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The synthesis of half-sandwich bis(pentafluorophenyl)boryl-substituted cyclopentadienyl zirconium, niobium and tantalum complexes and the isolation and molecular structure of a zwitterionic niobocene

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Reaction of $B(C_5H_4SiMe_3)(C_6F_5)_2$ with MCl_5 (M = Nb, Ta) leads to the first group 5 borylcyclopentadienyl half-sandwich complexes $MCl_4\{C_5H_4B(C_6F_5)_2\}$ (**1** and **2**). In contrast, the reaction with $ZrCl_4$ gives the metallocene $ZrCl_2\{C_5H_4B(C_6F_5)_2\}_2$ (**3**). The use of $ZrCl_4(SMe_2)_2$ instead of $ZrCl_4$ as starting material allows the isolation of the monocyclopentadienyl zirconium complex $ZrCl_3\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**4**). The utility of LiCp′ as a general route to zirconocenes is demonstrated by the synthesis of $ZrCl_2(Cp)\{C_5H_4B\ (C_6F_5)_2(SMe_2)\}$ (**5**) and $ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**6**) (Ind = η^5-indenyl). Boron-substituted niobocenes are prepared through the dehalostannylation reaction between the half-sandwich complexes and tin-substituted cyclopentadienes. They adopt zwitterionic structures in which a chloride ligand is transferred to boron, for example $Nb^{(+)}Cl_2(C_5H_4SiMe_3)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}$ (**9**). The crystal structure of **9** has been determined by X-ray crystallography. Reaction of the strong base, pyridine, with the borylcyclopentadienyl complexes $TiCl_3\{C_5H_4B(C_6F_5)_2\}$, $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2\}$ and **1**–**6** leads to the generation of a series of pyridine adducts (**10**–**17**) in which the pyridine is bound to boron. The solid-state structures of the four coordinate adducts $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}$ (**10**) and $TiCl_3\{C_5H_4B(C_6F_5)_2(py)\}$ (**14**) are described. The half-sandwich zirconium and niobium complexes **15** and **16** are shown by spectroscopic and structural methods to coordinate a further one (Nb) or two (Zr) equivalents of pyridine to attain an octahedral geometry at the metal centre. The zwitterionic complexes **8** and **9** do not react with pyridine.

Introduction

Early transition metal complexes with boron Lewis acid-substituted cyclopentadienyl ligands are of interest because of their unique structural and chemical properties. The first boryl half-sandwich titanium complexes $TiCl_3\{C_5H_3RBX_2\}$ (R = H, Me; X = Cl, Br, OEt, Me) (Structure **I**, Chart 1) were prepared in 1979 by a dehalosilylation route.[1] More recently a similar approach was used to prepare $TiCl_3\{C_5H_4BX_2\}$ ($X = C_6H_5, C_6F_5$).[2,3] A dehalosilylation route was also employed by Reetz to synthesise a series of boryl-substituted zirconocenes $ZrCl_2\{C_5H_4BX_2\}_2$ (**II**) and $ZrCl_2(Cp)\{C_5H_4BX_2\}$ (X = Me, Et, OEt, C_6F_5).[4] We reported the first synthesis of boryl-titanocenes, $TiCl_2(Cp')\{C_5H_4B(C_6F_5)_2\}$ (Cp′ = C_5H_5 (**III**), C_9H_7, $C_5H_4SiMe_3$), by reacting $TiCl_3\{C_5H_4B(C_6F_5)_2\}$ with LiCp′.[5]

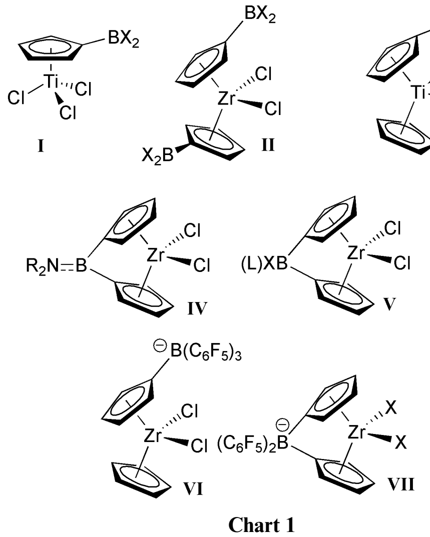

Chart 1

Other metallocene complexes with Lewis acidic substituents have been made by the hydroboration of allyl-Cp complexes with $HB(C_6F_5)_2$.[6,7] A number of related boron-bridged *ansa*-titanocenes and *ansa*-zirconocenes have been reported where the Lewis acidity is attenuated by a π-bonding substituent (**IV**)[8–10] or coordination of a base, L (**V**).[11,12] There are also examples of anionic borato-substituted complexes, introduced as borato-substituted cyclopentadienyl ligands[13,14] or formed through the electrophilic substitution reaction of a metallocene complex (**VI**).[15–17] Most recently borato-bridged *ansa*-zirconocenes of type (**VII**) have been prepared.[18,19]

Cyclopentadienyl complexes with Lewis acidic bis(pentafluorophenyl)boryl-substituents were initially of interest as self-activating alkene polymerisation catalysts.[3,4] However, both boron-based Lewis acids[20] and early transition metal cyclopentadienyl complexes are employed in an ever-increasing array of synthetic and catalytic reactions. There is increasing interest in using a combination of organometallic compounds with Lewis acids.[21] The attraction of borylcyclopentadienyl complexes stems from the intramolecular combination of metal and Lewis acid reactivity. One of the goals of our research is to utilise interactions between groups bound to the metal centre and the boron substituent. We have demonstrated that intramolecular Ti–Cl activation takes place in boryl-substituted titanocene complexes.[5] The object of the present study is to learn more about the prevalence of these interactions and how they depend upon both electronic (Lewis acidity of boron and metal) and steric (interligand distances and angles) parameters, in particular whether such interactions are possible for complexes other than titanocenes.

Here we present the synthesis of the first half-sandwich and metallocene borylcyclopentadienyl complexes of niobium, tantalum and zirconium. A general method for the preparation of borylcyclopentadienyl zirconocenes and the first niobocenes are described. The reactivity of borylcyclopentadienyl complexes towards Lewis bases is explored and a

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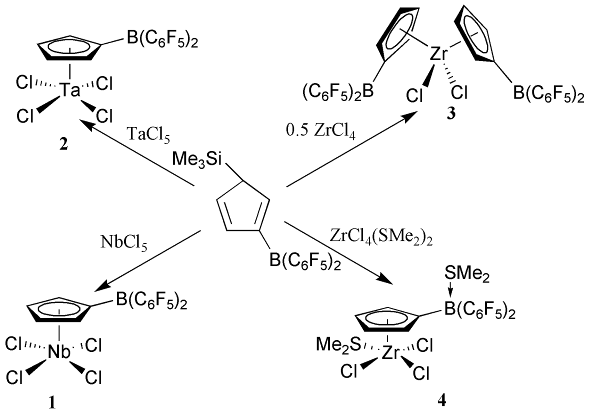
number of pyridine adducts have been isolated and structurally characterised.

Results and discussion

Synthesis and characterisation of new borylcyclopentadienyl complexes

We have previously reported that the reaction of $B(C_5H_4SiMe_3)(C_6F_5)_2$ with one equivalent of $TiCl_4$ leads to dehalosilylation and the formation of $TiCl_3\{C_5H_4B(C_6F_5)_2\}$.[3] The reaction with $NbCl_5$ or $TaCl_5$ (Scheme 1) in dichloromethane similarly leads to the orange–red $NbCl_4\{C_5H_4B(C_6F_5)_2\}$ (**1**) and yellow $TaCl_4\{C_5H_4B(C_6F_5)_2\}$ (**2**). These complexes are isolated following precipitation from the reaction medium and are sparingly soluble in hydrocarbon and halocarbon solvents. Solution NMR studies required solvation in THF-d_8. Spectroscopic data of all new compounds are collected in Table 1. The ^{11}B NMR signals are observed at δ 2.7 and 4.2 for **1** and **2** respectively, which is consistent with 4-coordinate boron following the formation of adducts with THF-d_8.

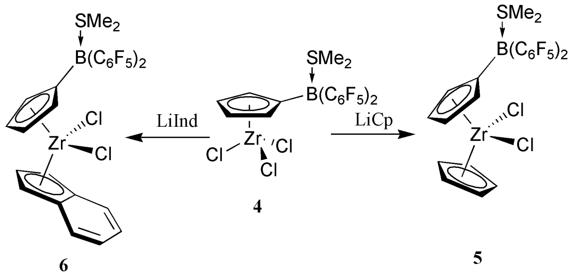


Scheme 1

The reaction with $ZrCl_4$ is not selective for the half-sandwich compound and leads to consecutive dehalosilylation reactions and formation of $ZrCl_2\{C_5H_4B(C_6F_5)_2\}_2$ (**3**). Although this compound has been described by Reetz,[4] full multinuclear NMR data were not given and are presented here in order to provide a comparison to the novel compounds. Purification of **3** proved difficult and a spectroscopically pure sample could only be obtained by recrystallisation from diethyl ether. No ^{11}B NMR signal for **3** was apparent at 20 °C in $CDCl_3$. At 80 °C in toluene-d_8 a broad peak at δ 60 was observed.

Dimethylsulfide has been demonstrated to modify the reactivity of $ZrCl_4$ towards dehalosilylation allowing the preparation of $ZrCl_3(Cp)\cdot L$ complexes.[22] The reaction of $ZrCl_4(SMe_2)_2$ with $B(C_5H_4SiMe_3)(C_6F_5)_2$ leads to the isolation of $ZrCl_3\{C_5H_4B(SMe_2)(C_6F_5)_2\}(SMe_2)$ (**4**). It appears that **4** slowly loses SMe_2 under vacuum, and integration of the ^1H NMR spectrum and elemental analysis indicates between 1 and 2 equivalents. Only one SMe_2 resonance is observed at 20 °C, implying rapid exchange between free SMe_2 and SMe_2 coordinated to the boron and zirconium Lewis acids. The ^{11}B NMR resonance is observed at δ 45, which is intermediate between three- and four-coordinate boron, again suggesting a rapid exchange.

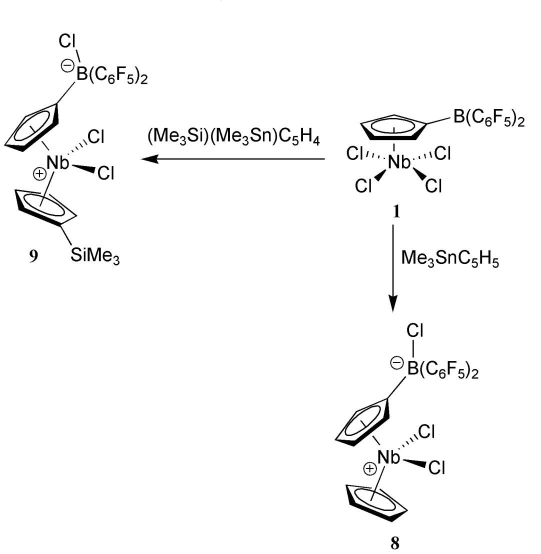
Reetz prepared $ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2\}$ by the dehalosilylation reaction between $ZrCl_3Cp$ and $B(C_5H_4SiMe_3)(C_6F_5)_2$. The application of this approach is restricted by the reduced tendency of substituted monocyclopentadienyl zirconium trichloride complexes to undergo dehalosilylation and the lack of accessibility of the base-free trichlorides.[23] Reaction of the half-sandwich complex **4** with LiCp′ (Cp′ = Cp or Ind) in a fashion analogous to that employed for boryl-substituted titanocenes facilitated the preparation of the representative zirconocene complexes $ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**5**) and $ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**6**) (Scheme 2). The presence of SMe_2 in the ^1H NMR spectra indicates that the complexes crystallise as the SMe_2 adducts. However, ^{11}B NMR ($CDCl_3$, 20 °C) chemical shifts at δ 45.0 and 39.7 for **5** and **6** respectively lie between the regions expected for three- and four-coordination and indicate partial dissociation in solution. Attempts to obtain a SMe_2-free sample by removing the SMe_2 under high vacuum or by repeated dissolution/solvent removal were not successful. The use of $B(C_6F_5)_3$ as a scavenger for SMe_2 did lead to the formation of $B(C_6F_5)_3\cdot SMe_2$ (**7**), which was confirmed by the preparation of an authentic sample (^{11}B NMR: δ 0.83). However, this approach, too, was unsatisfactory due to the similar solubility of **7** and the desired product.



Scheme 2

Unfortunately crystals suitable for X-ray diffraction were not obtained but the structure of these zirconocenes (Scheme 2) is clearly significantly different from that of the related titanocenes. It appears that the SMe_2 coordinated to boron is symptomatic of a reduced tendency to form Cp–B–Cl–M linkages of the sort exhibited by $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2\}$ (**III**). Indeed **III** does not form a SMe_2 adduct and the ^1H and ^{11}B NMR spectra remain largely unchanged on addition of several equivalents to a C_6D_6 solution.

Since the Cp–B–Cl–M interaction is not favourable in the boryl zirconocene dichlorides[24] we were interested in establishing whether such bridging chloride interactions were indeed unique to the boryl titanocenes. Having successfully prepared half-sandwich borylcyclopentadienyl complexes of niobium and tantalum, the corresponding metallocenes were an obvious target. It is well established that the reaction of monocyclopentadienyl complexes with LiCp, although successful for the group 4 metal complexes, is not suitable as a method of preparing niobium(V) metallocenes.[25] However, treatment of a dichloromethane suspension of **1**, with the non-reducing $SnMe_3(C_5H_5)$ (Scheme 3) gave a clear solution from which **8**



Scheme 3

Table 1 NMR data

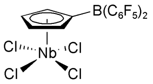
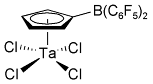
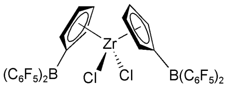
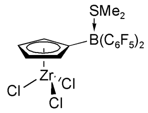
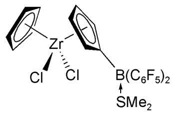
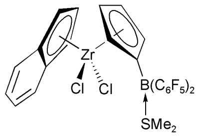
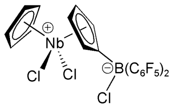
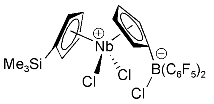
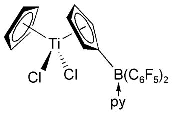
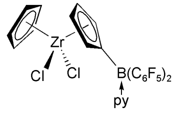
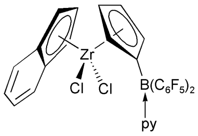
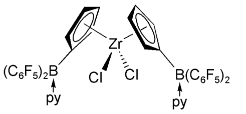
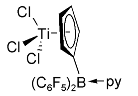
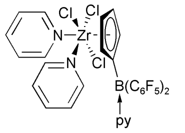
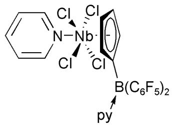
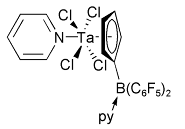
Complex	NMR data
$NbCl_4\{C_5H_4B(C_6F_5)_2\}$ (**1**)  	δ_H (300 MHz, THF-d_8, 20 °C) 7.72 (br, 2H, C_5H_4), 7.30 (br, 2H, C_5H_4) δ_C (75.47 MHz; THF-d_8, 20 °C) 139.09 (C_5H_4), 129.62 (C_5H_4) δ_B (96.29 MHz, THF-d_8, 20 °C) 2.7 δ_F (282.40 MHz, THF-d_8, 20 °C) −131.64 (br, 4F, *o*-F), −158.61 (d, 2F, *J*(FF) 20 Hz, *p*-F), −165.32 (t, 4F, *J*(FF) 18 Hz, *m*-F)
$TaCl_4\{C_5H_4B(C_6F_5)_2\}$ (**2**)  	δ_H (300 MHz, THF-d_8, 20 °C) 7.34 (br, 2H, C_5H_4), 6.90 (tr, 2H, *J* 2.5 Hz, C_5H_4) δ_C (75.47 MHz; THF-d_8; 20 °C) 134.85 (C_5H_4), 125.53 (C_5H_4) δ_B (96.29 MHz, THF-d_8, 20 °C) 4.2 δ_F (282.40 MHz, THF-d_8, 20 °C) −133.45 (t, 4F, *J*(FF) 19 Hz, *o*-F), −160.35 (d, 2F, *J*(FF) 20 Hz, *p*-F), −167.20 (t, 4F, *J*(FF) 21 Hz, *m*-F)
$ZrCl_2\{C_5H_4B(C_6F_5)_2\}_2$ (**3**)  	δ_H (300 MHz, $CDCl_3$, 20 °C) 6.40 (br, 4H, C_5H_4), 6.08 (tr, 2H, *J* 2.6 Hz, C_5H_4) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 126.93 (C_5H_4), 121.29 (C_5H_4) δ_B (96.29 MHz, $CDCl_3$, 20 °C) not observed δ_F (282.40 MHz, $CDCl_3$, 20 °C) −128.17 (d, 4F, *J*(FF) 20 Hz, *o*-F), −148.07 (t, 2F, *J*(FF) 21 Hz, *p*-F), −160.69 (d, 4F, *J*(FF) 20 Hz, *m*-F)
$ZrCl_3\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**4**)  	δ_H (300 MHz, $CDCl_3$, 20 °C) 6.91 (br, 2H, C_5H_4), 6.72 (tr, 2H, *J* 2.6 Hz, C_5H_4), 2.31 (s, 6H, $S(CH_3)_2$) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 126.69 (C_5H_4), 122.33 (C_5H_4), 21.05 ($S(CH_3)_2$) δ_B (96.29 MHz, $CDCl_3$, 20 °C) not observed δ_F (282.40 MHz, $CDCl_3$, 20 °C) −128.4 (br, 4F, *o*-F), −153.86 (br, 2F, *p*-F), −162.25 (br, 4F, *m*-F)
$ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**5**)  	δ_H (300 MHz, $CDCl_3$, 20 °C) 6.92 (br, 2H, C_5H_4), 6.74 (tr, 2H, *J* 2.6 Hz, C_5H_4), 6.50 (s, 5H, Cp), 2.14 (s, 6H, $S(CH_3)_2$) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 125.50 (C_5H_4), 120.70 (C_5H_4), 116.92 (Cp), 18.90 ($S(CH_3)_2$) δ_B (96.29 MHz, $CDCl_3$, 20 °C) 45.0 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −129.47 (d, 4F, *J*(FF) 23 Hz, *o*-F), −156.9 (t, 2F, *J*(FF) 20 Hz, *p*-F), −163.5 (d, 4F, *J*(FF) 21 Hz, *m*-F)
$ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (**6**)  	δ_H (300 MHz, $CDCl_3$, 20 °C) 7.66–7.63 (m, 2H, Ind), 7.35–7.32 (m, 2H, Ind) 6.80 (tr, 1H, *J* 3.4 Hz, Ind) 6.67 (br, 2H, C_5H_4), 6.51 (d, 2H, *J* 3.4 Hz, Ind) 6.32 (tr, 2H, *J* 2.5 Hz C_5H_4), 2.16 (s, 6H, $S(CH_3)_2$) δ_C (75.47 MHz; $CDCl_3$; 20 °C 126.93 (Ind), 125.44, 124.80 (C_5H_4), 122.02 (Ind), 119.79 (C_5H_4), 103.80 (Ind), 19.08 ($S(CH_3)_2$) δ_B (96.29 MHz, $CDCl_3$, 20 °C) 39.7 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −127.74 (d, 4F, *J*(FF) 22 Hz, *o*-F), −151.66 (t, 2F, *J*(FF) 21 Hz, *p*-F), −161.41 (d, 4F, *J*(FF) 21 Hz, *m*-F)
$B(C_6F_5)_3 \cdot SMe_2$ (**7**)	δ_H (300 MHz, $CDCl_3$, 20 °C) 2.17 δ_C (75.47 MHz; $CDCl_3$; 20 °C) 20.78 δ_B (96.29 MHz, $CDCl_3$, 20 °C) 0.83 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −130.15 (d, 6F, *J*(FF) 20 Hz, *o*-F), −154.41 (t, 3F, *J*(FF) 20 Hz, *p*-F), −162.45 (d, 6F, *J*(FF) 20 Hz, *m*-F)
$Nb^{(+)}Cl_2(Cp)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}$ (**8**)  	δ_H (300 MHz, $CDCl_3$, 20 °C) 7.59 (br, 2H, C_5H_4), 7.04 (s, 5H, Cp), 6.76 (br, 2H, C_5H_4) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 147.52 (d, *J*(CF) 235 Hz, *o*-C, C_6F_5), 139.74 (d, *J*(CF) 256 Hz, *p*-C, C_6F_5), 137.67 (d, *J*(CF) 254 Hz, *m*-C, C_6F_5), 130.96 (C_5H_4), 126.75 (C_5H_4), 123.10 (Cp). δ_B (96.29 MHz, $CDCl_3$, 20 °C) −2.9 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −131.4 (br, 4F, *o*-F), −158.9 (br, 2F, *p*-F), −164.0 (br, 4F, *m*-F)
$Nb^{(+)}Cl_2(C_5H_4SiMe_3)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}$ (**9**)  	δ_H (300 MHz, $CDCl_3$, 20 °C) 7.50 (m, 4H, C_5H_4B & C_5H_4Si), 6.95 (br, 2H, C_5H_4Si), 6.80 (br, 2H, C_5H_4B), 0.35 (s, 9H, $Si(CH_3)_3$) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 136.13 (C_5H_4Si), 129.74 (C_5H_4Si), −1.11 ($Si(CH_3)_3$)[b] δ_B (96.29 MHz, $CDCl_3$, 20 °C) −2.9 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −131.39 (d, 4F, *J*(FF) 17 Hz, *o*-F), −159.20 (tr, 2F, *J*(FF) 20 Hz, *p*-F), −164.34 (tr, 4F, *J*(FF) 23 Hz, *m*-F)
$TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}$ (**10**)  	δ_H (300 MHz, CD_2Cl_2, 20 °C) 9.00 (d, 2H, *J* 5.6 Hz, *o*-H, C_5H_5N), 8.19 (tr, 1H, *J* 7.7 Hz, *p*-H, C_5H_5N), 7.71 (tr, 2H, *J* 7.2 Hz, *m*-H, C_5H_5N), 6.51 (tr,2H *J* 2.6 Hz, C_5H_4), 6.46 (s, 5H, Cp), 6.36 (br, 2H, C_5H_4) δ_C (75.47 MHz; CD_2Cl_2; 20 °C) 147.86 *o*-C, C_5H_5N), 142. 77 (*p*-C, C_5H_5N), 127.83 (C_5H_4), 126.26 (*m*-C, C_5H_5N), 120.34 (Cp), 119.00 (C_5H_4) δ_B (96.29 MHz, CD_2Cl_2, 20 °C) 1.0 δ_F (282.40 MHz, CD_2Cl_2, 20 °C) −129.59 (d, 4F, *J*(FF) 23 Hz, *o*-F), −158.20 (t, 2F, *J*(FF) 20 Hz, *p*-F), −164.74 (d, 4F, *J*(FF) 20 Hz, *m*-F)

Table 1 (*Contd.*)

Complex	NMR data
$ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}$ (**11**) 	δ_H (300 MHz, $CDCl_3$, 20 °C) 8.78 (d, 2H, *J* 5.9 Hz, *o*-H, C_5H_5N), 8.18 (tr, 1H, *J* 7.7 Hz, *p*-H, C_5H_5N), 7.68 (tr, 2H, *J* 7.2 Hz, *m*-H, C_5H_5N), 6.49 (s, 5H, Cp), 6.38 (tr, 2H, *J* 2.6 Hz, C_5H_4), 6.21 (br, 2H, C_5H_4) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 147.86 *o*-C, C_5H_5N), 142.07 (*p*-C, C_5H_5N), 125.8 (*m*-C, C_5H_5N), 122.52 (C_5H_4)), 116.31 (C_5H_4), 115.99 (Cp) δ_B (96.29 MHz, $CDCl_3$, 20 °C) 1.3 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −129.47 (d, 4F, *J*(FF) 23 Hz, *o*-F), −156.9 (t, 2F, *J*(FF) 20 Hz, *p*-F), −163.5 (d, 4F, *J*(FF) 21 Hz, *m*-F)
$ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(py)\}$ (**12**) 	δ_H (300 MHz, $CDCl_3$, 20 °C) 8.77 (d, 2H, *J* 5.7 Hz, *o*-H, C_5H_5N), 8.15 (tr, 1H, *J* 7.7 Hz, *p*-H, C_5H_5N), 7.65 (tr, 2H, *J* 7.2 Hz, *m*-H, C_5H_5N), 7.64–7.60 (m, 2H, Ind), 7.30–7.25 (m, 2H, Ind), 7.19 (br, 2H, C_5H_4), 6.81 (tr, 1H, *J* 3.4 Hz, Ind), 6.42 (d, 2H, *J* 3.4 Hz, Ind) 6.08 (br, 2H, C_5H_4) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 147.85 *o*-C, C_5H_5N), 142.09 (*p*-C, C_5H_5N), 129.03 (C_5H_4B), 126.31 (Ind), 124.50 (*m*-C, C_5H_5N), 124.34 (Ind), 121.62 (Ind) 116.79 (C_5H_4B), 103.16 (Ind) δ_B (96.29 MHz, $CDCl_3$, 20 °C) 1.4 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −129.30 (d, 4F, *J*(FF) 24 Hz, *o*-F), −156.71 (t, 2F, *J*(FF) 21Hz, *p*-F), −163.46 (d, 4F, *J*(FF) 21 Hz, *m*-F)
$ZrCl_2\{C_5H_4B(C_6F_5)_2(py)\}$ (**13**) 	δ_H (300 MHz, $CDCl_3$, 20 °C) 8.78 (d, 2H, *J* 5.9 Hz, *o*-H, C_5H_5N), 8.17 (tr, 1H, *J* 7.7 Hz, *p*-H, C_5H_5N), 7.68 (tr, 2H, *J* 7.2 Hz, *m*-H, C_5H_5N), 6.39 (tr, 2H, *J* 2.6 Hz, C_5H_4), 6.21 (br, 2H, C_5H_4) δ_C (75.47 MHz; $CDCl_3$; 20 °C) 147.85 *o*-C, C_5H_5N), 142.07 (*p*-C, C_5H_5N), 125.8 (*m*-C, C_5H_5N), 122.56 (C_5H_4), 116.32 (C_5H_4) δ_B (96.29 MHz, $CDCl_3$, 20 °C) 1.2 δ_F (282.40 MHz, $CDCl_3$, 20 °C) −129.50 (d, 4F, *J*(FF) 23 Hz, *o*-F), −156.9 (t, 2F, *J*(FF) 20 Hz, *p*-F), −163.58 (d, 4F, *J*(FF) 21 Hz, *m*-F)
$TiCl_3\{C_5H_4B(C_6F_5)_2(py)\}$ (**14**) 	δ_H (300 MHz, CD_2Cl_2, 20 °C) 8.74 (d, 2H, *J* 5.8 Hz, *o*-H, C_5H_5N), 8.30 (tr, 1H, *J* 7.7 Hz, *p*-H, C_5H_5N), 7.79 (tr, 2H, *J* 7.7 Hz, *m*-H, C_5H_5N), 7.12 (tr, 2H, *J* 2.2 Hz, C_5H_4), 6.97 (tr, 2H, J 2.2 Hz, C_5H_4) δ_C (75.47 MHz; CD_2Cl_2; 20 °C) 147.65 *o*-C, C_5H_5N), 143.69 (*p*-C, C_5H_5N), 129.87 (C_5H_4), 127.71 (C_5H_4), 126.80 (*m*-C, C_5H_5N) δ_B (96.29 MHz, CD_2Cl_2, 20 °C) 0.80 δ_F (282.40 MHz, CD_2Cl_2, 20 °C) −127.85 (d, 4F, *J*(FF) 22 Hz, *o*-F), −150.65 (t, 2F, *J*(FF) 20 Hz, *p*-F), −161.03 (d, 4F, *J*(FF) 23 Hz, *m*-F)
$ZrCl_3\{C_5H_4B(C_6F_5)_2(py)\}\cdot py_2$ (**15**) 	δ_H (300 MHz, $CDCl_3$, 50 °C) 9.15 (d, 2H, *J* 4.7 Hz, *o*-H, C_5H_5N–B), 8.94 (d, 4H, *J* 4.5 Hz, *o*-H, C_5H_5N–Zr), 8.20 (tr, 1H, *J* 7.3 Hz, *p*-H, C_5H_5N–B), 7.75 (br, 4H, *p*-H, C_5H_5N–Zr, *m*-H, C_5H_5N–B), 7.30–7.24 (m, 4H, *m*-H, C_5H_5N–Zr), 6.59 (tr, 2H, *J* 2.4 Hz, C_5H_4), 6.38 (br, 2H, C_5H_4) δ_C (75.47 MHz; $CDCl_3$; 50 °C) 151.42 *o*-C, C_5H_5N–Zr) 148.63 *o*-C, C_5H_5N–B), 142.1 (*p*-C, C_5H_5N–B), 137.99 (*p*-C, C_5H_5N–Zr), 127.0 (C_5H_4), 125.66 (*m*-C, C_5H_5N–B), 123.84 (*m*-C, C_5H_5N–Zr), 121.04 (C_5H_4) δ_B (96.29 MHz, $CDCl_3$, 20 °C) 1.6 δ_F (282.40 MHz, $CDCl_3$, 50 °C) −129.99 (d, 4F, *J*(FF) 21 Hz, *o*-F), −157.67 (t, 2F, *J*(FF) 21 Hz, *p*-F), −163.90 (d, 4F, *J*(FF) 21 Hz, *m*-F)
$NbCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (**16**) 	δ_H (300 MHz, THF-d_8, 20 °C) 9.56 (br, 2H, *o*-H, C_5H_5N–Nb), 9.09 (br, 2H, *o*-H, C_5H_5N–B), 8.44 (tr, 1H, *J* 7.6 Hz, *p*-H, C_5H_5N–B), 7.93–7.85 (m, 3H, *p*-H, C_5H_5N–Nb, *m*-H, C_5H_5N–B), 7.46 (br, 2H, *m*-H, C_5H_5N–Nb), 7.20 (br, 2H, C_5H_4), 6.98 (br, 2H, C_5H_4) δ_C (75.47 MHz; THF-d_8, 20 °C) 150.85 br, *o*-C, C_5H_5N–Nb) 149.62 *o*-C, C_5H_5N–B), 144.81 (*p*-C, C_5H_5N–B), 139.47 (br, *p*-C, C_5H_5N–Nb), 129.01 (br, C_5H_4), 127.50 (*m*-C, C_5H_5N–B), 123.88 (br, *m*-C, C_5H_5N–Nb), 122 (v br, C_5H_4) δ_B (96.29 MHz, THF-d_8, 20 °C) 1.0 δ_F (282.40 MHz, THF-d_8, 20 °C) −129.72 (br, 4F, *o*-F), −159.12 (t, 2F, *J*(FF) 24 Hz, *p*-F), −165.61 (t, 4F, *J*(FF) 20 Hz, *m*-F)
$TaCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (**17**) 	δ_H (300 MHz, THF-d_8, 20 °C) 9.61 (v br, 2H, *o*-H, C_5H_5N–Ta), 9.09 (d, 2H, *J* 7.7 Hz, *o*-H, C_5H_5N–B), 8.45 (tr, 1H, *J* 7.7 Hz, *p*-H, C_5H_5N–B), 7.97 (br, 1H, *p*-H, C_5H_5N–Ta), 7.87 (tr, 2H, *J* 7.0 Hz, *m*-H, C_5H_5N–B), 7.51 (br, 2H, *m*-H, C_5H_5N–Ta), 6.82 (tr, 2H, *J* 2.1 Hz C_5H_4), 6.98 (tr, 2H, *J* 2.4 Hz, C_5H_4) δ_C (75.47 MHz; THF-d_8, 20 °C) 149.65 *o*-C, C_5H_5N–B), 144.74 (*p*-C, C_5H_5N–B), 131.59 (C_5H_4), 129.68 (*m*-C, C_5H_5N–B), 124.76(C_5H_4)[b] δ_B (96.29 MHz, THF-d_8, 20 °C) 0.6 δ_F (282.40 MHz, THF-d_8, 20 °C) −129.75 (d, 4F, *J*(FF) 23 Hz, *o*-F), −159.33 (t, 2F, *J*(FF) 20 Hz, *p*-F), −165.71 (t, 4F, *J*(FF) 24 Hz, *m*-F)

[a] The ^1H, ^{13}C and ^{11}B NMR data of complex **3** were first published in ref. 4 but are included here for comparison. [b] Other resonances not observed.

was isolated as a red oil, which solidified on drying to give a glass. Although this material could not be induced to crystallise, satisfactory elemental analyses were obtained, and the complex could be characterised by multinuclear NMR. The ^1H NMR spectrum consists of a single resonance for the Cp ligand and broad peaks integrating to 2 protons for the 2,5 and 3,4 positions of the boron-substituted cyclopentadienyl ligand, confirming the expected composition. The more informative indicator in determining whether there is any B–Cl interaction is the ^{11}B chemical shift. At δ −2.9 this is clearly in the region consistent with four-coordinate boron, at even higher field than the ^{11}B resonance of **III** (δ 7.0).

In order to unequivocally demonstrate the presence and nature of a B–Cl interaction a molecular structure determination was required. Since crystallisation of **8** proved difficult we prepared the trimethylsilyl substituted analogue, **9**, from **1** and $(SnMe_3)(SiMe_3)C_5H_4$. Complex **9** exhibits the expected ^1H NMR spectrum for a metallocene with two different monosubstituted cyclopentadienyl rings and the ^{11}B chemical shift is identical to that for **8**, indicating the same basic structure. X-ray quality crystals were grown from toluene solution. The bonding and geometry in **9** is discussed in detail later but the crystallographic study reveals a zwitterionic structure, $Nb^{(+)}Cl_2(C_5H_4SiMe_3)\{(C_5H_4)B^{(-)}(Cl)(C_6F_5)_2\}$, where one chloride ion has been abstracted to give a formally anionic $-B(Cl)(C_6F_5)_2$ substituent and a cationic niobium centre, Fig. 1. In the light of the strong spectroscopic similarities, **8** is therefore formulated as $Nb^{(+)}Cl_2(Cp)\{(C_5H_4)B^{(-)}(Cl)(C_6F_5)_2\}$ (Scheme 3).

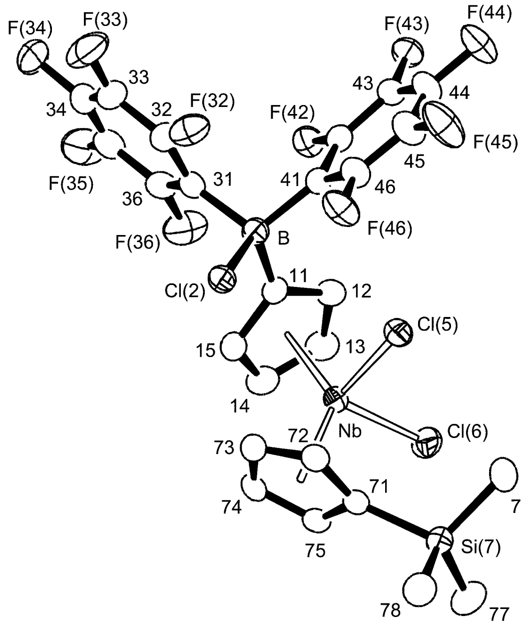
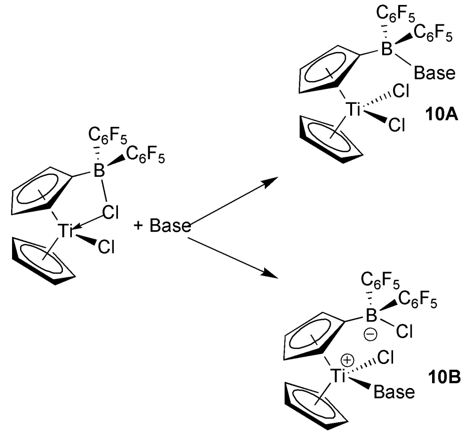


Fig. 1 View of a molecule of $Nb^{(+)}Cl_2(C_5H_4SiMe_3)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}$ (**9**), indicating the atom numbering scheme. In all the figures, atoms labelled '*n*' represent the carbon atoms C(*n*); hydrogen atoms are omitted for clarity; and thermal ellipsoids are drawn at the 50% probability level.

Having found that boryl niobocenes were capable of quantitative self-ionisation, we wished to determine whether a similar reaction could be promoted for $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2\}$ (**III**, Chart 1). Examination of the bond lengths in the crystallographically characterised indenyl analogue suggests that the bonding is best described as Cp–B–Cl⟶Ti.[5] Reaction with a base was expected to break the linkage between B–Cl or Ti–Cl to give either a neutral titanocene with a $\{C_5H_4B(py)(C_6F_5)_2\}$ ligand or a zwitterion similar to **9**, with a basic ligand occupying the vacated coordination site at titanium (Scheme 4). However, the addition of excess tetrahydrofuran to **III** did not produce a significant change in the solution ^1H and ^{11}B solution NMR.[26] In contrast, addition of a stoichiometric amount of pyridine to a toluene suspension of **III** caused the metallocene to dissolve to give a very dark red solution from which red crystals were obtained. The ^1H NMR of these crystals (Table 1) shows one equivalent of pyridine downfield shifted *versus* free pyridine, which is consistent with coordination to a Lewis acid. The borylcyclopentadienyl resonances adopt the expected AA′BB′ pseudotriplets for a freely rotating mono-substituted cyclopentadienyl ligand. The ^{11}B NMR signal was observed at 1.0 *vs.* 7.0 ppm for $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2\}$. The latter value is consistent with formation of a neutral adduct **10A**, rather than an ionic product **10B** (Scheme 4). This was confirmed by the X-ray structure of $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}$ (**10**), Fig. 2.



Scheme 4

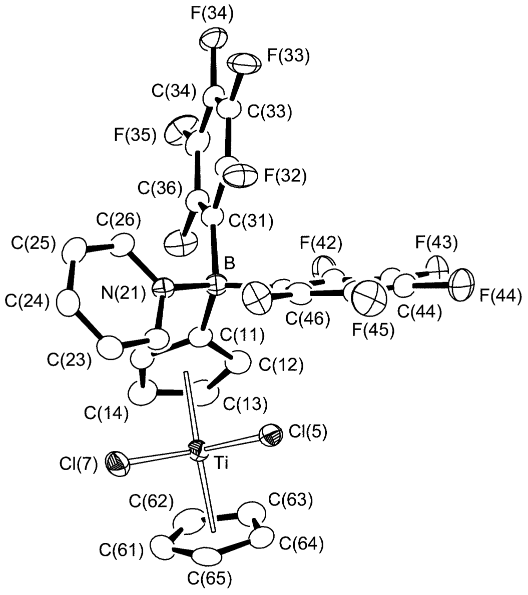


Fig. 2 View of a molecule of $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}$ (**10**).

The high basicity and modest steric hindrance of the pyridine ligand coupled with good crystallinity and stability of the resulting complexes encouraged us to prepare a series of pyridine adducts of the borylcyclopentadienyl complexes. Not surprisingly, pyridine displaces SMe_2 in the zirconocenes **5** and **6** to give the pyridine adducts $ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}$ (**11**) and $ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(py)\}$ (**12**). While **11** was obtained as pale yellow crystals, **12** separates from solution as a dark yellow oil and as a consequence the elemental analysis result is relatively poor. Both Lewis acidic boron sites in **3** accept a pyridine donor to give $ZrCl_2\{C_5H_4B(C_6F_5)_2(py)\}_2$ (**13**). In each of the complexes **10**–**13**, pyridine coordination is obvious from the downfield shifts in the ^1H NMR spectra of the pyridine ligand and the ^{11}B chemical shifts which are remarkably similar and occur within a narrow range from δ 1.0 to 1.4.

One can envisage the zwitterionic niobocene **9** reacting with a Lewis base either to reverse the zwitterion formation and form a $-B(C_6F_5)_2(py)$ adduct, or with coordination to the cationic niobium. In practice neither reaction occurs, and **9** can be recrystallised unchanged from a toluene solution containing an excess of pyridine.[27]

The half-sandwich complex, $TiCl_3\{C_5H_4B(C_6F_5)_2\}$, reacts with an excess of pyridine to give exclusively the mono-adduct, $TiCl_3\{C_5H_4B(C_6F_5)_2(py)\}$ (**14**). The coordination of pyridine to the boron centre was indicated by a ^{11}B chemical shift of 0.8 *versus* 59.8 for the free compound. The presence of only one molecule of pyridine indicated by the ^{1}H NMR spectrum and elemental analysis was confirmed by X-ray crystallography, Fig. 3. Presumably the titanium remains uncomplexed due to steric congestion. By contrast, the zirconium complex, **4**, reacts with excess pyridine in toluene to give, $ZrCl_3\{C_5H_4B(C_6F_5)_2(py)\}\cdot py_2$ (**15**), as colourless crystals. The ^{1}H NMR spectrum clearly indicates three equivalents of pyridine, one of which shows the strong down-field shift associated with coordination to the boron centre, while the other two pyridine molecules give rise to only one slightly broad signal in the ^{1}H NMR. The structure of **15** was determined by single crystal X-ray diffraction, Fig. 4, and the bonding and geometry is described below.

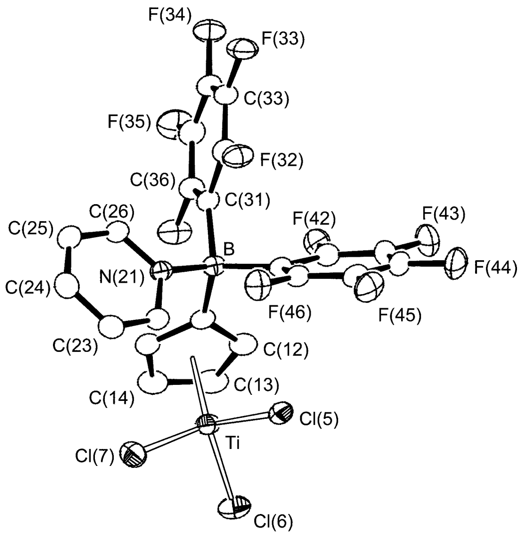


Fig. 3 View of a molecule of $TiCl_3\{C_5H_4B(C_6F_5)_2(py)\}$ (**14**).

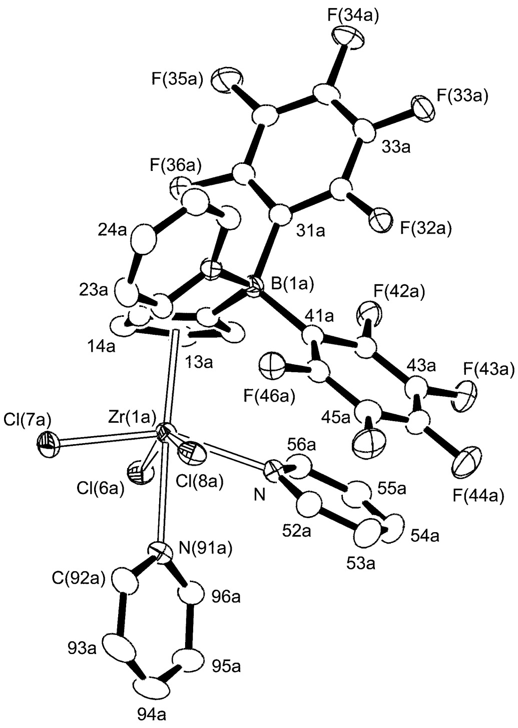


Fig. 4 View of a molecule of $ZrCl_3\{C_5H_4B(C_6F_5)_2(py)\}\cdot py_2$ (**15**).

Complexes **1** and **2** are poorly soluble in toluene but when suspensions are treated with excess pyridine they dissolve before crystallising as the adducts $NbCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (**16**) and $TaCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (**17**) from solution. The spectroscopic details for the two complexes are similar and closely related to **15**. The ^{11}B signals indicate pyridine coordination which is maintained in THF solution. The ^{1}H NMR spectra show two inequivalent pyridines suggesting one coordinated to the boron centre and the second to the metal. The octahedral structure of the niobium complex was confirmed by X-ray diffraction, Fig. 5.

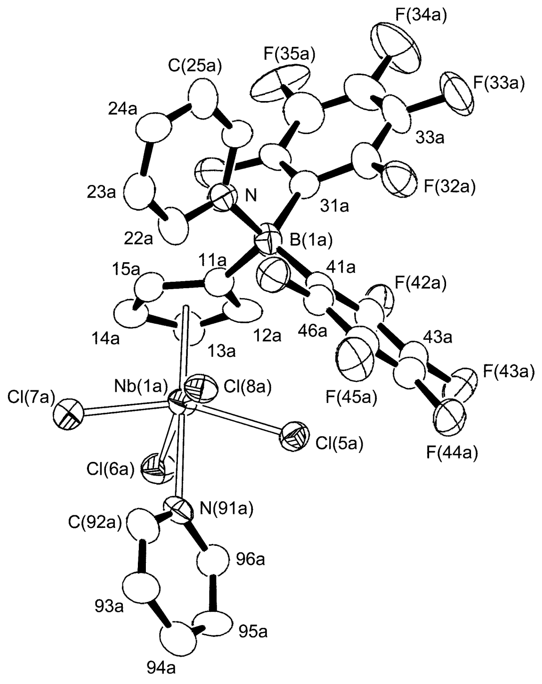


Fig. 5 View of a molecule of $NbCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (**16**).

X-Ray crystallographic analysis of complexes 9, 10 and 14–16

Complexes **9**, **10** and **14** were shown by X-ray methods to have a number of structural similarities. In each, the metal atom (Nb, Ti and Ti respectively) are tetrahedral, assuming that the both the Cp′ and Cp^B ligands (where Cp^B is a boron-substituted cyclopentadienyl ligand) are considered to occupy a single coordination site. The boron atom in each is also tetrahedral. Selected geometric parameters are collated in Table 2.

The Nb–Cl(5) and Nb–Cl(6) distances in complex **9** at 2.3367(9) and 2.3615(11) Å are typical for cationic niobocene dichlorides.[28] Cl(2) is bonded to the boron atom at a distance of 1.929(4) Å,[29,30] the bond is directed away from the Nb atom [torsion angle Cl(2)–B–C(11)–Nb is −43.8(3)°] and the Nb ··· Cl(2) distance is 3.996(8) Å; hence there is no bridging B–Cl–Nb contact in this molecule. A similar arrangement has been noted in $[W(H)_3\{C_5H_4B(Cl)(C_6F_5)_2\}]$ where the B–Cl distance is 1.915(5).[16] This contrasts with the arrangement in $[TiCl(Ind)\{C_5H_4B(Cl)(C_6F_5)_2\}]$[5] where the boron atom is displaced to the same side of the C_5 ring as the metal atom and the chloride ligand forms a B–Cl–Ti bridge, with a B–Cl distance of 2.007(4) and a Ti–Cl distance of 2.4641(9) Å.

The chloride group on the boron atom in the zwitterion **9** is replaced in the neutral adducts **10** and **14** by a pyridyl group, but the orientation of the C_6F_5 rings is similar in all three molecules. About the metal atoms, the ligands, *viz.* $(Cp^B)Cl_3$, $(Cp^B)Cl_2(Cp)$ and $(Cp^B)Cl_2(Cp')$, have very similar orientations. In the Cp^B groups, the boron atom in each complex is displaced slightly from the C_5 mean-plane away from the metal atom. As one would have expected from the consistency of the ^{11}B NMR data, the B–N distances in **10** and **14** are similar.

The Ti–C(11) bond in complex **10** at 2.546(2) Å is significantly longer than those to the other cyclopentadienyl carbons, which are otherwise comparable to the average Ti–Cp distance of 2.31 Å in $TiCl_2Cp_2$.[31] This is in sharp contrast with the shortening of the Ti–C(B) bond in $TiCl_2(Ind)\{C_5H_4B(C_6F_5)_2\}$. The

Table 2 Selected dimensions in the four-coordinate complexes **9**, **10** and **14**. Bond lengths are in Ångströms, angles in degrees. E.s.d.s are in parentheses [a]

9		**10**		**14**	
Nb–C(11)	2.501(3)	Ti–C(11)	2.546(2)	Ti–C(11)	2.4182(19)
Nb–C(12)	2.455(3)	Ti–C(12)	2.403(2)	Ti–C(12)	2.348(2)
Nb–C(13)	2.442(3)	Ti–C(13)	2.351(2)	Ti–C(13)	2.332(2)
Nb–C(14)	2.374(3)	Ti–C(14)	2.340(2)	Ti–C(14)	2.324(2)
Nb–C(15)	2.402(3)	Ti–C(15)	2.444(2)	Ti–C(15)	2.360(2)
Nb–C(71)	2.470(3)	Ti–C(61)	2.393(2)		
Nb–C(72)	2.440(3)	Ti–C(62)	2.372(2)		
Nb–C(73)	2.389(3)	Ti–C(63)	2.362(2)		
Nb–C(74)	2.405(3)	Ti–C(64)	2.409(2)		
Nb–C(75)	2.433(3)	Ti–C(65)	2.401(2)		
Nb–C(1x)	2.115	Ti–C(1x)	2.097	Ti–C(1x)	2.024
Nb–Cl(5)	2.3367(9)	Ti–Cl(5)	2.3629(6)	Ti–Cl(5)	2.2483(8)
Nb–Cl(6)	2.3615(11)	Ti–C(6x)	2.069	Ti–Cl(6)	2.2399(7)
Nb–C(7x)	2.109	Ti–Cl(7)	2.3733(7)	Ti–Cl(7)	2.2426(7)
B–Cl(2)	1.929(4)	B–N(21)	1.632(3)	B–N(21)	1.623(3)
C(1x)–Nb–Cl(5)	105.9	C(1x)–Ti–Cl(5)	107.2	C(1x)–Ti–Cl(5)	115.37
C(1x)–Nb–Cl(6)	106.1	C(1x)–Ti–C(6x)	131.4	C(1x)–Ti–Cl(6)	116.46
C(1x)–Nb–C(7x)	130.0	C(1x)–Ti–Cl(7)	107.4	C(1x)–Ti–Cl(7)	115.96
Cl(5)–Nb–Cl(6)	97.90(4)	C(6x)–Ti–Cl(5)	105.7	Cl(6)–Ti–Cl(5)	101.51(3)
Cl(5)–Nb–C(7x)	107.8	Cl(5)–Ti–Cl(7)	94.78(2)	Cl(7)–Ti–Cl(5)	103.11(3)
Cl(6)–Nb–C(7x)	104.7	C(6x)–Ti–Cl(7)	104.4	Cl(6)–Ti–Cl(7)	102.32(3)

[a] *N.B.* C(1x), C(6x) and C(7x) are the centroids of the Cp^B and Cp rings.

Ti–Cl distances in **10** are very similar to those observed for $TiCl_2Cp_2$.

Although the longest of the Ti–C bonds in **14**, the Ti–C(11) bond length, at 2.4182(19) is much shorter than that in **10** and only a little longer than that determined for the pyridine-free $TiCl_3\{C_5H_4B(C_6F_5)_2\}$.[3] The Ti–Cl distances are also slightly longer in **14** than in $TiCl_3\{C_5H_4B(C_6F_5)_2\}$. This is consistent with a reduction in electron-deficiency at the titanium centre on base coordination to the electron-withdrawing substituent on the cyclopentadienyl ligand.

The two six-coordinate complexes, **15** and **16**, also share many geometrical features (Fig. 4 and 5).[32] With respect to the B–C(11) bond, the orientations of the C_6F_5 and pyridine groups bound to boron are almost identical in both complexes. The tilt of the Cp^B ring, and the arrangements of the other five ligands, about the Zr or Nb atoms are also very similar. The metal atoms are displaced by *ca.* 0.61 Å (Zr) or 0.53 Å (Nb) from the mean-planes through the chlorine atoms which form the 'equatorial' planes in each complex; in both molecules, the Cp^B ligand is *trans* to a pyridine. Selected geometric parameters are collated in Table 3.

To the best of our knowledge pyridine complexes of the type $NbCl_4(Cp){\cdot}py$ or $ZrCl_3(Cp){\cdot}py_2$ have not been crystallographically characterised. The octahedral geometry around zirconium and tetrahedral environment of the boron atom is reminiscent of $[NEt_4]_2[Zr(\mu\text{-}Cl)Cl_2\{C_5H_4B(C_6F_5)_3\}]_2$, where the terminal Zr–Cl distances were slightly shorter than those of **15** at 2.4200(8) and 2.4603(8) Å.[14] In contrast, a very similar Zr–Cl distance, 2.504(1) was observed for monocyclopentadienyl imido complex $ZrCl(C_5Me_5)(N\text{-}2,6\text{-}^iPrC_6H_3)(py)_2$. The Zr–N distances 2.435(4) and 2.414(4) Å for the pyridine ligands in this complex are inside the range defined by the equatorial and axial Zr–N distances in **15**.[33]

Conclusion

Half-sandwich complexes of zirconium, niobium and tantalum with the $\{C_5H_4B(C_6F_5)_2\}$ ligand are readily accessible from the metal chlorides and $B(C_5H_4SiMe_3)(C_6F_5)_2$ by selective dehalosilylation. Borylcyclopentadienyl zirconocenes can be prepared by reaction of the half-sandwich complex with LiCp′, but unlike the analogous titanocenes there is no interaction between the boron and the chloride ligands. In contrast, the preparation of niobocenes requires a dehalostannylation route, and they relieve the steric congestion by chloride transfer to boron to become zwitterions. The monocyclopentadienyl complexes react with excess pyridine to form adducts. The titanium complex coordinates pyridine only at the boron, whereas the zirconium, niobium and tantalum complexes coordinate pyridine both at boron and at the metal centre to attain octahedral geometries. Pyridine displaces boron-bound SMe_2 in the borylcyclopentadienyl zirconocenes and splits the Ti–Cl–B bridge in borylcyclopentadienyl titanocenes, to give group 4 metallocenes with the $\{C_5H_4B(C_6F_5)_2(py)\}$ ligand, whereas the zwitterionic niobocenes do not react with pyridine.

Experimental

General experimental

All manipulations were performed under a dinitrogen atmosphere using Schlenk techniques. Solvents were distilled under N_2 over sodium (toluene), Na/K alloy (light petroleum (bp 40–60 °C)), CaH_2 (dichloromethane) or sodium/benzophenone (diethyl ether). NMR solvents were dried over 4 Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded on a Bruker Avance DPX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C NMR) or external $BF_3{\cdot}OEt_2$ (^{11}B) and $CFCl_3$ (^{19}F). Titanium tetrachloride, niobium pentachloride, tantalum pentachloride, and anhydrous SMe_2 were purchased from Aldrich and used as supplied. Zirconium tetrachloride (Acros) was sublimed immediately prior to use. Pyridine (Aldrich) was dried over activated 4 Å molecular sieves. $TiCl_3\{C_5H_4B(C_6F_5)_2\}$,[3] and $TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2\}$[5] were prepared according to literature procedures.

Synthesis

$NbCl_4\{C_5H_4B(C_6F_5)_2\}$ (1). To a dichloromethane solution of $B(C_5H_4SiMe_3)(C_6F_5)_2$ (51.7 cm^3, 0.45 M, 32.3 mmol) was added $NbCl_5$ (8.72 g, 32.3 mmol). The solid dissolved quickly, and within minutes a fine orange–red solid precipitated from the deep red solution. The reaction was stirred at room temperature for 3 h. The product was allowed to settle overnight, separated by filtration, washed with light petroleum and dried under vacuum to give **1** as a very fine orange–red powder (15 g, 23.3

Table 3 Selected dimensions in the six-coordinate complexes **15** and **16**. Bond lengths are in Ångströms, angles in degrees. E.s.d.s are in parentheses[a]

			16 (major component molecules)		
15	Mol. A	Mol. B		Mol. A	Mol. B
Zr(1a)–C(11a)	2.651(2)	2.647(2)	Nb(1a)–C(11a)	2.576(5)	2.588(5)
Zr(1a)–C(12a)	2.547(2)	2.547(2)	Nb(1a)–C(12a)	2.489(5)	2.493(5)
Zr(1a)–C(13a)	2.514(2)	2.504(3)	Nb(1a)–C(13a)	2.427(5)	2.440(6)
Zr(1a)–C(14a)	2.497(2)	2.484(3)	Nb(1a)–C(14a)	2.396(6)	2.398(5)
Zr(1a)–C(15a)	2.546(2)	2.544(2)	Nb(1a)–C(15a)	2.447(5)	2.448(5)
Zr(1a)–C(1a)	2.250	2.243	Nb(1a)–C(1a)	2.157	2.162
Zr(1a)–N(51a)	2.412(2)	2.418(2)	Nb(1a)–Cl(5a)	2.4140(12)	2.4384(16)
Zr(1a)–Cl(6a)	2.5067(7)	2.5260(7)	Nb(1a)–Cl(6a)	2.419(2)	2.4169(15)
Zr(1a)–Cl(7a)	2.4994(7)	2.4893(7)	Nb(1a)–Cl(7a)	2.427(2)	2.4168(14)
Zr(1a)–Cl(8a)	2.4855(7)	2.4852(8)	Nb(1a)–Cl(8a)	2.4209(15)	2.4263(14)
Zr(1a)–N(91a)	2.492(2)	2.494(2)	Nb(1a)–N(91a)	2.391(5)	2.388(5)
B(1a)–N(21a)	1.631(3)	1.635(3)	B(1a)–N(21a)	1.620(7)	1.644(7)
N(51a)–Zr(1a)–C(1a)	102.10	100.76	Cl(5a)–Nb(1a)–C(1a)	101.74	101.53
Cl(6a)–Zr(1a)–C(1a)	102.95	101.73	Cl(6a)–Nb(1a)–C(1a)	103.28	103.37
Cl(7a)–Zr(1a)–C(1a)	102.57	103.51	Cl(7a)–Nb(1a)–C(1a)	101.96	101.78
Cl(8a)–Zr(1a)–C(1a)	105.76	106.01	Cl(8a)–Nb(1a)–C(1a)	103.90	103.83
N(91a)–Zr(1a)–C(1a)	175.91	174.49	N(91a)–Nb(1a)–C(1a)	179.98	179.56
N(51a)–Zr(1a)–Cl(6a)	85.09(5)	86.15(5)	Cl(5a)–Nb(1a)–Cl(6a)	87.60(6)	86.94(6)
N(51a)–Zr(1a)–Cl(7a)	155.26(5)	155.66(5)	Cl(5a)–Nb(1a)–Cl(7a)	156.29(6)	156.69(6)
N(51a)–Zr(1a)–Cl(8a)	85.49(5)	85.92(5)	Cl(5a)–Nb(1a)–Cl(8a)	88.35(5)	88.01(5)
N(51a)–Zr(1a)–N(91a)	74.50(7)	74.55(7)	N(91a)–Nb(1a)–Cl(5a)	78.26(10)	78.03(11)
Cl(7a)–Zr(1a)–Cl(6a)	87.59(2)	87.24(2)	Cl(6a)–Nb(1a)–Cl(7a)	86.82(7)	88.18(5)
Cl(8a)–Zr(1a)–Cl(6a)	151.06(2)	152.10(2)	Cl(6a)–Nb(1a)–Cl(8a)	152.78(7)	152.80(6)
N(91a)–Zr(1a)–Cl(6a)	74.68(5)	75.29(5)	N(91a)–Nb(1a)–Cl(6a)	76.73(11)	76.61(12)
Cl(8a)–Zr(1a)–Cl(7a)	89.64(3)	89.07(3)	Cl(8a)–Nb(1a)–Cl(7a)	86.16(6)	85.98(5)
N(91a)–Zr(1a)–Cl(7a)	80.77(5)	81.11(5)	N(91a)–Nb(1a)–Cl(7a)	78.03(11)	78.66(11)
Cl(8a)–Zr(1a)–N(91a)	76.44(5)	76.82(5)	N(91a)–Nb(1a)–Cl(8a)	76.10(11)	76.19(12)
Deviation of metal from 'equatorial' plane	0.6169(2)	0.6003(2)		0.5331(10)	0.5321(9)

[a] *N.B.* C(1a) is the centroid of the Cp^b ring. The metals of Mol. B in both complexes are Zr(2b) and Nb(2b); all other atoms have labels corresponding to those in Mol. A, *viz.* C(11b), C(12b), *etc.*

mmol, 72%). (Found: C, 30.76; H, 0.75; Cl, 22.85. $C_{17}H_4BCl_4F_{10}Nb$ requires C, 31.72; H 0.63; Cl, 22.03%.)

$TaCl_4\{C_5H_4B(C_6F_5)_2\}$ (2). Following a very similar procedure to **1**, the reaction of $B(C_5H_4SiMe_3)(C_6F_5)_2$ (14.8 cm^3, 0.45 M, 6.6 mmol) with $TaCl_5$ (2.38 g, 6.6 mmol) gave **2** as a fine pale yellow solid (3 g, 4.1 mmol, 62%). (Found: C, 28.36; H, 0.57; Cl, 19.77. $C_{17}H_4BCl_4F_{10}Ta$ requires C, 27.90; H 0.55; Cl, 19.38%.)

$ZrCl_2\{C_5H_4B(C_6F_5)_2\}_2{\cdot}0.5(Et_2O)$ (3). A solution of $B(C_5H_4SiMe_3)(C_6F_5)_2$ (20 g, 41.4 mmol) in toluene (100 cm^3) was added to a suspension of $ZrCl_4$ (4.66 g, 20 mmol) in toluene (40 cm^3). The mixture was warmed to 60 °C for 4 h and stirred at room temperature overnight. Removal of the volatiles under vacuum gave a viscous brown oil. Trituration with light petroleum yielded a tan-coloured solid which was recrystallised from diethyl ether to give very small off-white crystals (4.5 g, 4.4 mmol, 22%). (Found: C, 42.54; H, 1.33; Cl, 7.56. $C_{36}H_{13}B_2Cl_2F_{20}O_{0.5}Zr$ requires C, 42.51; H 1.29; Cl, 6.97%.)

$ZrCl_3\{C_5H_4B(C_6F_5)_2(SMe_2)\}{\cdot}0.25(C_7H_8)$ (4). To a dichloromethane solution of $B(C_5H_4SiMe_3)(C_6F_5)_2$ (56 cm^3, 0.45 M, 25.2 mmol) was added $ZrCl_4(SMe_2)_2$ (8.9 g, 25 mmol). The pale orange solution was stirred overnight. Concentration of the solution and cooling to −25 °C overnight gave small yellow crystals, which were filtered off and washed with light petroleum. The material was recrystallised from toluene to give **4** (10.5 g, 15.2 mmol, 61%). The crystals slowly lose solvent of crystallisation under vacuum. (Found: C, 35.82; H, 1.91; Cl, 14.06. $C_{20.75}H_{12}BCl_3F_{10}SZr$ requires C, 36.03; H 1.75; Cl, 15.38%.)

$ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(SMe_2)\}{\cdot}0.66(C_7H_8)$ (5). To a suspension of **4** (2.8 g, 4.2 mmol) in toluene (30 cm^3) was added solid LiCp (0.30 g, 4.2 mmol) in one portion. A yellow solution resulted, together with and a small amount of fine white precipitate. The reaction was stirred for a further 2 h and the solids were filtered off. The filtrate was concentrated to 15 cm^3 and cooled to −25 °C overnight to afford **5** as small off-white crystals (1.5 g, 1.98 mmol, 47%). (Found: C, 45.47; H, 2.68; Cl, 9.53. $C_{28.62}H_{20.28}BCl_2F_{10}SZr$ requires C, 45.28; H 2.69; Cl, 9.34%.)

$ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (6). Following the procedure given for compound **5**: **6** was made from 2.6 g (3.98 mmol) of **4** and 0.49 g (3.98 mmol) LiInd in toluene (20 cm^3). Removal of the solvent gave as an orange solid (2.5 g, 3.3 mmol, 83%). An analytically pure sample was obtained by addition of SMe_2 to a saturated solution of the crude material and cooling to −25 °C overnight (Found: C, 45.23; H, 2.45; Cl, 9.33. $C_{28}H_{17}BCl_2F_{10}SZr$ requires C, 44.94; H 2.29; Cl, 9.47%.)

$B(C_6F_5)_3{\cdot}SMe_2$ (7). Tris(pentafluorophenyl)boron (2.3 g, 4.5 mmol) was dissolved in toluene (30 cm^3) at 60 °C. The solution was then treated with dimethylsulfide (1.0 cm^3, 0.85 g, 13.7 mmol) and the mixture was stirred to ensure uniform mixing. Cooling the solution overnight (−25 °C) afforded cubic colourless crystals of $B(C_6F_5)_3{\cdot}SMe_2$ (2.0 g, 3.5 mmol, 78%). (Found: C, 41.77; H, 0.97. $C_{20}H_6BF_{15}S$ requires C, 41.84; H, 1.05%.)

$Nb^{(+)}Cl_2(Cp)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}$ (8). To a stirred suspension of 4.78 g (7.43 mmol) **1** in dichloromethane (30 cm^3) was added $Me_3SnC_5H_5$ (1.83 g, 8.0 mmol). The suspended solids dissolved within 1 h to give a very dark red solution. After a further 2 h the solution was filtered to separate a small amount of dark solid. The product was isolated by concentrating to 10 cm^3 and precipitating with 40 cm^3 of light petroleum to give a dark red oil that dried to a glassy solid, yield 3.5 g (5.2 mmol, 70%). The ^{1}H NMR indicated that the material retains some solvents even after extended periods of drying under high vacuum. Repeated attempts to purify by recrystallisation from toluene and dichloromethane/light petroleum mixtures were unsuccessful. (Found: C, 40.25; H, 2.06. $C_{22}H_9BCl_3F_{10}Nb$ requires C, 39.24; H 1.35%.)

$Nb^{(+)}Cl_2(C_5H_4SiMe_3)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}$ (9). Following a similar procedure to that outlined for **8**, a stirred suspension of **1** (3.08 g, 4.8 mmol) was treated with 1.5 g (5 mmol) $(SnMe_3)(SiMe_3)C_5H_4$. The product was isolated by removing the volatiles and washing the solid with light petroleum to give **9** as a dark red solid, yield 2 g (2.7 mmol, 56%). (Found: C, 39.65; H, 2.59; Cl, 14.62. $C_{25}H_{17}BCl_3F_{10}NbSi$ requires C, 40.28; H, 2.30; Cl, 14.27%.) Dark red crystals suitable for X-ray diffraction were obtained by recrystallisation from 20 cm^3 toluene at −25 °C overnight.

$TiCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}\cdot 0.5(C_7H_8)$ (10). To a solution of $TiCl_3\{C_5H_4B(C_6F_5)_2\}$, (1.62 g, 2.74 mmol) in toluene (20 cm^3) was added pyridine (0.24 g, 3.0 mmol). There was an appreciable exotherm but no significant colour change. The solution was left to stand at room temperature for 30 min. A microcrystalline red solid precipitated which was filtered off and dried to give **10** (1.2 g, 1.7 mmol, 62%). (Found: C, 50.44; H, 2.34; N, 2.07; Cl, 10.40. $C_{30.5}H_{18}BCl_2F_{10}NTi$ requires C, 51.02; H, 2.53; N, 1.95; Cl, 9.87%.) Crystals suitable for X-ray analysis were obtained by cooling a saturated toluene solution to −25 °C overnight.

$ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(py)\}\cdot 0.5(C_7H_8)$ (11). Following the procedure given for **10**, compound **11** was made from $ZrCl_2(Cp)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (1.0 g, 1.43 mmol) and pyridine (1.0 cm^3) as pale yellow crystals (0.5 g, 0.66 mmol, 46%). (Found: C, 48.05; H, 2.20; N, 2.24; Cl, 9.90. $C_{30.5}H_{18}BCl_2F_{10}NZr$ requires C, 48.11; H, 2.38; N, 1.84; Cl, 9.31%.)

$ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(py)\}\cdot(C_7H_8)(C_5H_5N)$ (12). Following the procedure outlined for **10**, compound **12** was made from $ZrCl_2(Ind)\{C_5H_4B(C_6F_5)_2(SMe_2)\}$ (0.5 g, 0.67 mmol) and pyridine (1 cm^3) as a dark yellow oil. Decanting the supernatant and drying under vacuum produced a dry yellow foam (0.5 g, 0.53 mmol, 80%). (Found: C, 53.49; H, 2.96; N, 3.17; Cl, 6.39. $C_{43}H_{29}BCl_2F_{10}N_2Zr$ requires C, 55.14; H, 3.12; N, 2.99; Cl, 7.57%.)

$ZrCl_2\{C_5H_4B(C_6F_5)_2(py)\}_2\cdot(C_7H_8)$ (13). Following a similar procedure as for **10**, compound **13** was prepared from $ZrCl_2\{C_5H_4B(C_6F_5)_2\}_2$ (0.5 g, 0.51 mmol) and pyridine (0.5 cm^3). A fine colourless solid precipitate formed almost immediately. This was redissolved by adding further pyridine (1 cm^3) followed by gentle heating. Almost colourless crystals were obtained after cooling the solution to 5 °C overnight (0.5 g, 0.44 mmol, 86%). (Found: C, 49.60; H, 2.17; N, 2.63; Cl, 6.32. $C_{51}H_{26}B_2Cl_2F_{20}N_2Zr$ requires C, 49.78; H, 2.13; N, 2.28; Cl, 5.76%.)

$TiCl_3\{C_5H_4B(C_6F_5)_2(py)\}\cdot 0.5(C_7H_8)$ (14). To a solution of $TiCl_3\{C_5H_4B(C_6F_5)_2\}$ (2.24 g, 3.9 mmol) in toluene (20 cm^3) was added pyridine (1 cm^3). Allowing the solution to stand at room temperature afforded needle-like red crystals, fragments of which were suitable for X-ray analysis (1.7 g, 2.5 mmol, 63%). (Found: C, 43.76; H, 1.68; N, 2.07; Cl, 16.36. $C_{25.5}H_{13}BCl_3F_{10}NTi$ requires C, 44.49; H 1.90; N, 2.03; Cl, 15.45%.)

$ZrCl_3\{C_5H_4B(C_6F_5)_2(py)\}\cdot py_2\cdot(C_7H_8)$ (15). Following a similar procedure as for **10**, compound **15** was made from $ZrCl_3\{(C_5H_4)B(SMe_2)(C_6F_5)_2\}$ (1.2 g, 1.8 mmol) and pyridine (1 cm^3) and obtained as very small colourless needle-shaped crystals (1 g, 1.1 mmol, 61%). (Found: C, 49.21; H, 2.95; N, 4.84; Cl, 10.74. $C_{29}H_{27}BCl_3F_{10}N_3Zr$ requires C, 50.04; H, 2.91; N, 4.49; Cl, 11.36%.) Crystals suitable for X-ray analysis were obtained by recrystallisation from $CDCl_3$.

$NbCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (16). Pyridine (1 cm^3) was added to a suspension of **1** (2.8 g, 4.3 mmol) in dichloromethane (20 cm^3) to produce a dark red solution. A small amount of insoluble residue was removed by filtration. On standing at room temperature the solution afforded dark red crystals (3.3 g, 4.1 mmol, 95%). (Found: C, 40.11; H, 1.77; N, 3.55; Cl, 17.89. $C_{27}H_{14}BF_{10}N_2Nb$ requires C, 40.44; H, 1.76; N, 3.49; Cl, 17.68%.)

$TaCl_4\{C_5H_4B(C_6F_5)_2(py)\}\cdot py$ (17). Following the procedure described for **16** reaction of **2** (4.4 g, 6.6 mmol) with pyridine (2 cm^3) gave pale yellow crystals (4 g, 4.5 mmol, 68%). Although this sample did not give a satisfactory elemental analysis, the compound was identified spectroscopically and by comparison with the Nb analogue **16**.

Crystal structure analyses

The X-ray analysis of $[Nb^{(+)}Cl_2(C_5H_4SiMe_3)\{C_5H_4B^{(-)}(Cl)(C_6F_5)_2\}]\cdot 1.5(toluene)$, complex **9**, is described here; the analyses of the other complexes followed similar procedures, except where stated below. Crystal data are collated in Table 4.

Crystals of **9** are orange–brown, diamond-shaped plates. From a sample under oil, one, *ca.* 0.55 × 0.32 (across diagonals) and 0.15 mm thick, was mounted on a glass fibre and fixed in the cold nitrogen stream (140 K) on a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating anode X-ray source (Mo–Kα radiation $\lambda = 0.71069$ Å) and graphite monochromator. Using 4° oscillations, 48 exposures of 54 min each were made.

Data were processed using the DENZO/SCALEPACK programs.[34] The structure was determined by the direct methods routines in the SHELXS program[35] and refined by full-matrix least-squares methods, on F^2s with SHELXL.[35] In addition to the Nb complex molecule in the asymmetric unit, there is one ordered toluene molecule plus a further toluene molecule which is disordered about a centre of symmetry. The disordered solvent molecule was refined with geometrical restraints. The non-hydrogen atoms (except those of partial occupancy in the disordered toluene) were refined with anisotropic thermal parameters. Hydrogen atoms in the complex and ordered toluene were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms; H atoms were not included in the disordered toluene molecule. At the conclusion of the refinement, $wR_2 = 0.112$ and $R_1 = 0.047$ [35] for all 6318 reflections, weighted $w = [\sigma^2(F_o^2) + (0.0656P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, $R_1 = 0.039$. In the final difference map, the highest peaks (to *ca.* 0.60 e Å^{-3}) were in the disordered solvent region.

In complex **10**, the carbon atoms of the toluene solvent molecule, which is disordered about a twofold symmetry axis, were refined isotropically. Hydrogen atoms in this solvent molecule were included in idealised positions.

There are two independent Zr-complex molecules in the asymmetric unit of the cell of complex **15**, together with three solvent $CDCl_3$ molecules (one of which is disordered).

During the refinement of two independent molecules of complex **16**, the principal difference peaks (*ca.* 12 e Å^{-3}) were identified as alternative molecules and were included with a site occupancy which was adjusted to 0.15 (and that of the major molecules to 0.85). In the minor component molecules, only the Nb and Cl atoms were refined anisotropically and no hydrogen atoms were included.

Scattering factors for neutral atoms were taken from ref. 36. Computer programs used in these analyses include those noted above, those in Table 4 of ref. 37, and the SHELXTL suite,[38] and were run on a Silicon Graphics Indy at the University of East Anglia, or a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

CCDC reference numbers 201466–201470.

See http://www.rsc.org/suppdata/dt/b3/b300552f/ for crystallographic data in CIF or other electronic format.

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26 There is a typographical error in ref. 5, the NMR data for complex **2** in Table 1 should read '6.31 (br, 2H) C_5H_4B', not '6.13 (br, 2H) C_5H_4B'.
27 Indeed X-ray quality crystals were obtained in such a fashion and the structure determined. The molecular structure is almost identical to that described for **9** but there is only one molecule of toluene solvent per niobium molecule. *Crystal data:* $C_{25}H_{17}BCl_3F_{10}NbSi{\cdot}C_7H_8$, M = 837.7. Monoclinic, space group $P2_1/c$ (no. 14), a = 13.801(1), b = 15.892(1), c = 15.892(1) Å, β = 110.45(1)°, V = 3265.9(4) Å^3. Z = 4, D_c = 1.704 g cm^{-3}, $F(000)$ = 1672, T = 140(1) K, μ(Mo-Kα) = 7.3 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. Intensity data from a Rigaku R-Axis IIc image plate diffractometer. Refinement gave final wR_2 = 0.089 and R_1 = 0.036 [35] for all 5959 unique reflections; for the 5347 'observed' data, R_1 = 0.033.
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Table 4 Crystal and structure refinement data from X-ray diffraction analysis for $[NbCl_2(C_5H_4SiMe_3)\{C_5H_4B(Cl)(C_6F_5)_2\}]{\cdot}1.5tol$ (**9**), $[TiCl_2(Cp)\{C_5H_4B(py)(C_6F_5)_2\}]{\cdot}0.5tol$ (**10**), $[TiCl_3\{C_5H_4B(py)(C_6F_5)_2\}]{\cdot}tol$, (**14**), $[ZrCl_3(py)_2\{C_5H_4B(py)(C_6F_5)_2\}]{\cdot}1.5(CDCl_3)$ (**15**) and $[NbCl_4(py)\{C_5H_4B(py)(C_6F_5)_2\}]$ (**16**)

	9	**10**	**14**	**15**	**16**
Elemental formula	$C_{25}H_{17}BCl_3F_{10}NbSi{\cdot}1.5(C_7H_8)$	$C_{27}H_{14}BCl_2F_{10}NTi{\cdot}0.5(C_7H_8)$	$C_{22}H_9BCl_3F_{10}NTi{\cdot}C_7H_8$	$C_{32}H_{19}BCl_3F_{10}N_3Zr{\cdot}1.5(CDCl_3)$	$C_{27}H_{14}BCl_4F_{10}N_2Nb$
Formula weight	883.8	718.1	734.5	1024.4	801.9
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$I2/a$ (equiv. to no 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	9.601(2)	12.545(1)	8.799(1)	11.201(1)	18.553(2)
b/Å	14.492(4)	13.546(1)	13.523(1)	18.241(1)	15.695(1)
c/Å	15.252(8)	34.000(4)	13.626(3)	21.174(3)	21.135(2)
α/°	116.58(3)	90	107.44(1)	67.46(1)	90
β/°	99.60(2)	95.04(1)	92.97(1)	76.82(1)	112.14(1)
γ/°	96.390(10)	90	103.27(1)	84.93(1)	90
V/Å^3	1829.2(11)	5755.4(9)	1492.8(4)	3890.5(7)	5700.5(9)
Z	2	8	2	4	8
D_c/Mg m^{-3}	1.605	1.657	1.634	1.749	1.869
$F(000)$	886	2872	732	2020	3152
μ/mm^{-1}	0.658	0.573	0.640	0.877	0.887
Reflections (not absences)	10730	16585	8342	22856	30927
Unique reflections	6318	5208	4926	13163	9754
R_{int} for equivalents	0.039	0.051	0.0543	0.045	0.072
'Observed' reflections ($I > 2s_I$)	5315	4083	4224	11449	5979
Final R_1, wR_2 ('observed')	0.039, 0.109	0.033, 0.086	0.036, 0.097	0.037, 0.097	0.063, 0.151
Final R_1, wR_2 (all data)	0.047, 0.112	0.046, 0.090	0.042, 0.100	0.042, 0.100	0.095, 0.170

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