Cationic species derived from the η^1-amidosilyl-η^5-cyclopentadienyl dimethyl titanium complex.
Crystal structure of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}\{CH_2B(C_6F_5)_2\}(C_6F_5)]$
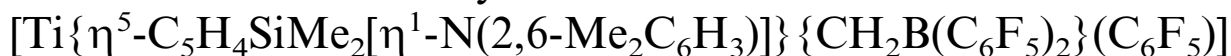
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Abstract

Reactions of the η^5-cyclopentadienyl-η^1-amido dimethyl titanium derivative $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}Me_2]$ (1) with tris(pentafluorophenyl)borane $B(C_6F_5)_3$ in hexane at room temperature yield a thermally stable bright yellow microcrystaline solid identified by elemental analysis as $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}Me\{MeB(C_6F_5)_3\}]$ (2). A solution of 1 in CD_2Cl_2 at $-78°C$ affords the ion-pair complex 2, while in C_6D_6 it is slowly converted into the new neutral complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2\text{-}[\eta^1\text{-}N(C_6H_3Me_2)]\}\{CH_2B(C_6F_5)_2\}(C_6F_5)]$ (3). Complex 3 is the unique product obtained after stirring compound 2 or a mixture of complex 1 and $B(C_6F_5)_3$ in toluene or benzene for 12 h at room temperature. The molecular structure of complex 3 has been determined by diffraction methods. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Amido-silylcyclopentadienyl; Cationic alkyltitanium complexes; Titanium

1. Introduction

Currently there is interest in the synthesis of η^5-cyclopentadienyl-η^1-amido metal catalysts (CGC) derived from the *ansa*-metallocene by replacement of one of the cyclopentadienyl rings by a three-electron-donor amido group. These compounds are alternatives to Kaminsky and Brintzinger type catalysts, and provide highly active systems that produce ethylene/α-olefin copolymerisation with remarkable properties [1]. Two general strategies are employed to develop efficient synthetic procedures for these complexes. The metathetical reaction of the dilithium salt of the $[(C_5R_4)SiMe_2NR']^{2-}$ dianions affords dichloro derivatives $[M\{(C_5R_4)\text{-}SiMe_2NR'\}Cl_2]$ (M = Ti, Zr, Hf) [2], and the reaction of homoleptic metal amides $M(NR'_2)_4$ with the bifunctional $[(C_5R_4H)SiMe_2NHR']$ ligand via amine elimination produces diamido compounds $[M\{(C_5R_4)\text{-}$

$SiMe_2NR'\}(NR'_2)_2]$ [3]. A less general synthetic route restricted to titanium and non-substituted cyclopentadienyl rings [4,5] uses the reaction of the suitable chlorodimethylsilyl-substituted monocyclopentadienyl titanium complex $[Ti(C_5H_4SiMe_2Cl)Cl_3]$ [6] with primary alkyl or aryl amines to give the dichloro derivatives.

Very recently, we have shown that complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}Cl_2]$ can be readily converted, at room temperature, into the dialkyl and diamido complexes $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3\text{-}Me_2)]\}X_2]$ (X = alkyl or NMe_2) or into the monoalkyl derivative $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}MeCl]$ by salt metathesis using Grignard, organolithium or organoaluminium reagents [4b]. The dialkyl complexes are precursors of the active cationic species when treated with perfluoroaryl boranes and borates [7]. However, few studies have been reported for this type of η^5-cyclopentadienylsilyl-η^1-amido titanium derivative [8]. Here, we present the reactions of the dialkyl titanium derivative $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3\text{-}Me_2)]\}Me_2]$ (1) with tris(pentafluorophenyl)borane $B(C_6F_5)_3$ in different solvents.

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2. Results and discussion

The reaction of the dimethyl complex [Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N($C_6H_3Me_2$)]}Me$_2$] (1) with the strong Lewis acid B(C_6F_5)$_3$ has been studied using different solvents. A mixture of compound 1 and B(C_6F_5)$_3$ in hexane at room temperature afforded a high yield of a thermally stable bright yellow microcrystalline solid, which was identified as [Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N($C_6H_3Me_2$)]}Me{MeB(C_6F_5)$_3$}] (2) by elemental analysis. Crystals of this compound were not suitable for X-ray diffraction studies and therefore its structure could only be investigated in solution.

The ^{1}H-NMR spectrum of a CD$_2$Cl$_2$ solution of this compound recorded at $-78°$C indicated that the [MeB(C_6F_5)$_3$]$^-$ anion was coordinated to the acidic titanium centre, as evidenced by the broad signal due to the Ti–CH$_3$B system observed at δ 0.38 and the large chemical shift difference of $\Delta\delta = \delta m - \delta p = 5.03$ between the m- and p-resonances observed in the ^{19}F-NMR spectrum [9]. Moreover, exactly the same spectral data were obtained from a CD$_2$Cl$_2$ solution prepared by mixing compound 1 and B(C_6F_5)$_3$ in a molar ratio of 1:1 in a sealed NMR tube at $-60°$C. This behaviour allows the species present in solution to be formulated as the ion-pair complex [Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N($C_6H_3Me_2$)]}Me{MeB(C_6F_5)$_3$}] (2). This formulation is consistent with the other signals observed in the ^{1}H-NMR spectrum, which shows an ABCD spin system for the cyclopentadienyl ring protons as well as two different methyl groups for the SiMe$_2$ bridging group and for the N($C_6H_3Me_2$) fragment. These results indicate the presence of a chiral metal center. One singlet was also observed for the titanium bound terminal methyl group. The ^{13}C{^{1}H}-NMR spectrum shows a resonance at δ 72.0 due to the Ti–Me carbon, along with the rest of the signals attributed to the ancillary dianionic ligand {η^5-$C_5H_4SiMe_2[\eta^1$-N($C_6H_3Me_2$)]}$^{2-}$ consistent with the indicated symmetry. The chemical shift of the cyclopentadienyl C$_{ipso}$ atom is typically shifted upfield from the other ring carbon resonances and is therefore diagnostic of chelation of the appended amido group in complex (2) [6]. A similar ion-pair coordination has been suggested for the more electron rich and sterically encumbered complex [Ti{η^5-$C_5Me_4SiMe_2(\eta^1$-N^{t}Bu)}Me{MeB(C_6F_5)$_3$}] [8b].

When the reaction of 1 with B(C_6F_5)$_3$ was carried out in an aromatic solvent (toluene or benzene), a mixture of complex 2 and a new compound [Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N($C_6H_3Me_2$)]}{CH$_2$B(C_6F_5)$_2$}(C_6F_5)] (3) was formed in less than 5 min. When the mixture was allowed to stir for longer periods only 3 was detected. Complex 2 decomposes over a number of hours via methane evolution to give 3 as orange crystals after extraction into hexane and cooling at $-40°$C. Similar

behaviour has been observed in the reaction of either the chelating diamido complex [Ti{(2,6-^{i}Pr$_2C_6H_3$)-N(CH$_2$)$_3$N(2,6-^{i}Pr$_2C_6H_3$)}Me$_2$] or o-arylphenoxide-cyclopentadienyl complexes [Ti(C_5H_5)(OAr)Me$_2$] with B(C_6F_5)$_3$ to afford [Ti{(2,6-^{i}Pr$_2C_6H_3$)N(CH$_2$)$_3$N(2,6-^{i}Pr$_2C_6H_3$)}{CH$_2$B(C_6F_5)$_2$}(C_6F_5)] [10] or [Ti(C_5H_5)-(OAr){CH$_2$B(C_6F_5)$_2$}(C_6F_5)] [11], respectively. The ^{1}H- and ^{13}C-NMR spectra of 3 are consistent with C_1 symmetry. The diastereotopic methylene protons Ti–CH$_2$–B appear as two broad resonances at δ 3.92 and 3.14 in the ^{1}H-NMR spectrum and one broad signal at δ 110.5 is observed in the corresponding ^{13}C-NMR spectrum. The ^{19}F-NMR spectrum at room temperature shows the presence of two different pentafluorophenyl groups, consistent with the migration of one C_6F_5 group to the titanium atom. The Ti–C_6F_5 resonances at δ 115.3 (2F, $ortho$), 154.2 (1F, $para$) and 164.0 (2F, $meta$) and the CH$_2$B(C_6F_5)$_3$ resonances compare well with those found in the [Ti{(2,6-^{i}Pr$_2C_6H_3$)N-(CH$_2$)$_3$N(2,6-^{i}Pr$_2C_6H_3$)}{CH$_2$B(C_6F_5)$_2$}(C_6F_5)] [10] complex discussed above and in other similar complexes [12].

The structures proposed for the new complexes 2 and 3 are shown in Scheme 1 and their spectroscopic and analytical data are collected in Section 4.

Orange crystals of 3, suitable for X-ray diffraction, were obtained from its hexane solution after slow cooling. The molecular structure of 3 is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1.

The titanium centre is in a pseudo-tetrahedral environment defined by a chelate silylamido σ-N coordinated η^5-cyclopentadienyl ligand, a pentafluorophenyl group and a methylboron fragment. The Ti–Cp$_{cent}$ distance of 2.033 Å is slightly longer than the corresponding distance in [Ti{η^5-$C_5H_4SiMe_2[\eta^1$-N($C_6H_3Me_2$)]}Cl$_2$] (2.016 Å), although the Ti–N bond distance of 1.911(4) Å and the Cp$_{cent}$–Ti–N angle of 105.3° are comparable to those found in this complex (1.914(3) Å and 105.1°, respectively) [4b] and in other related η^5-cyclopentadienylsilyl-η^1-amido metal derivatives [5,13]. However, the Cp$_{cent}$–Ti–N angle in 3 is considerably smaller than in similar unlinked Cp-amido or Cp-arylphenoxide complexes such as [Ti(C_5H_5)(N^{i}Pr$_2$)Cl$_2$] (116.2°) [14] or [Ti(C_5H_5)(OAr)Cl$_2$] (123.7°) [11], or than the N–Ti–N angle in diamido complexes such as [Ti{N-(SiMe$_3$)$_2$}$_2$(CH$_2$Ph)$_2$] (120.6°) [15], but larger than that observed in bidentate diamide derivatives of the type [Ti{η^1-N(2,6-^{i}Pr$_2C_6H_3$)(CH$_2$)$_3\eta^1$-N(2,6-^{i}Pr$_2C_6H_3$)}Cl$_2$] (99.2(2)°) [16]. The coordination geometry of both N and B atoms is trigonal planar, consistent with sp^2 hybridization. The Ti–C6–B angle of 114.9(4)° is close to sp^3 hybridization for the methylene carbon atom but is smaller than that found in the analogous bidentate diamide [Ti{η^1-N(2,6-^{i}Pr$_2C_6H_3$)(CH$_2$)$_3\eta^1$-N(2,6-^{i}Pr$_2C_6H_3$)}{CH$_2$B(C_6F_5)$_2$}(C_6F_5)] (125.1(3)°) [10]

Scheme 1.
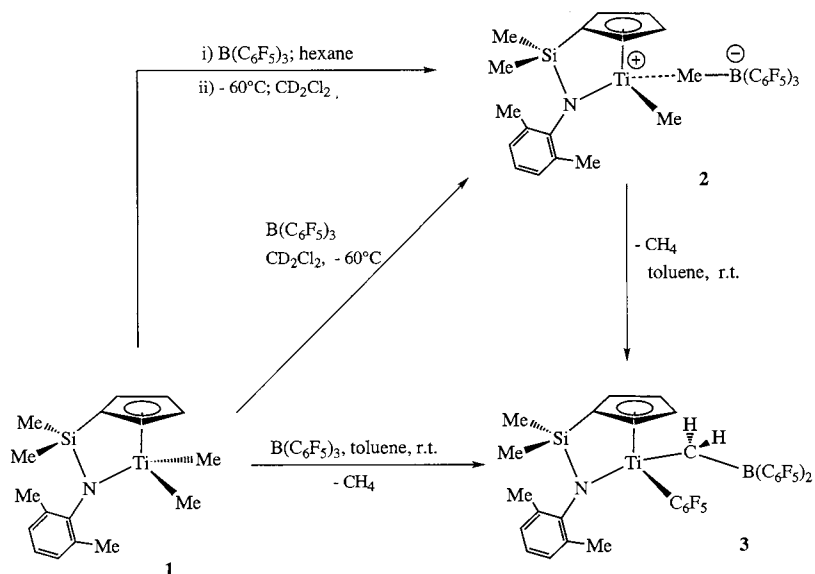
where the deviation is due to steric interaction between the $B(C_6F_5)_2$ moiety and the C_6F_5 group bonded to titanium. The Ti–CH$_2$ bond distance in **3** (2.169(5) Å) is slightly larger than that observed in the latter compound (2.111(4) Å) and this is probably the reason for an acute angle in **3**.

3. Conclusions

The reaction of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}\text{-}Me_2]$ (**1**) with $B(C_6F_5)_3$ has been investigated in different solvents. The ion-pair complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}Me\{MeB(C_6F_5)_3\}]$ (**2**) was detected in the polar and poorly coordinating solvent CD_2Cl_2 at low temperature, but decomposed to unidentified complexes above −10°C. However, **2** was formed at r.t. in aromatic solvents although it decomposed slowly to give the neutral compound $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(C_6H_3Me_2)]\}\{CH_2B(C_6F_5)_2\}(C_6F_5)]$ (**3**) with evolution of methane. This behaviour is different from that observed for the analogous cationic metallocene complexes, but similar to the decomposition pathway observed for analogous monocyclopentadienyl-arylphenoxide $[Ti(C_5H_5)(OAr)Me_2]$, chelating diamido or $[Ti\{(2,6\text{-}^iPr_2C_6H_3)N(CH_2)_3N(2,6\text{-}^iPr_2C_6H_3)\}\text{-}Me_2]$ complexes with $B(C_6F_5)_3$.

4. Experimental

4.1. General considerations

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model HE-63 or MBraun. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane, sodium-benzophenone for THF and CaH_2 for acetonitrile). The tris(pentafluorophenyl)-borane [17] and $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6\text{-}H_3)]\}Me_2]$ (**1**) [4b] were prepared according to literature procedures. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. NMR spectra were recorded on a Varian Unity 300 (^{1}H-NMR at 300 MHz, ^{19}F-NMR at 282 MHz and ^{13}C-NMR at 75 MHz) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in δ units relative to a TMS standard while ^{19}F was referenced to $CFCl_3$.
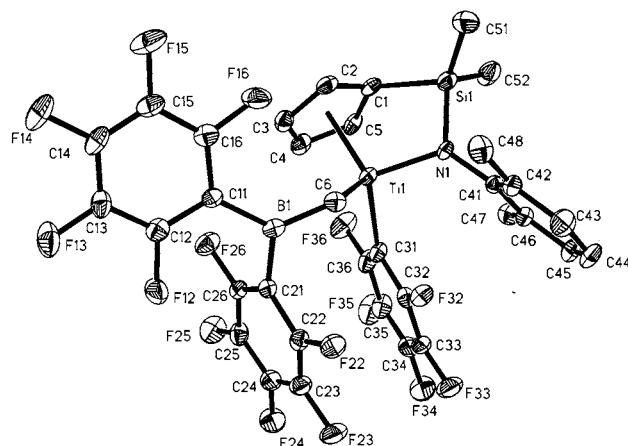

Fig. 1. ORTEP view of the molecular structure of compound **3** with atom-numbering scheme.

Table 1
Bond lengths (Å) and angles (°) for **3**

Bond lengths	
Ti(1)–N(1)	1.911(4)
Ti(1)–C(6)	2.169(5)
Ti(1)–C(31)	2.204(5)
Ti(1)–C(1)	2.304(5)
Ti(1)–C(5)	2.327(5)
Ti(1)–C(2)	2.336(5)
Ti(1)–C(3)	2.408(5)
Ti(1)–C(4)	2.418(5)
Ti(1)–Si(1)	2.948(2)
Si(1)–N(1)	1.749(4)
Si(1)–C(51)	1.829(6)
Si(1)–C(52)	1.845(6)
Si(1)–C(1)	1.853(6)
N(1)–C(41)	1.439(5)
B(1)–C(6)	1.483(8)
B(1)–C(11)	1.602(8)
B(1)–C(21)	1.596(7)
Ti(1)–Cp	2.033
Bond angles	
N(1)–Ti(1)–C(6)	107.35(18)
N(1)–Ti(1)–C(31)	102.79(17)
C(6)–Ti(1)–C(31)	107.66(19)
N(1)–Si(1)–C(51)	113.5(3)
N(1)–Si(1)–C(52)	115.7(2)
C(51)–Si(1)–C(52)	110.1(3)
N(1)–Si(1)–C(1)	89.6(2)
C(41)–N(1)–Si(1)	127.5(3)
C(41)–N(1)–Ti(1)	125.3(3)
Si(1)–N(1)–Ti(1)	107.23(18)
C(6)–B(1)–C(11)	125.6(5)
C(6)–B(1)–C(21)	117.0(5)
C(11)–B(1)–C(21)	117.3(5)
B(1)–C(6)–Ti(1)	114.9(4)
N(1)–Ti(1)–Cp	105.3
C(31)–Ti(1)–Cp	116.6
C(6)–Ti(1)–Cp	115.9
Si(1)–C(19–Cp	151.3

4.2. Synthesis of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Me\{MeB(C_6F_5)_3\}]$ (2)

A mixture of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Me_2]$ (1) (50 mg, 0.156 mmol) and $B(C_6F_5)_3$ (80 mg, 0.156 mmol) in hexane (100 ml) was stirred at r.t. for 12 h in a glovebox affording a bright yellow precipitate slowly. After the solvent was completely removed by filtration, the solid was washed with hexane and dried in vacuo to give complex **2** (113 mg, 87%) as yellow microcrystals. Anal. Calc. for. $C_{35}H_{25}F_{15}NBSiTi$: C: 50.56; H: 3.03; N: 1.68. Found: C: 50.94; H: 3.41; N: 2.12%.

4.2.1. In situ generation of 2
$[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}Me_2]$ (1) (50 mg, 0.156 mmol) and $B(C_6F_5)_3$ (80 mg, 0.156 mmol) was dissolved in CD_2Cl_2 at $-78°C$ in a sealed NMR

tube. The NMR spectrum was recorded at $-60°C$ to give complex **2** as the sole spectroscopic compound. ^{1}H-NMR (C_6D_6, 293 K): δ 6.90 (m, $2H_{meta}$, $C_6H_3Me_2$); 6.79 (m, $1H_{para}$, $C_6H_3Me_2$); 6.47 (m, 1H, C_5H_4); 6.20 (m, 1H, C_5H_4); 6.02 (m, 1H, C_5H_4); 5.44 (m, 1H, C_5H_4); 1.54 (s, 3H, $C_6H_3Me_2$); 1.26 (s, 3H, $C_6H_3Me_2$); 0.94 (s, 3H, TiMe); 0.65 (br, 3H, $MeB(C_6F_5)_3$); -0.16 (s, 3H, $SiMe_2$); -0.22 (s, 3H, $SiMe_2$). ^{1}H-NMR (CD_2Cl_2, 213 K): δ 7.61 (m, 1H, C_5H_4); 7.19 (m, $1H_{meta}$, $C_6H_3Me_2$, $J_{H-H} = 7.0$ Hz); 7.05 (t, $1H_{para}$, $C_6H_3Me_2$, $J_{H-H} = 7.7$ Hz); 6.87 (m, $1H_{meta}$, $C_6H_3Me_2$, $J_{H-H} = 7.3$ Hz); 6.60 (m, 2H, C_5H_4); 6.30 (m, 1H, C_5H_4); 1.93 (s, 3H, $C_6H_3Me_2$); 1.37 (s, 3H, $C_6H_3Me_2$); 1.29 (s, 3H, TiMe); 0.51 (s, 3H, $SiMe_2$); 0.46 (s, 3H, $SiMe_2$); 0.38 (br, 3H, $MeB(C_6F_5)_3$). ^{13}C-NMR (CD_2Cl_2, 213 K): δ 147.5 (d, C_{ortho} of C_6F_5, $J_{C-F} = 232.6$ Hz); 144.8 (C_{ipso} of $C_6H_3Me_2$); 138.5 (d, C_{para} of C_6F_5, $J_{C-F} = 238.0$ Hz); 136.1 (d, C_{meta} of C_6F_5, $J_{C-F} = 249.1$ Hz); 130.6 (C_{ortho} of $C_6H_3Me_2$); 129.2, 128.6, 128.1 ($C_6H_3Me_2$ or C_5H_4); 127.7 (C_{ortho} of $C_6H_3Me_2$); 126.2, 124.6, 124.3, 120.5 ($C_6H_3Me_2$ or C_5H_4); 111.1 (C_{ipso} of C_5H_4); 72.0 (TiMe); 40.5 ($MeB(C_6F_5)_3$); 19.0 ($C_6H_3Me_2$); 18.5 ($C_6H_3Me_2$); -1.1 ($SiMe_2$); 1.3 ($SiMe_2$). ^{19}F-NMR (CD_2Cl_2, 213 K): δ -136.0 ($6F_{ortho}$, C_6F_5); -161.1 ($3F_{para}$, C_6F_5); -166.15 ($6F_{meta}$, C_6F_5); ($\Delta\delta = \delta_{meta} - \delta_{para} = 5.0$).

4.3. Synthesis of $[Ti\{\eta^5\text{-}C_5H_4SiMe_2[\eta^1\text{-}N(2,6\text{-}Me_2C_6H_3)]\}\{CH_2B(C_6F_5)_2\}(C_6F_5)]$ (3)

4.3.1. Method A
A solution of complex **2** (113 mg, 0.136 mmol) in toluene (15 ml) was stirred at r.t. for 12 h in a glovebox. After the solvent was completely removed under vacuum, the oily material was extracted into hexane (50 ml) and the solution filtered. The solution was concentrated and cooled to $-40°C$ to give complex **3** (97 mg, 83%) as red–orange crystals.

4.3.2. Method B
A mixture of complex **1** (50 mg, 0.156 mmol) and $B(C_6F_5)_3$ (80 mg, 0.156 mmol) in toluene (15 ml) was stirred at r.t. for 12 h. Following the procedure described above, complex **3** was obtained (0.1 g, 85%). Anal. Calc. for $C_{34}H_{21}F_{15}NBSiTi$: C: 50.08; H: 2.59; N: 1.72. Found: C: 49.76; H: 2.91; N: 2.03%. ^{1}H-NMR (C_6D_6, 298 K): δ 7.35 (m, 1H, C_5H_4); 7.07 (m, 1H, C_5H_4); 6.88–6.97 (m, 3H, $C_6H_3Me_2$); 6.48 (m, 1H, C_5H_4); 6.43 (m, 1H, C_5H_4); 4.15 (br, 1H, $TiCH_2B$); 3.15 (br, 1H, $TiCH_2B$); 1.92 (s, 3H, $C_6H_3Me_2$); 1.24 (s, 3H, $C_6H_3Me_2$); -0.02 (s, 3H, $SiMe_2$); -0.08 (s, 3H, $SiMe_2$). ^{1}H-NMR (CD_2Cl_2, 298 K): δ 7.53 (m, 1H, C_5H_4); 7.30 (m, 1H, C_5H_4); 7.17 (m, 1H, $C_6H_3Me_2$, $J_{H-H} = 6.6$ Hz); 7.02 (m, 2H, $C_6H_3Me_2$, $J_{H-H} = 6.6$ Hz); 6.88 (m, 1H, C_5H_4); 6.79 (m, 1H, C_5H_4); 3.92 (br, 1H, $TiCH_2B$); 3.14 (br, 1H, $TiCH_2B$); 2.08 (s, 3H, $C_6H_3Me_2$); 1.41 (s, 3H, $C_6H_3Me_2$); 0.52 (s, 3H, $SiMe_2$);

0.45 (s 3H, SiMe$_2$). ^{13}C-NMR (CD$_2$Cl$_2$, 298 K): δ 150–134 (C$_6$F$_5$); 148.5 (C$_{ipso}$ of C$_6$H$_3$Me$_2$); 131.3 (C$_6$H$_3$Me$_2$ or C$_5$H$_4$); 130.1 (C$_{ortho}$ of C$_6$H$_3$Me$_2$); 129.3, 128.8 (C$_6$H$_3$Me$_2$ or C$_5$H$_4$); 128.6 (C$_{ortho}$ of C$_6$H$_3$Me$_2$); 128.4, 125.9, 125.4, 120.8 (C$_6$H$_3$Me$_2$ or C$_5$H$_4$); 110.8 (C$_{ipso}$ of C$_5$H$_4$); 110.5 (C of TiCH$_2$B); 19.6 (C$_6$H$_3$Me$_2$); 19.5 (C$_6$H$_3$Me$_2$); −0.6 (SiMe$_2$); −1.3 (SiMe$_2$). ^{19}F-NMR (CD$_2$Cl$_2$, 298°K): δ −115.3 (d, 2F$_{ortho}$, TiC$_6$F$_5$); −132.0 (br, 4F$_{ortho}$, B(C$_6$F$_5$)$_2$); −151.0 (br, 2F$_{para}$, B(C$_6$F$_5$)$_2$); −154.2 (t, 1F$_{para}$, TiC$_6$F$_5$); −164.0 (t, 2F$_{meta}$, TiC$_6$F$_5$); −164.3 (br, 4F$_{meta}$, B(C$_6$F$_5$)$_2$).

4.4. X-ray structure determination of 3

Crystals of compound **3** were obtained by crystallisation from hexane and a suitable sized crystal was mounted in a Lindemann tube, which was then mounted in an Enraf–Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystallographic and experimental details are summarised in Table 2. Data

Table 2
Crystal, experimental data and structure refinement procedures for compound **3**

Formula	C$_{34}$H$_{21}$F$_{15}$,B,N,Si,Ti
M$_w$	815.32
Crystal habit	Prismatic
Colour	Red–orange
Crystal size (mm)	$0.25 \times 0.28 \times 0.30$
Symmetry	Monoclinic $P2_1/n$
Unit cell dimensions	
a (Å)	11.292(3), 17.166(4), 18.057(5)
b (Å)	
c (Å)	
β (°)	105.54(1)
V (Å^3)	3372(1)
Z	4
D_{calc} (g cm^{-3})	1.606
$F(000)$	1632
μ (cm^{-1})	4.00
Scan mode	$\omega/2\theta$ $2.22 < \theta < 25.02$
No. of reflections measured	6254
Independent observed	5937 ($R_{int} = 0.037$)
Observed	2711 ($I > 2\sigma(I)$)
Range of hkl	$0 < h < 13$, $0 < k < 20$, $-21 < l < 20$
Standard reflections	3 every 200 reflections
Refinement method	Full matrix least squares on F^2.
Final R indices ($I > 2\sigma(I)$) [a]	$R_1 = 0.0585$, $wR_2 = 0.1147$
Weighting scheme	Calc $w = 1/[s^2(F_o^2) + (0.0630P)_2 + 0P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole (e Å^{-3})	0.262, −0.271
Goodness of fit on F^2	0.979

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; $wR_2 = \{[\Sigma \omega((F_o^2 - F_c^2)/[\Sigma \omega(F_o^2)_2]\}^{1/2}$.

were collected at r.t. Intensities were corrected for Lorenz and polarisation effects in the usual manner. No absorptions or extinctions were made. The structure was solved by direct methods (SHELXL90) [18] and refined by least squares against F^2 (SHELXL93) [19]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with fixed thermal parameters. Calculations were carried out on an ALPHA AXP (Digital) workstation.

5. Supplementary material

The supplementary material includes a list of the positional parameters and their standard deviations, a complete list of bond lengths and angles, anisotropic displacement parameters, the calculated fractional coordinates of the hydrogen atoms and a list of observed and calculated structure factors. This is available on request from the authors. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre, CCDC no. 116437. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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