SYNTHESIS AND CRYSTAL STRUCTURES OF DIMETHYLSILYLENE-BRIDGED (AMIDOCYCLOPENTADIENYL)DICHLOROTITANIUM(IV) COMPLEXES WITH VARIOUS SUBSTITUENTS ON THE CYCLOPENTADIENYL LIGAND

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(Amidocyclopentadienyl)dichlorotitanium(IV) complexes of the general formula [$TiCl_2\{\eta^5:\eta^1(N)\text{-}C_5(1\text{-}SiMe_2Nt\text{-}Bu\text{-}2,3,4\text{-}Me_3\text{-}5\text{-}R)\}$], where R = H (**6b**), Ph (**6c**), 4-fluorophenyl (**6d**) and 1-methylallyl (**6e**) were synthesized and characterized by spectral methods. Solid-state structure of [$TiCl_2\{\eta^5:\eta^1(N)\text{-}C_5Me_4(SiMe_2Nt\text{-}Bu)\}$] (**6a**) and **6d** determined by single-crystal X-ray diffraction showed that variation of the ring substituent R has only a negligible effect on the molecular structure of the complexes. The NMR spectra indicate that motion of the bulky substituent R in compounds **6c**, **6d** and **6e** is hindered below *ca* 50 °C.

Keywords: Titanium; Half-sandwich complexes; Cyclopentadienyl ligands; (Amidocyclopentadienyl)dichlorotitanium(IV) complexes; Substituent effects; X-Ray diffraction; NMR spectroscopy; Alkene polymerization catalysts.

An introduction of (*tert*-butylamido)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane as the $\eta^5:\eta^1(N)$-dianionic ligand in the synthesis of *ansa*-($\eta^5:\eta^1(N)$-((*tert*-butylamido)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane))chloroscandium(III)[1] resulted in discovery of a new class of alkene polymerization catalysts called "constrained geometry catalysts" (CGC)[2,3]. Active single-site catalysts formed from these *ansa*-amidocyclopentadienyl complexes in the presence of excess methylalumoxane (MAO) offer an alternative to the well-known group 4 metallocene catalysts by pro-

viding generally more acidic and less sterically encumbered cationic centres[4] that display very high activities especially in the copolymerization of ethene with terminal alkenes[5], cycloalkenes[6] and styrene[7], where both the traditional Ziegler–Natta multi-site and metallocene-based single-site catalysts are ineffective. Particularly, catalysts based on an archetypal titanium(IV) complex $[TiCl_2\{\eta^5:\eta^1(N)\text{-}C_5Me_4(SiMe_2N\textit{t}\text{-}Bu)\}]$[8] (**6a**) showed industrially explorable properties[9]. Analogous titanium complexes with unsubstituted cyclopentadienyl- (refs[9b,10]), indenyl- (ref.[11]) or fluorenylamidosilane ligands[11], however, were found to be precursors of poorer catalyst than is **6a** (refs[2–4,12]). Similarly, replacement of *tert*-butyl substituent on the amido nitrogen atom by Me, i-Pr, CH_2Ph, CHMePh, cyclohexyl, 1-adamantyl or cyclododecyl group[4,13] as well as attachment of a further tether bearing nitrogen or oxygen donor atom[14] did not improve the catalyst performance. On the other hand, a replacement of the bridging dimethylsilylene group by ethane-1,2-diyl link in the CGC-type polymerization catalyst precursors suppresses the catalyst activity towards propene while slightly enhancing that towards ethene[15].

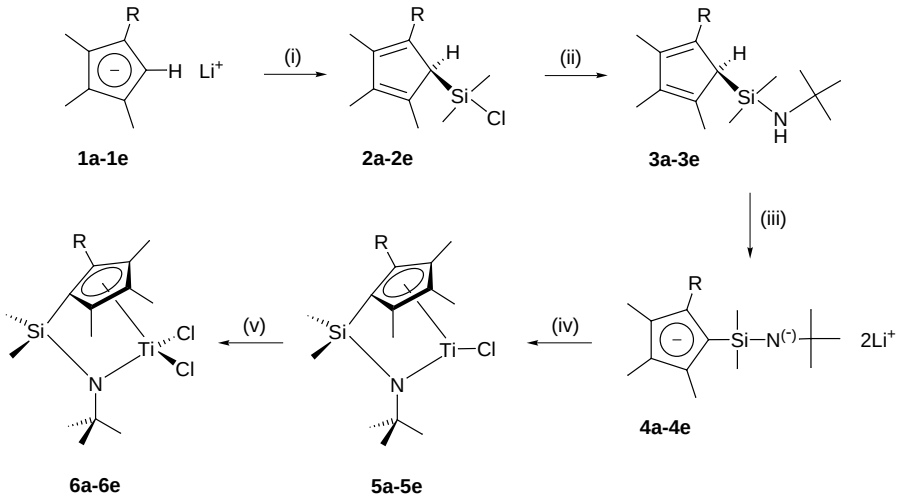
To the best of our knowledge, a fine tuning of properties of the catalytic centre derived from compound **6a** by changing a single substiuent on otherwise fully methylated cyclopentadienyl ligand has not yet been attempted. Hence, in this work we report the synthesis of analogues of complex **6a** bearing various substituents in the position adjacent to the dimethylsilylene bridge.

RESULTS AND DISCUSSION

Synthesis and Spectroscopy

Synthesis of (amidocyclopentadienyl)dichlorotitanium(IV) complexes $[TiCl_2\{\eta^5:\eta^1(N)\text{-}C_5(1\text{-}SiMe_2NCMe_3\text{-}2,3,4\text{-}Me_3\text{-}5\text{-}R)\}]$ largely follows the general procedure described for the synthesis of complex **6a** (R = Me, Scheme 1)[9b]. The starting trimethylcyclopentadienes $C_5H_2Me_3R$ (R = H, Ph, 4-fluorophenyl and $CH(Me)CH{=}CH_2$) were obtained by iodine-catalyzed dehydration of alcohols synthesized from 2,3,4-trimethylcyclopent-2-en-1-one and the appropriate R^- source ($LiAlH_4$ for **6b** and the corresponding Grignard reagents for **6c**–**6e**)[16]. The cyclopentadienes $C_5H_2Me_3R$ were deprotonated by one equivalent of BuLi and the formed monoanions (**1**) were reacted with one equivalent of dichlorodimethylsilane to give the corresponding chloro(cyclopentadienyl)dimethylsilanes ($C_5HMe_3R)SiMe_2Cl$ (**2**). The latter were added directly to one equivalent of lithium *tert*-butyl-

amide (prepared by mixing stoichiometric amounts of *tert*-butylamine and BuLi) since this protocol proved to be less time consuming than the generally used refluxing of the silanes with an excess of *tert*-butylamine[9b]. The resulting cyclopentadienyl(*tert*-butylamino)dimethylsilanes (**3**) were isolated



(i) Me_2SiCl_2, THF
(ii) $LiNHCMe_3$, Et_2O
(iii) 2 BuLi, THF-hexane
(iv) $[TiCl_3(THF)_3]$, THF
(v) 1/2 $PbCl_2$, THF

1-6	R
a	Me
b	H
c	Ph
d	4-FC_6H_4
e	$CH(Me)CH=CH_2$

SCHEME 1

as yellow fluorescent oily liquids by hexane extraction in the absence of air (removal of LiCl), evaporation of the extracts and distillation of the residues in vacuum. The silanes **3** were further converted to dianions by reacting with 2 equivalents of BuLi and the obtained lithium salts **4** were mixed with a slurry of one equivalent $[TiCl_3(THF)_3]$ in THF. After refluxing for 6 h, one half of molar equivalent of $PbCl_2$ was added[17] to oxidize a titanium(III) intermediates **5**. Thereupon the initially green reaction mixtures turned yellow (after 3 h at room temperature) and black metallic lead deposited at the bottom of reaction vessels. The solvents were evaporated *in vacuo* and the residues were extracted with dry hexane. After evaporation, the extracted products were sublimed *in vacuo* at temperature increasing up to 210 °C. Finally, the (amidocyclopentadienyl)dichlorotitanium complexes **6b**–**6e**

were separated from organic byproducts by crystallization from hexane. Pure titanium(IV) complexes were thus obtained as intense yellow crystalline materials in yields not exceeding 19%. The parent compound of this series, complex **6a** was also synthesized by this procedure as the reference.

Compounds **6a**–**6e** were characterized by ^{1}H and ^{13}C NMR, mass and IR spectra. The NMR spectra of **6b**–**6e** are unexceptional, differing from the spectra of **6a** mainly by signals of the substituents R. More interestingly, compounds with bulky aromatic substituents **6c** and **6d** exhibit broad resonances due to the substituent R (Ph or 4-C_6H_4F) in both ^{1}H and ^{13}C NMR spectra. As indicated by a variable temperature ^{1}H NMR study, the broadening results from a hindered motion of these substituents (Fig. 1). At room temperature and in benzene-d_6 solution, a movement of the phenyl group in **6c** is slow on the NMR time scale and results in a separation of phenyl resonances so that they consist of a sharp multiplet (3 H) and two well separated broad signals (2 × 1 H). Examination of ^{1}H NMR spectra in a temperature range of 0–60 °C showed the coalescence temperature of this two-site exchange to be *ca* 45 °C.

Similarly to its non-fluorinated analogue, complex **6d** exhibits in its NMR spectra a typical two-site exchange of the aromatic CH groups adjacent to the cyclopentadienyl ring with coalescence temperature of *ca* 45 °C. Upon lowering temperature to 0 °C, further signals of the 4-fluorophenyl substituent, which are well-resolved at room temperature, become broad. It appears likely that a motion of the 1-methylallyl substituent in **6e** is hindered as well since this compound features unresolved broad resonances due to the CH(Me)CH=CH_2 moiety in ^{1}H NMR spectra. However, as the complex **6e** is obtained as a mixture of two diastereisomers, the observed broadening of NMR signals may be also attributed to overlapping of two signals sets.

Mass spectra of complexes **6a**–**6e** display only poorly abundant molecular ions which fragment by a loss of one methyl group with subsequent elimination of *t*-Bu group (**6c**–**6e**) or by an elimination of 2-methylpropene (**6a** and **6b**). In infrared spectra of the CGC complexes, typical absorption bands of the phenyl and 4-fluorophenyl groups at 1 600 cm^{-1} and in the region 3 000–3 100 cm^{-1} as well as the ν(C=C) band of the 1-methylallyl group at 1 640 cm^{-1} are well observable. The common framework of the complexes gives rise to strong single bands at 984 ± 4 and 1 181 ± 3 cm^{-1} whose positions are virtually independent of the substituents R on the cyclopentadienyl ring. On the other hand, the bands due to the dimethylsilylene group are influenced by the varying substituents: compounds **6c**–**6e** show a band at 850 ± 1 cm^{-1} and doublets 1 258/1 262 cm^{-1} for **6c**,

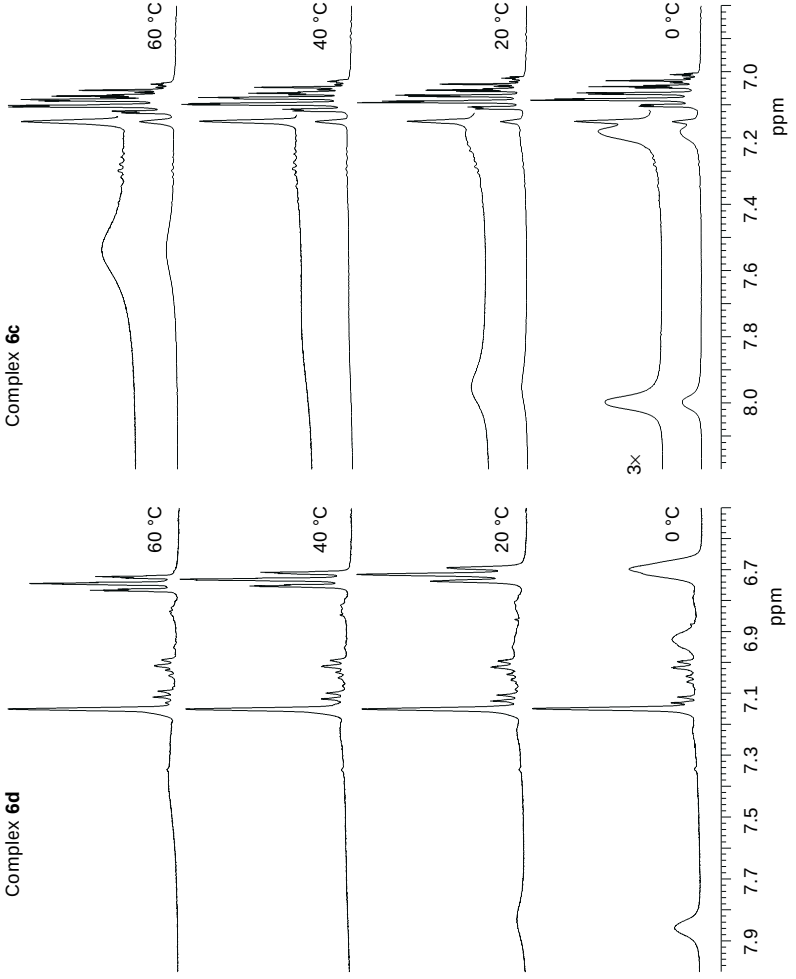


FIG. 1
Temperature dependent ^{1}H NMR spectra of complex **6c** and **6d**. A broad signal at δ_H 7.15 is due to the solvent

1 251/1 260 cm^{-1} for **6d** and 1 252/1 259 cm^{-1} for **6e**, while complexes **6a** and **6b** exhibit only single bands at 841 and 1 253 cm^{-1}, and at 838 and 1 255 cm^{-1}, respectively. The splitting of the band at 1 250–1 260 cm^{-1} in infrared spectra of **6c**–**6e** can be related to a steric hindrance imposed by the bulky substituents R whose hindered rotation has been established by NMR spectroscopy (*vide supra*).

Structures of compounds **6a** and **6d** were determined by X-ray diffraction of single crystals. We have redetermined the crystal structure of **6a** because the data reported previously are accessible only with difficulty[8,10c].

*Crystal Structures of **6a** and **6d***

Molecular structure **6a** is largely dictated by the symmetry of unit cell since the molecule is located so that a crystallographic mirror plane passes the Ti, C1, Si, N, C7 and C9 atoms (Fig. 2). The molecule of 4-fluorophenyl derivative **6d** (Fig. 3) shows planar chirality due to the presence of the non-methyl substituent on the cyclopentadienyl ring. Hence, the racemic unit cell consists of two pairs of enantiomeric molecules. The bond lengths and angles for **6a** and **6d** (Table I) indicate that the 4-fluorophenyl substituent has almost no effect on the geometry of the molecular skeleton. The bite angles N–Ti–Cg (Cg denotes centroid of the cyclopentadienyl ring) in **6a**

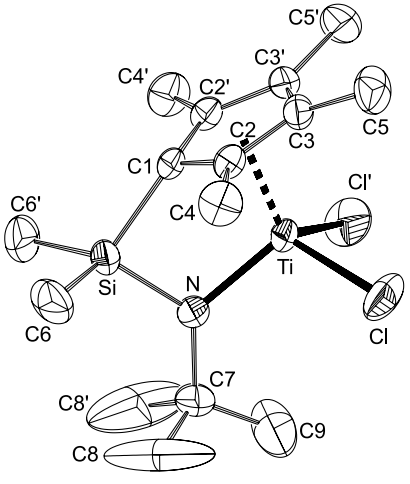


FIG. 2
Structure of compound **6a** drawn at the 30% probability level with the atom labelling scheme. All hydrogen atoms are omitted for clarity

(107.8(2)°) and **6d** (107.6(2)°) do not differ within the precision of measurement and their values are only slightly larger than the bite angle in $[TiCl_2\{\eta^5:\eta^1(N)\text{-}C_5H_4(SiMe_2N\textit{t}\text{-}Bu)\}]$ (107.0°)[10c]. Similarly, other skeletal angles, N–Si–C1 and Si-N–Ti, are virtually equal in both compounds. The asymmetry induced by the 4-fluorophenyl substituent results in a slight rotation of the η^5-cyclopentadienyl ligand from an arrangement perpendicular to a plane defined by Ti, N and Si atoms. The corresponding dihedral angle is 86.9(2)°, the side bearing the aromatic substituent being more distant from the titanium atom. The least-squares 4-fluorophenyl and cyclopentadienyl planes subtend an angle 52.7(2)° and the aromatic group is disposed out of the latter plane: the C15 *ipso*-carbon atom is shifted 0.200(7) Å from the cyclopentadienyl-ring plane away from the titanium centre. The asymmetry of **6d** is also manifested by dihedral angles between the Ti, Cl1, Cl1′ and Ti, Cl1, Cl2 planes, respectively, and the least-squares cyclopentadienyl plane: 47.8(1)° for **6a** and 52.7(2)° for **6d**. Similarly, the angle between the Ti, Cl1, Cl2 and Ti, N, Si planes in **6d** (88.4(1)°) differs slightly from the perpendicular angle in compound **6a** which reflects crystallographic symmetry.

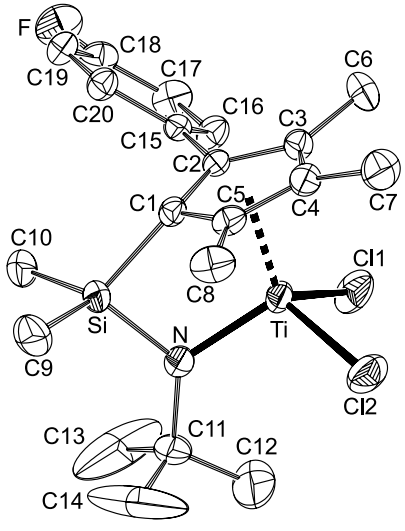


FIG. 3
Structure of compound **6d** drawn at the 30% probability level showing the atom labelling scheme. All hydrogen atoms are omitted for clarity

These results show that the substituents on the cyclopentadienyl ring do not affect the skeleton of the studied CGC complexes, particularly the magnitude of the N–Ti–Cg bite angle which is believed to determine polymerization activity of the catalysts prepared thereof[9b]. The magnitude of the bite angle is somewhat more affected by substituents on the nitrogen atoms as their stereoelectronic effect instantly influences the Ti–N bond[3,9b].

TABLE I
Selected bond lengths (in Å) and angles (in °) for complexes **6a** and **6d**

Atoms	**6a**	**6d**
	Lengths	
Ti–C1	2.264(4)	2.284(4)
Ti–C2	2.329(3)	2.373(4)
Ti–C3	2.445(3)	2.452(4)
Ti–C4	–	2.425(4)
Ti–C5	–	2.316(4)
Ti–Cg[a]	2.033(3)	2.040(4)
C_{ring}–C_{ring}	1.405–1.430(4)	1.409–1.432(6)
Ti–N	1.910(4)	1.910(3)
Si–N	1.745(4)	1.744(4)
Si–C1	1.866(4)	1.875(4)
Ti–Cl1	2.265(1)	2.269(2)
Ti–Cl2	–	2.274(2)
	Angles	
Cg–Ti–N	107.8(2)	107.6(2)
Cg–Ti–Cl1	114.55	115.94
Cg–Ti–Cl2	–	114.87
Cl1–Ti–Cl1′(Cl2)[b]	103.17(8)	100.68(6)
N–Si–C1	90.4(2)	90.8(2)
Si–N–Ti	105.3(2)	105.6(2)

[a] Centroid of the C1-C5 cyclopentadienyl ring. [b] Position of the Cl1′ atom is generated by the (x, 1/2 + y, z) symmetry operation.

EXPERIMENTAL

General Comments

Syntheses of cyclopentadienes from ketones and $LiAlH_4$ or Grignard reagents were performed under nitrogen; the reactions of lithium cyclopentadienides or lithium *tert*-butylamide were carried out in argon atmosphere. All manipulations with the (amidocyclopentadienyl)titanium complexes were carried out on a high vacuum-argon line operated by glass-to-metal sealed valves (Hoke) in all-sealed glass devices equipped with breakable seals. NMR samples were prepared in evacuated all-glass devices from which the NMR tubes were sealed off by flame. The adjustment of single crystals into Lindemann glass capillaries for X-ray analyses as well as the preparation of samples for IR and MS measurements was made under nitrogen in a glovebox (mBraun, O_2 and H_2O concentrations lower than 2.0 ppm).

Infrared spectra of samples in KBr pellets were recorded on a Specord IR-75 spectrometer (Carl Zeiss, Jena, Germany) in a closed cell under nitrogen (wavenumbers in cm^{-1}). ^1H (399.95 MHz) and ^{13}C (100.58 MHz) NMR spectra were measured on a Varian UNITY Inova 400 spectrometer in C_6D_6 solutions at 298 K. Chemical shifts (δ, ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.0). Coupling constants (*J*) are given in Hz. Mass spectra were measured on a VG 7070E spectrometer at 70 eV using a direct inlet probe (samples in sealed capillaries were opened and inserted into the probe in an argon flow). GC analyses were performed on a CHROM 5 gas chromatograph (Laboratory Instruments, Prague, Czech Republic) equipped with a 10% SE-30/Chromaton N-AW-DMCS column. GC-MS analyses were carried out on a Hewlett–Packard gas chromatograph (5890 series II; capillary column SPB-1 (Supelco)) interfaced to a mass spectrometric detector (5791 A). Melting points were determined for samples in nitrogen-filled sealed capillaries on a Kofler apparatus and are uncorrected.

Diethyl ether and tetrahydrofuran (THF) used for the synthesis of (*tert*-butylamino)-(cyclopentadienyl)dimethylsilanes were dried by refluxing over $LiAlH_4$ in argon atmosphere. THF and hexane for the synthesis and purification of (amidocyclopentadienyl)titanium complexes were refluxed with $LiAlH_4$ in argon atmosphere, carefully degassed and stored as solutions of green dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)\{(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H)\}_2]$ (ref.[18]) on a vacuum line. C_6D_6 for NMR spectroscopy was degassed and stored as a solution of green dimeric titanocene on a vacuum line.

The starting trimethylcyclopentadienes were obtained from 2,3,4-trimethylcyclopent-2-en-1-one by reduction with $LiAlH_4$ (refs[16,19]) or, in the case of $C_5Me_3RH_2$ derivatives (R = Ph, 4-fluorophenyl and $CH(Me)CH{=}CH_2$), from alkylation with corresponding Grignard reagents, and subsequent iodine-catalyzed dehydration of the resulting alcohols[16]. This procedure is analogous to the synthesis of C_5Me_4RH, where R = Ph (ref.[20]), 4-fluorophenyl (ref.[21]) or $CH(Me)CH{=}CH_2$ (ref.[22]). Titanium tetrachloride (International Enzymes) was degassed, refluxed over copper turnings, and distilled *in vacuo* into ampoules. Crude $[TiCl_3(THF)_3]$ was obtained by reduction of $TiCl_4$ with equimolar amount of BuLi in THF (ref.[23]). Lead dichloride (powder, Aldrich) was heated to 100 °C *in vacuo* and then stored under argon. Butyllithium (1.6 M solution in hexanes), *tert*-butylamine, bromobenzene, 4-fluorobromobenzene and dichlorodimethylsilane (all Aldrich) were used as received.

Synthesis of {η^5:η^1(*N*)-1-[(*tert*-Butylamido)dimethylsilyl)]-2,3,4-trimethylcyclopentadienyl}dichlorotitanium(IV) (**6b**)

Butyllithium (31.3 ml 1.6 mol l^{-1}, 50.0 mmol) was added to a stirred solution of isomeric 1,2,3-trimethylcyclopentadienes[19] (5.4 g, 50.0 mmol) in THF (300 ml) in a three-necked flask equipped with a magnetic stirring bar and a reflux condenser. A voluminous white precipitate of lithium cyclopentadienide, which separated immediately, was stirred at room temperature for 2 h. Then, it was treated with neat dichlorodimethylsilane (6.3 ml, 52.0 mmol) and the reaction mixture was refluxed for 1 h. The reaction volume was reduced to *ca* 20 ml by distillation at normal pressure and the remaining volatiles were distilled off at room temperature in oil-pump vacuum. Finally, chlorodimethyl(1,2,3-trimethylcyclopenta-1,3-dien-5-yl)silane (**2b**) was obtained by distillation from boiling water bath at 15 Pa as a yellowish liquid (8.5 g, 85%). This product was stored under argon prior to use.

Simultaneously, BuLi (26.0 ml of 1.6 M solution in hexane, 42.0 mmol) was slowly added to a vigorously stirred solution of *tert*-butylamine (4.7 ml, 42.0 mmol) in dry THF (200 ml) in a three-necked flask equipped with a magnetic stirring bar and a reflux condenser. The colourless solution was stirred at room temperature for 2 h and the chlorosilane **2b** (8.5 g, 42.3 mmol) was slowly introduced. A white precipitate slowly formed overnight. Most of THF was distilled off and hexane (50 ml) was added to the remaining 20 ml of the reaction mixture. The solution was separated from the precipitated LiCl and the extraction was repeated by another 50 ml of hexane. Combined hexane extracts were evaporated at reduced pressure on a rotary evaporator and the remaining liquid was distilled at 10 Pa from boiling water bath to provide silane **3b** as a yellow viscous liquid showing green fluorescence. Yield 8.7 g (88%). GC-MS, *m/z* (relative abundance): 237 ($M^{\bullet+}$, 12), 222 ($[M - Me]^+$, 6), 165 (13), 131 (18), 130 ($[Me_2SiNH(t\text{-}Bu)]^+$, 100), 114 (32), 105 (11), 100 (12), 93 (14), 91 (41), 79 (13), 77 (15), 75 (12), 74 (82), 73 (71), 59 (26), 58 (33), 41 (26). IR (neat): 3 043 (w), 2 953 (vs), 2 924 (sh), 2 900 (s), 2 854 (s), 1 612 (w), 1 533 (w), 1 460 (m), 1 440 (m), 1 393 (m), 1 373 (vs), 1 357 (s), 1 247 (vs), 1 223 (vs), 1 148 (w), 1 120 (m), 1 090 (w), 1 014 (vs), 977 (s), 937 (m), 896 (w), 847 (vs), 824 (vs), 767 (s), 720 (w), 687 (w), 673 (w), 637 (w), 540 (w), 500 (m), 483 (m), 450 (w).

In the next step, the silane **3b** (8.5 g, 36.0 mmol) was dissolved in THF (300 ml), BuLi (45.0 ml of 1.6 M solution in hexanes, 72.0 mmol) was added with stirring and the resulting yellow solution was stirred for 2 h. A suspension of $[TiCl_3(THF)_3]$ (prepared from $TiCl_4$ (4.0 ml, 36.0 mmol) and BuLi (22.5 ml 1.6 mol l^{-1}, 36.0 mmol)) was added to the solution of the lithium salt and the mixture was refluxed for 8 h. The solvents were distilled off to reduce the reaction volume to about 50 ml and, after cooling to room temperature, dry $PbCl_2$ (5.0 g, 18.0 mmol) was added into the reaction mixture and stirring was continued at 40 °C for 2 h. The reaction vessel was then attached to a vacuum-argon line under argon where the remaining volatiles were removed in vacuum and the reaction products were extracted into hexane (100 ml portions; hexane was added by distillation on the vacuum-argon line). Combined brown extracts were concentrated to approximately 30 ml and distributed into 3 ampoules, whose contents were distilled on a high-vacuum line. The volatiles distilling up to 70 °C were collected in a cooled trap but discarded. Temperature was successively increased to about 210 °C and a red oil which partly solidified at room temperature was collected in a trap cooled with liquid nitrogen at a pressure of 2 Pa. After cooling to room temperature, hexane (10 ml) was distilled into the trap to dissolve the distillate and to separate a small amount of a white insoluble solid. The volume of the clear hexane

solution was reduced to 5 ml and cooled to –18 °C overnight. Yellow crystals that separated from a brown-red solution were isolated and recrystallized from hexane. After analogous workup of all the three parts a total yield of bright yellow crystalline **6b** was 2.41 g (19%).

Data for **6b**: M.p. 124 °C. MS (115 °C, m/z (relative abundance)): 353 ($M^{\bullet+}$, 0.5), 342 (16), 341 (18), 340 (73), 339 (32), 338 ($[M - Me]^+$, 100), 337 (11), 336 (10), 284 (9), 283 (6), 282 ($[M - Me - Me_2C{=}CH_2]^+$, 13), 162 (6). ^{1}H NMR (C_6D_6): 0.29, 0.38 (2 × s, 3 H, $SiMe_2$); 1.41 (s, 9 H, CMe_3); 1.95, 1.96, 2.09 (3 × s, 3 H, Me_3C_5); 5.90 (Me_3C_5**H**). ^{13}C{^{1}H} NMR ($CDCl_3$): 0.89, 3.04 ($SiMe_2$); 12.3, 15.1, 16.0 (**Me**$_3C_5$); 32.7 (C**Me**$_3$); 62.8 (CMe_3); 105.9 (C-Si, Me_3C_5); 127.0 (CH, Me_3C_5); 138.0, 139.0, 141.0 (C-Me, Me_3C_5). IR (KBr): 3 060 (w), 2 958 (vs), 2 912 (s), 2 860 (m), 1 466 (m,b), 1 400 (vw), 1 389 (vw), 1 373 (w), 1 363 (m), 1 359 (m), 1 340 (w), 1 282 (vw), 1 255 (s), 1 231 (vw), 1 213 (w), 1 180 (s), 1 135 (m), 1 032 (m), 987 (s), 922 (w,b), 837 (vs), 812 (m), 780 (s), 767 (vs), 685 (vw), 657 (w), 539 (vw), 506 (w), 497 (m), 486 (w), 426 (m).

Synthesis of {η^5:η^1(*N*)-1-[(*tert*-butylamido)dimethylsilyl)]-2,3,4-trimethyl-5-phenylcyclopentadienyl}dichlorotitanium(IV) (**6c**)

1,2,3-Trimethyl-4-phenylcyclopentadiene (a mixture of isomers) was obtained by the reaction of phenylmagnesium chloride with 2,3,4-trimethylcyclopent-2-en-1-one followed by dehydration catalyzed with iodine according to the general procedure[24]. Recrystallization from hexane afforded slightly yellow crystals of the cyclopentadienes in 61% yield. GC-MS, *m/z* (relative abundance): 185 (16), 184 ($M^{\bullet+}$, 100), 183 (10), 170 (12), 169 (79), 168 (10), 167 (14), 165 (16), 155 (17), 154 (34), 153 (22), 152 (18), 141 (32), 129 (18), 128 (30), 127 (10), 115 (27), 105 (11), 91 (38), 78 (10), 77 (24), 76 (11), 65 (11), 63 (14), 51 (22), 43 (12), 41 (11). IR (KBr): 3 066 (vw), 3 040 (w), 3 021 (w), 2 980 (vw), 2 952 (m), 2 930 (w), 2 905 (m), 2 880 (w), 2 867 (w), 2 847 (m), 1 947 (vw), 1 887 (vw), 1 635 (vw), 1 593 (m), 1 585 (w), 1 560 (w), 1 485 (m), 1 435 (s), 1 373 (m), 1 363 (s), 1 180 (m), 1 115 (w), 1 095 (w), 1 081 (w), 1 060 (m), 1 025 (w), 973 (w), 913 (w), 860 (w), 754 (vs), 703 (vs), 561 (w), 529 (m).

The cyclopentadiene (7.37 g, 40.0 mmol) was converted to the lithium salt **1c** with BuLi (26.0 ml of 1.6 M solution in hexane, 41 mmol), the salt was stirred for 2 h and treated with dichlorodimethylsilane (4.85 ml, 40.0 mmol). The mixture was refluxed for 1 h, THF and hexane were distilled off and the product was distilled at 126 °C/4 Pa and stored under argon. Yield of 1,2,3-trimethyl-4-phenylcyclopentadienyldimethylchlorosilane (**2c**) 8.5 g (87%).

All this silane was reacted with *t*-BuNHLi (from *tert*-butylamine (3.67 ml, 35.0 mmol) and BuLi (21.8 ml of 1.6 M solution in hexanes, 35.0 mmol)) to give, after distillation at 125 °C/2 Pa, the silane **3c** as a yellow fluorescent oily liquid. Yield 8.4 g (81%). GC-MS *m/z* (relative abundance): 313 ($M^{\bullet+}$, 6), 167 (9), 165 (9), 152 (6), 131 (15), 130 ($[Me_2SiNH$*t*-$Bu]^+$, 100), 114 (8), 75 (7), 74 (55), 73 (35), 59 (8), 58 (14), 41 (8). IR spectrum (neat): 3 067 (vw), 3 047 (w), 3 015 (w), 2 958 (vs), 2 904 (s), 2 857 (m), 1 933 (vw), 1 867 (vw), 1 800 (vw), 1 741 (vw), 1 700 (w), 1 593 (m), 1 570 (vw), 1 540 (w), 1 483 (m), 1 460 (m), 1 440 (s), 1 398 (m), 1 376 (vs), 1 355 (s), 1 247 (vs), 1 223 (vs), 1 147 (w), 1 113 (w), 1 087 (w), 1 058 (m), 1 013 (vs), 970 (s), 903 (w), 843 (vs), 817 (vs), 779 (s), 758 (m), 697 (vs), 633 (w), 520 (w), 492 (w), 457 (w).

The synthesis of **6c** was carried out as given above for **6b** starting from the above silane **3c** (36.0 mmol). Distillation of the crude product *in vacuo* and crystallization from hexane at low temperature afforded **6c** as a yellow crystalline solid (2.02 g, 13%).

Data for **6c**: M.p. 143 °C. MS (125 °C, m/z (relative abundance)): 429 ($M^{\bullet+}$, not observed), 418 (19), 417 (25), 416 (78), 415 (39), 414 ([M – Me]$^+$, 100), 413 (12), 412 (10), 359 (13), 357 ([M – Me – *t*-Bu]$^+$, 16), 342 (7), 324 (10), 323 (16), 322 (25), 321 (27), 320 (7), 223 (8), 209 (9), 73 (8), 59 (9), 58 (19), 57 (23), 43 (12). ^{1}H NMR (C_6D_6): –0.23, 0.44 (2 × s, 3 H, $SiMe_2$); 1.38 (s, 9 H, CMe_3); 2.01, 2.03, 2.14(Me_3C_5); 7.00–7.13 (m, 3 H, Ph); 7.19, 7.92 (2 × br s, 1 H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): 4.1, 4.8 ($SiMe_2$); 13.1, 13.3, 16.8 (**Me**$_3C_5$); 32.7 (C**Me**$_3$); 63.0 (CMe_3); 104.3, 135.9, 137.2, 137.6, 142.3, 147.9 (C_{ipso}, Me_3C_5 and Ph); 128.4, 130.7 (br), 132.7 (br) (CH, Ph). IR (KBr): 3 050 (m), 2 958 (vs), 2 910 (sh), 2 855 (s), 1 600 (w), 1 572 (vw), 1 497 (w), 1 463 (m), 1 443 (s), 1 402 (m), 1 390 (sh), 1 378 (s), 1 360 (s), 1 323 (m), 1 309 (w), 1 255 (vs), 1 229 (m), 1 214 (m), 1 180 (vs), 1 094 (m,b), 1 075 (m), 1 024 (s), 981 (vs), 926 (sh), 918 (m), 847 (vs), 822 (s), 805 (s), 792 (sh), 769 (vs), 702 (vs), 681 (m), 641 (w), 589 (w), 547 (s), 500 (m), 480 (s), 430 (s).

Synthesis of {η^5:η^1(*N*)-1-[(*tert*-Butylamido)dimethylsilyl)]-2-(4-fluorophenyl)-3,4,5-trimethylcyclopentadienyl}dichlorotitanium(IV) (**6d**)

1-(4-Fluorophenyl)-2,3,4-trimethylcyclopentadiene (a mixture of isomers) was synthesized from (4-fluorophenyl)magnesium chloride and 2,3,4-trimethylcyclopent-2-en-1-one according to the general procedure[21]. Recrystallization from hexane afforded slightly yellow crystals of the cyclopentadiene in the yield of 82%. GC-MS, *m/z* (relative abundance): 203 (16), 202 ($M^{\bullet+}$, 100), 188 (15), 187 (99), 185 (9), 183 (14), 173 (14), 172 (31), 171 (19), 170 (17), 167 (23), 166 (14), 165 (27), 159 (26), 153 (9), 152 (24), 147 (12), 146 (21), 133 (22), 109 (21), 91 (15), 41 (10), 39 (16). IR (KBr): 3 051 (vw), 3 032 (vw), 2 967 (m), 2 933 (w), 2 907 (s), 2 850 (m), 1 893 (vw), 1 637 (vw), 1 598 (w), 1 585 (m), 1 561 (m), 1 500 (vs), 1 440 (m), 1 403 (w), 1 377 (s), 1 325 (w), 1 297 (w), 1 227 (vs), 1 177 (m), 1 154 (s), 1 117 (w), 1 103 (m), 1 073 (m), 1 007 (w), 981 (w), 860 (m), 830 (vs), 810 (s), 730 (w), 713 (w), 573 (m), 560 (m), 527 (m), 474 (w).

Subsequent reactions follow the same protocol as given for the synthesis of compound **6b**. Thus, using the cyclopentadiene (12.4 g, 49.0 mmol), the corresponding chlorosilane **2d** was obtained (11.1 g, 77%) and immediately converted to the aminosilane **3d** (9.6 g, 78%). GC-MS, *m/z* (relative abundance): 331 ($M^{\bullet+}$, 4), 202 (7), 201 (6), 200 (6), 185 (10), 184 (5), 183 (10), 165 (16), 131 (19), 130 ([Me_2SiNH*t*-Bu]$^+$, 100), 114 (11), 74 (52), 73 (32), 58 (14), 41 (8). IR (neat): 3 037 (w), 2 973 (vs), 2 907 (s), 2 860 (m), 1 887 (vw), 1 600 (w), 1 547 (m), 1 500 (s), 1 467 (w), 1 447 (m), 1 400 (w), 1 387 (s), 1 360 (m), 1 247 (s), 1 230 (vs), 1 153 (m), 1 117 (w), 1 073 (w), 1 017 (s), 973 (m), 953 (w), 839 (vs), 824 (s), 776 (m), 747 (vw), 733 (vw), 633 (w), 580 (w), 567 (m), 527 (w), 500 (m), 427 (w).

The titanium(IV) complex **6d** was prepared from silane **3d** (11.9 g, 36 mmol) by the procedure described above. Yield: 2.25 g (14%), yellow crystalline solid. M.p. 170 °C. MS (135 °C, *m/z* (relative abundance)): 447 ($M^{\bullet+}$, 1), 437 (6), 436 (20), 435 (26), 434 (85), 433 (46), 432 ([M – Me]$^+$, 100), 431 (13), 430 (11), 377 ([M – Me – *t*-Bu]$^+$, 98), 375 (9), 342 (8), 341 (12), 340 (19), 339 (19), 191 (7), 58 (66), 57 (16), 55 (7), 43 (10), 42 (9), 41 (33). ^{1}H NMR (C_6D_6): –0.29, 0.42 (2 × s, 3 H, $SiMe_2$); 1.36 (s, 9 H, Me_3C); 1.98, 2.00, 2.11 (3 × s, 3 H, Me_3C_5); 6.68–8.00 (m consisting of sharp multiplets (2 H) and a broad doublet (2 H), C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): 4.1, 4.8 ($SiMe_2$); 13.1, 13.2, 16.8 (**Me**$_3C_5$); 32.7 (**Me**$_3$C); 63.0 (Me_3C); 104.3 (C_{ipso}, C_5Me_3); 114.9 (d, $^2J_{FC}$ = 21, γ-CH); 131.7 (d, $^4J_{FC}$ = 3, α-C); 133.4 (br d, $\Delta\nu_{1/2} \approx 250$, β-CH); 137.2, 137.7, 142.2, 146.3 (C_{ipso}, C_5Me_3); 163.0 (d, $^1J_{FC}$ = 248, δ-CF). IR (KBr): 3 040 (w), 2 964 (vs), 2 916 (s), 2 860 (m), 1 913 (vw), 1 662 (vw), 1 602 (s), 1 511

(vs), 1 464 (m), 1 439 (w), 1 402 (m), 1 388 (s), 1 375 (m), 1 360 (s), 1 312 (w), 1 260 (s), 1 251 (s), 1 228 (vs), 1 179 (vs), 1 157 (m), 1 093 (m), 1 033 (w), 1 014 (w), 980 (s), 916 (w), 848 (vs,b), 820 (m), 790 (vs), 780 (vs), 767 (vs), 726 (w), 682 (w), 642 (vw), 627 (vw), 587 (w), 577 (m), 545 (m), 507 (s), 465 (m), 434 (s).

Synthesis of {η^5:η^1(*N*)-1-[(*tert*-Butylamido)dimethylsilyl)]-2,3,4-trimethyl-5-(1-methylallyl)cyclopentadienyl}dichlorotitanium(IV) (**6e**)

Grignard reagent prepared from 3-chlorobut-1-ene was reacted with 2,3,4-trimethylcyclopent-2-en-1-one in diethyl ether and the alcohol obtained was instantly dehydrated with a catalytic amount of iodine according to the general procedure[22]. A mixture of isomeric 1,2,3-trimethyl-4-(1-methylallyl)cyclopentadienes was obtained as a colourless liquid in 80% yield (based on the ketone). GC-MS, *m/z* (relative abundance): 162 ($M^{\bullet+}$, 12), 147 (18), 133 (6), 119 (20), 107 (18), 106 (8), 105 (38), 93 (14), 91 (74), 79 (34), 77 (44), 65 (32), 63 (10), 55 (51), 53 (36), 51 (36), 41 (94), 40 (11), 39 (100). IR (neat): 3 067 (m), 2 960 (vs), 2 907 (vs), 2 852 (s), 1 812 (w), 1 650 (sh), 1 630 (s), 1 440 (vs), 1 408 (m), 1 372 (s), 1 330 (w), 1 158 (m), 1 087 (m), 993 (s), 903 (vs), 850 (m), 773 (w), 682 (m), 508 (w).

Subsequent reaction of $C_5H_2Me_3(CHMeCH{=}CH_2)$ (8.5 g, 53.0 mmol) with equimolar amount of dichlorodimethylsilane afforded chlorosilane **2e** (8.5 g, 68%) and finally, upon reacting with *t*-BuNHLi, the silane **3e** (8.3 g, 79%) as a yellow fluorescent liquid distilling at 120 °C/2 Pa. Data for **3e**: GC-MS, *m/z* (relative abundance): 290 ($M^{\bullet+}$, 1), 132 (5), 131 (19), 130 ($[Me_2SiNH\textit{t}\text{-}Bu]^+$, 100), 128 (6), 115 (6), 114 (9), 91 (9), 75 (9), 74 (81), 73 (65), 60 (7), 59 (21), 58 (12), 57 (15), 55 (32), 53 (8), 46 (15), 45 (11), 44 (13), 42 (11), 41 (29). IR (neat): 3 072 (w), 2 953 (vs), 2 927 (s), 2 907 (sh), 2 860 (m), 1 630 (m), 1 450 (s), 1 400 (m), 1 380 (vs), 1 360 (s), 1 250 (vs), 1 229 (vs), 1 017 (vs), 980 (m), 962 (w), 906 (s), 847 (vs), 828 (s), 798 (m), 773 (s), 680 (w), 634 (w), 513 (vw), 472 (w).

The reaction of **3e** (10.5 g, 36.0 mmol) with $[TiCl_3(THF)_3]$ (from 4.0 ml (36.0 mmol) $TiCl_4$), $PbCl_2$ oxidation and workup as given above gave **6e** (1.32 g, 9%) as a yellow crystalline solid. M.p. 112 °C. MS (90 °C, *m/z* (relative abundance)): 407 ($M^{\bullet+}$, 4), 396 (18), 395 (23), 394 (76), 393 (37), 392 ($[M - Me]^+$, 100), 391 (12), 390 (10), 376 (8), 339 (12), 338 (13), 337 (47), 336 (22), 335 ($[M - Me - \textit{t}\text{-}Bu]^+$, 66), 334 (8), 333 (7), 322 (7), 320 (10), 319 (6), 301 (7), 300 (13), 299 (12), 285 (7), 73 (17), 59 (21), 57 (21), 41 (25). ^{1}H NMR (C_6D_6): 0.39, 0.43 (2 × s, 3 H, $SiMe_2$); 1.37 (s, 9 H, Me_3C); 2.01, 2.07, 2.08 (3 × s, 3 H, Me_3C_5); 1.49 (dq, J_{HH} = 5.6, 1.1, 3 H, CH(**Me**)CH=CH_2); 3.24–3.33 (br m, 1 H, C**H**(Me)CH=CH_2); 5.12 (q, J_{HH} = 1.6, 1 H, CH(Me)CH=C$\mathbf{H}_2$); 5.35–5.39 (m, 1 H, CH(Me)CH=C$\mathbf{H}_2$); 5.41 (qq, 1 H, J_{HH} = 1.5, 6.7, CH(Me)C**H**=CH_2). ^{13}C{^{1}H} NMR (C_6D_6): 5.0 ($SiMe_2$); 13.1, 13.2, 16.8 (**Me**$_3C_5$); 13.9 (CH(**Me**)CH=CH_2); 32.8 (**Me**$_3$C); 62.8 (Me_3C); 70.8 (CH(Me)CH=CH_2); 103.5 (C_{ipso}, C_5Me_3); 117.4 (CH(Me)CH=CH_2); 128.6 (CH(Me)CH=CH_2); 131.4, 136.5, 141.6, 152.2 (C_{ipso}, C_5Me_3). IR (KBr): 3 055 (vw), 3 020 (sh), 2 957 (s), 2 940 (sh), 2 902 (m), 2 860 (w), 1 640 (w), 1 465 (m), 1 453 (w), 1 439 (m), 1 404 (w), 1 389 (m), 1 373 (m), 1 360 (s), 1 333 (vw), 1 306 (m), 1 260 (s), 1 252 (s), 1 229 (w), 1 215 (m), 1 182 (vs), 1 107 (vw), 1 052 (w), 1 034 (w), 1 022 (vw), 983 (s), 908 (w), 850 (vs), 817 (m), 791 (s), 770 (vs), 687 (w), 639 (w), 627 (vw), 594 (vw), 549 (m), 497 (m), 466 (w), 432 (s).

TABLE II
Crystal and structure refinement data for **6a** and **6d**

Parameter	**6a**[a]	**6d**
Formula	$C_{15}H_{27}Cl_2NSiTi$	$C_{20}H_{28}Cl_2NSiTi$
Formula weight, g mol^{-1}	368.27	448.32
Crystal system	orthorhombic	monoclinic
Space group	*Pnma* (No. 62)	$P2_1/c$ (No. 14)
a, Å	11.608(5)	13.620(3)
b, Å	13.500(5)	8.5715(9)
c, Å	12.181(5)	20.183(3)
α, °	90	90
β, °	90	107.033(15)
γ, °	90	90
V, Å^3; *Z*	1 909(1); 4	2 253.0(6); 4
d_{calc}, g cm^{-3}	1.281	1.322
μ(MoKα), mm^{-1}	0.783	0.683
F(000)	776	936
Crystal size, mm^3	0.6 × 0.4 × 0.2	0.5 × 0.3 × 0.2
Range of θ, °	2.86–25.02	1.56–24.94
Range of *h*,*k* and *l*	–1→30, –16→15, 0→14	–16→15, 0→10, 0→23
Reflections collected	3 183	4 051
Independent reflections	1 754	3 924
No. of data/parameters	1 754/118	3 924/314
S	1.059	1.006
R, *wR* (all data)	0.0686, 0.1472	0.1304, 0.1321
R, *wR* (observed diffractions)[b]	0.0492, 0.1340	0.0469, 0.1080
Δρmap, eÅ^{-3}	0.493; –0.329	0.435; –0.316

$R(F) = 3|F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^2$, $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$. [a] Crystallographic data for **6a** agree with those published earlier[10c]. [b] $I > 2\sigma(I)$.

{η^5:η^1(*N*)-1-[(*tert*-Butylamido)dimethylsilyl]-2,3,4,5-tetramethylcyclopentadienyl}-dichlorotitanium(IV) (**6a**)

MS (115 °C, *m/z* (relative abundance)): 367 ($M^{\bullet+}$, 0.4), 356 (18), 355 (20), 354 (73), 353 (34), 352 ([M – Me]$^+$, 100), 351 (11), 350 (10), 298 (9), 297 (7), 296 ([M – Me – $Me_2C{=}CH_2$]$^+$, 12), 295 (7), 169 (5), 73 (7), 59 (10), 58 (7), 57 (6), 41 (10). ^{1}H NMR (C_6D_6): 0.43 (s, 6 H, $SiMe_2$); 1.42 (s, 9 H, CMe_3); 1.99, 2.00 (2 × s, 6 H, Me_4C_5). $^{13}C\{^1H\}$ NMR (C_6D_6): 5.4 ($SiMe_2$); 13.0, 13.1 (**Me**$_4C_5$); 32.7 (C**Me**$_3$); 62.1 (CMe_3); 104.0 (Me_4C_5, C-Si); 137.9, 140.6 (Me_4C_5, C-Me) (*cf*. ref.[9c]). IR (KBr): 2 954 (vs), 2 900 (s), 2 860 (s), 1 466 (s), 1 390–1 360 (s,b), 1 320 (s), 1 254 (vs), 1 230 (w), 1 214 (m), 1 180 (vs), 1 087 (m), 1 020 (s), 986 (vs), 920 (m), 840 (vs), 814 (s), 793 (s), 766 (vs), 687 (m), 660 (m), 540 (w), 514 (vs), 497 (m).

Crystal Structure Analysis of **6a** and **6d**

Fragments of yellow crystals of complexes **6a** and **6d** were inserted into Lindemann glass capillaries in a glove box. Diffraction data for **6a** were collected on a Nonius KappaCCD diffractometer with CCD area detector and those for **6d** on an Enraf–Nonius CAD-4 MACH III diffractometer using graphite monochromated MoKα radiation (λ = 0.71069 Å), both at room temperature. The structures were solved by direct methods (SIR-92, ref.[25]). The non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **6a** were included in calculated positions. Hydrogen atoms in **6d** were identified on difference Fourier electron density maps and isotropically refined with the exception of hydrogen atoms of the *tert*-butyl group which were fixed in calculated positions. Refinement by full-matrix least-squares on F^2 was performed using the SHELXL97 program[26]. Crystallographic data, details of their collection and the structure refinement are given in Table II. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers: CCDC-158989 (for **6a**) and CCDC-158988 (for **6d**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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