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The first silyl- and germylboryl complexes: synthesis from novel (dichloro)silyl- and (dichloro)germylboranes, structure and reactivity

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A series of silyl- and germyl(dichloro)boranes Cl_2B-ER_3 (**5**, $ER_3 = Si(SiMe_3)_3$; **6**, $ER_3 = Ge(SiMe_3)_3$; **7**, $ER_3 = Si(SiMe_3)_2-Si(SiMe_3)_3$; **8**, $ER_3 = SiPh_3$) was obtained in good yields from the corresponding bis(dimethylamino)boranes $(Me_2N)_2B-ER_3$ (**1**, $ER_3 = Si(SiMe_3)_3$; **2**, $ER_3 = Ge(SiMe_3)_3$; **3**, $ER_3 = Si(SiMe_3)_2-Si(SiMe_3)_3$; **4**, $ER_3 = SiPh_3$) upon reaction with BCl_3, and fully characterised in solution. These compounds proved to be versatile starting materials for the synthesis of the first silyl- and germylboryl complexes by salt elimination reactions starting from anionic transition metal complexes of the type $Na[(\eta^5-C_5R_5)Fe(CO)_2]$ and $K[(\eta^5-C_5R_5)Mn(H)(CO)_2]$. The novel iron and manganese boryl complexes $[(\eta^5-C_5R_4R')(OC)_2Fe-B(Cl)Si(SiMe_3)_3]$ (**9a**, $R = R' = H$; **9b**, $R = H$, $R' = Me$; **9c**, $R = R' = Me$), $[(\eta^5-C_5H_5)(OC)_2Fe-B(Cl)Ge(SiMe_3)_3]$ (**9d**), $[(\eta^5-C_5H_5)(OC)_2Fe-B(Cl)Si(SiMe_3)_2Si(SiMe_3)_3]$ (**9e**), $[(\eta^5-C_5H_4Me)(OC)_2(H)Mn-B(Cl)Si(SiMe_3)_3]$ (**10a**) and $[(\eta^5-C_5H_4Me)(OC)_2(H)Mn-B(Cl)Ge(SiMe_3)_3]$ (**10b**) were obtained in yields between 35 and 70%, fully characterised in solution and in the case of **9a**, **d**, and **10a** also in the crystalline state. They are all characterised by metal–boron σ-bonds without indication of any metal-to-boron π-backdonation. There is, however, spectroscopical and structural evidence for the presence of a Mn–H–B bridge in the case of the manganese complexes **10a**, **b**. The first transhalogenation of a metal coordinated boryl ligand was achieved by reaction of **9a** with TlF affording the fluoroboryl complex $[(\eta^5-C_5H_5)(OC)_2Fe-B(F)Si(SiMe_3)_3]$ (**11**), which was characterised in solution and in the solid state.

Introduction

Over the past decade transition metal complexes of boron have become established as a novel class of compounds made up by direct metal–boron interactions. In contrast to the other three major groups in this area *i.e.* borides, metallaboranes, and π-complexes with boron-containing ligands, transition metal complexes of boron are characterised by electron-precise two-centre two-electron bonds between boron and the metal centre. According to this pattern of metal–boron interaction, a variety of different coordination modes for boron-centred ligands was realised, allowing for a systematic classification of those compounds into borane, boryl, and borylene complexes.[1] The particular interest in boryl complexes L_xM-BR_2 is due to their importance for the functionalisation of hydrocarbons by metal-catalysed hydroboration of olefins[2] and photochemically induced selective α-borylation of alkanes by C–H activation.[3]

The phenylene-1,2-dioxo or catechol group as a ligand to boron has had a pivotal role in establishing these compounds, and the vast majority of structurally authentic boryl complexes derive from either catecholborane or dicatecholdiborane(4).[1] In the course of our investigations in this field we reported on a series of boryl,[4] diborane(4)yl,[5] and η^1-borazine complexes[6] which were obtained *via* salt elimination reactions from anionic transition metal complexes and amino(halo)boranes. In these compounds and in the aforementioned catecholboryl complexes, the electron deficiency at the three coordinate boron centre is relieved by π-interaction with the boron bound O- or N-donors, thus competing with a possible π-backdonation from the metal into the p_z-orbital at boron. Boryl complexes L_xM-BR_2 (R = alkyl, aryl) without ligand-to-boron π-interaction are very rare, but have received significant interest in studies, which addressed the nature of the metal–boron linkage and the role of metal–boron π-interaction in particular.[1,7] Due to the obvious difficulties accompanying the synthesis of alkyl- and arylboryl complexes, corresponding silyl- or germylboranes could provide a useful alternative.

With this in mind, we recently communicated on the use of the bulky (dichloro)silylborane $(Me_3Si)_3SiBCl_2$ for the synthesis of the first coordinatively and electronically unsaturated terminal borylene complex $[(OC)_5Cr=B-Si(SiMe_3)_3]$.[8] In the present paper, we report on full experimental and spectroscopic details for $(Me_3Si)_3SiBCl_2$, a series of related new silyl- and germylboranes, and their facile use as starting materials for the preparation of the first silyl- and germylboryl complexes.

Experimental

General

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques, unless otherwise stated. Solvents and reagents were dried by standard procedures, distilled and stored under nitrogen over molecular sieves. $(Me_2N)_2BSi(SiMe_3)_3$,[9] $Li[Ge(SiMe_3)_3]$,[10] $ClB(NMe_2)_2$,[11] $K[Si_2(SiMe_3)_5]$,[12] $(Me_2N)_2BSiPh_3$,[13] $Na[(\eta^5-C_5H_5)Fe(CO)_2]$,[14] $Na[(\eta^5-C_5H_4Me)Fe(CO)_2]$,[14] $Na[(\eta^5-C_5Me_5)Fe(CO)_2]$,[14] $K[(\eta^5-C_5H_4Me)Mn(CO)_2H]$[15] were synthesised according to literature

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procedures. NMR: Varian Unity 500 at 499.834 MHz (^{1}H, standard TMS internal), 125.639 MHz (^{11}B, standard $BF_3{\cdot}OEt_2$ in C_6D_6 external), 125.639 MHz (^{13}C{^{1}H}, APT, standard TMS internal), 99.263 MHz (^{29}Si, standard TMS internal); all NMR spectra were recorded in C_6D_6 as solvent, unless otherwise stated. Elemental analyses were obtained from a Carlo-Erba elemental analyser, model 1106 and IR spectra were recorded on a Nicolet FT-IR AVATAR 360. Mass spectra were recorded on a Finnigan MAT 95 (70 eV).

Syntheses

Bis(dimethylamino){tris(trimethylsilyl)germyl}borane (2). $Li[Ge(SiMe_3)_3]$ (13.94 g, 27.00 mmol) was dissolved in 125 ml of hexane at −78 °C. $ClB(NMe_2)_2$ (3.63 g, 27.00 mmol) was added dropwise within 10 min. The white suspension was allowed to come to ambient temperature within 2 h and stirred overnight. The suspension was filtered and the colourless solid rinsed twice with 30 ml of hexane. All volatiles of the bright yellow filtrate were removed under vacuum and pure **2** (10.27 g, 97%) was obtained as a bright yellow, air and moisture sensitive solid, which can be stored at −30 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 0.23$ (s, 27 H, $Ge\{Si(CH_3)_3\}_3$), 2.70 (s, 12 H, 2 $N(CH_3)_2$); ^{11}B-NMR: $\delta = 39.3$; ^{13}C-NMR: $\delta = 3.28$ ($Ge\{Si(CH_3)_3\}_3$), 42.38 ($N(CH_3)_2$). $C_{13}H_{39}BN_2GeSi_3$ (391.13): found C 39.55, H 9.82, N 6.85; requires C 39.92, H 10.05, N 7.16%.

Bis(dimethylamino){pentakis(trimethylsilyl)disilyl}borane (3). As described for **2**, $K[Si_2(SiMe_3)_5]$ (13.05 g, 21.59 mmol) was treated with $ClB(NMe_2)_2$ (2.76 g, 20.54 mmol). After filtration, the filtrate was concentrated under vacuum to 20 ml and stored at −80 °C for 3 d. Pure **3** (5.93 g, 53%) was obtained as a colourless, air and moisture sensitive solid, which can be stored at −30 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 0.23$ (s, 27 H, $Si\{Si(CH_3)_3\}_3$), 0.27 (s, 18 H, $Si\{Si(CH_3)_3\}_2$), 2.67 (s, 12 H, 2 $N(CH_3)_2$); ^{11}B-NMR: $\delta = 38.9$; ^{13}C-NMR: $\delta = 4.22$ ($Si\{Si(CH_3)_3\}_3$), 5.18 ($Si\{Si(CH_3)_3\}_2$), 42.98 ($N(CH_3)_2$). $C_{19}H_{57}BN_2Si_7$ (521.09): found C 43.11, H 10.41, N 5.29; requires C 43.79, H 11.03, N 5.38%.

Dichloro{tris(trimethylsilyl)silyl}borane (5). Bis(dimethylamino){tris(trimethylsilyl)silyl}borane (**1**) (5.80 g, 16.73 mmol) was dissolved in 70 ml of hexane at −78 °C. A solution of BCl_3 (3.92 g, 33.46 mmol) in 10 ml hexane was added dropwise within 10 min. The white suspension was allowed to come to ambient temperature within 2 h and was stirred overnight. All volatiles of the bright yellow, clear solution were removed under vacuum and the colourless residue was sublimed at 60 °C/0.001 Torr into a cold sublimation tube (−78 °C). Pure **5** (4.93 g, 89.5%) was obtained as a colourless, air and moisture sensitive solid, which can be stored at −30 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 0.27$ (s, 27 H, $Si\{Si(CH_3)_3\}_3$); ^{11}B-NMR: $\delta = 79.2$; ^{13}C-NMR: $\delta = 1.9$ ($Ge\{Si(CH_3)_3\}_3$). $C_9H_{27}BCl_2Si_4$ (329.38): found C 32.43, H 8.67; requires C 32.82, H 8.26%.

Dichloro{tris(trimethylsilyl)germyl}borane (6). As described for **5**, bis(dimethylamino){tris(trimethylsilyl)germyl}borane (**2**) (10.27 g, 26.26 mmol) was treated with BCl_3 (6.77 g, 57.78 mmol, 10% excess). After removing all volatiles under vacuum the bright yellow residue was dried for 3 h at ambient temperature under vacuum. Pure **6** (9.52 g, 97%) was obtained as a bright yellow, extremely air and moisture sensitive, pyrophoric solid, which can be stored at −30 °C. ^{1}H-NMR ($CDCl_3$): $\delta =$ 0.30 (s, 27 H, $Ge\{Si(CH_3)_3\}_3$); ^{11}B-NMR: $\delta = 80.0$; ^{13}C-NMR: $\delta = 2.46$ ($Ge\{Si(CH_3)_3\}_3$). $C_9H_{27}BCl_2GeSi_3$ (373.88): found C 28.55, H 6.94; requires C 28.91, H 7.28%.

Dichloro{pentakis(trimethylsilyl)disilyl}borane (7). As described for **5**, bis(dimethylamino){pentakis(trimethylsilyl)disilyl}borane (**3**) (5.93 g, 11.40 mmol) was treated with BCl_3 (2.94 g, 25.10 mmol, 10% excess). After removing all volatiles under vacuum, the colourless oily residue was dried for 3 h at 50 °C under vacuum. Pure **7** (5.40 g, 94%) was obtained as a colourless, air and moisture sensitive oil, which can be strored at −30 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 0.28$ (s, 27 H, $Si\{Si(CH_3)_3\}_3$), 0.33 (s, 18 H, $Si\{Si(CH_3)_3\}_2$); ^{11}B-NMR: $\delta = 79.7$; ^{13}C-NMR: $\delta = 3.27$ ($Si\{Si(CH_3)_3\}_2$), 3.68 ($Si\{Si(CH_3)_3\}_3$), ^{29}Si-NMR: $\delta = -9.04$ ($Si\{\mathit{Si}(CH_3)_3\}_3$), −9.59 ($Si\{\mathit{Si}(CH_3)_3\}_2$), −104.76 ($B\mathit{Si}\{Si(CH_3)_3\}_2$), −126.19 ($\mathit{Si}\{Si(CH_3)_3\}_3$). $C_{15}H_{45}BCl_2Si_7$ (503.84): found C 35.36, H 8.72; requires C 35.76, H 9.00%.

Dichloro(triphenylsilyl)borane (8). As described for **5**, bis(dimethylamino)(triphenylsilyl)borane (**4**) (20.38 g, 51.75 mmol) was treated with BCl_3 (18.19 g, 155.25 mmol, threefold excess). After removing all volatiles under vacuum, the brown oily residue was prepurified by condensation at 100 °C in high vacuum into a cooled trap (−78 °C). The colourless crude material, which is a 1 : 1 mixture of **8** and $(Me_2N)_2BCl$, is distilled under vacuum affording pure **8** (8.41 g, 48%) at 54 °C/14 mbar as a colourless, air and moisture sensitive liquid. ^{1}H-NMR ($CDCl_3$): $\delta = 7.50$ (m, 6 H, *m*-C_6H_5), 7.68 (m, 3 H, *p*-C_6H_5), 8.17 (m, 6 H, *o*-C_6H_5); ^{11}B-NMR: $\delta = 55.5$; ^{13}C-NMR: $\delta = 128.14$ (*m*-C_6H_5), 135.07 (*p*-C_6H_5), 136.86 (*o*-C_6H_5). $C_{18}H_{15}BCl_2Si$ (341.11): found C 63.36, H 4.23; requires C 63.38, H 4.43%.

[Chloro{tris(trimethylsilyl)silyl}boryl]dicarbonyl(η^5-cyclopentadienyl)iron (9a). $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (1.15 g, 5.7 mmol) was suspended in 30 ml of toluene at 0 °C. A solution of **3** (1.90 g, 5.77 mmol) in 10 ml of toluene was added dropwise within 10 min. After stirring for another 5 min at 0 °C all volatiles were removed under vacuum. The red–brown residue was suspended in 30 ml of hexane and the mixture was centrifuged. The clear, red–brown solution was decanted from the light solid, concentrated under vacuum to 10 ml and stored at −80 °C. After 24 h pure **9a** (1.87 g, 69%) was obtained as yellow, air and moisture sensitive crystals, which have to be stored at −30 °C. ^{1}H-NMR: $\delta = 0.40$ (s, 27 H, $Si(CH_3)_3$), 4.12 (s, 5 H, C_5H_5); ^{11}B-NMR: $\delta = 141.2$; ^{13}C-NMR: $\delta = 3.18$ ($Si(CH_3)_3$), 85.43 (C_5H_5), 213.69 (CO). IR (toluene): $\nu = 2009$, 1956 cm^{-1} (CO). $C_{16}H_{32}BClFeO_2Si_4$ (470.88): found C 40.08, H 7.08; requires C 40.81, H 6.85%. MS *m*/*z* = 470 (M^+), 455 ($M^+ - CH_3$), 442 ($M^+ - CO$), 414 ($M^+ - 2CO$), 427 ($M^+ - CH_3 - CO$), 73 ($SiMe_3$).

[Chloro{tris(trimethylsilyl)silyl}boryl]dicarbonyl(η^5-methylcyclopentadienyl)iron (9b). As described for **9a**, $Na[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]$ (0.56 g, 2.62 mmol) was treated with **3** (0.86 g, 2.62 mmol). After decantation all volatiles were removed under vacuum and almost pure **9b** (0.64 g, 50%) was obtained as a brown, air and moisture sensitive oil, which has to be stored at −30 °C. ^{1}H-NMR: $\delta = 0.41$ (s, 27 H, $Si(CH_3)_3$), 1.49 (s, 3 H, $C_5H_4\mathit{CH}_3$), 4.09 (s, 4 H, $C_5\mathit{H}_4CH_3$); ^{11}B-NMR: $\delta = 140.1$; ^{13}C-NMR: $\delta = 3.26$ ($Si(CH_3)_3$), 12.74 ($C_5H_4\mathit{C}H_3$), 84.74, 86.01 ($\mathit{C}_5H_4CH_3$), 103.06 (ipso-C, $\mathit{C}_5H_4CH_3$), 214.15 (CO). IR (toluene): $\nu = 2008$, 1957 cm^{-1} (CO). $C_{17}H_{34}BClFeO_2Si_4$ (484.91): found C 43.78, H 6.98; requires C 42.11, H 7.07%.

[Chloro{tris(trimethylsilyl)silyl}boryl]dicarbonyl(η^5-pentamethylcyclopentadienyl)iron (9c). As described for **9a**, $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ (0.50 g, 1.85 mmol) was treated with **3** (0.61 g, 1.85 mmol). Pure **9c** (0.52 g, 52%) was obtained as brown–yellow, air and moisture sensitive crystals, which have to be stored at −30 °C. ^{1}H-NMR: $\delta = 0.49$ (s, 27 H, $Si(CH_3)_3$), 1.49 (s, 15 H, $C_5(CH_3)_5$); ^{11}B-NMR: $\delta = 138.9$; ^{13}C-NMR: $\delta = 3.59$ ($Si(CH_3)3$), 9.91 ($C_5(\mathit{C}H_3)_5$), 97.18 ($\mathit{C}_5(CH_3)_5$), 215.89 (CO). IR (toluene): $\nu = 1990$, 1939 cm^{-1} (CO). $C_{21}H_{42}BClFeO_2Si_4$ (541.02): found C 46.54, H 8.05; requires C 46.62, H 7.83%.

[Chloro{tris(trimethylsilyl)germyl}boryl]dicarbonyl(η^5-cyclopentadienyl)iron (9d). As described for **9a**, $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (0.49 g, 2.43 mmol) was treated with **4** (0.91 g, 2.43 mmol). Pure **9d** (0.44 g, 35%) was obtained as brown–yellow, extremely air and moisture sensitive crystals, which have to be stored at −30 °C. ^{1}H-NMR: δ = 0.42 (s, 27 H, $\mathrm{Ge\{Si(CH_3)_3\}_3}$), 4.14 (s, 5 H, $\mathrm{C_5H_5}$); ^{11}B-NMR: δ = 139.0; ^{13}C-NMR: δ = 3.73 ($\mathrm{Ge\{Si(CH_3)_3\}_3}$), 85.56 ($\mathrm{C_5H_5}$), 213.65 (CO). IR (toluene): ν = 2009, 1956 cm^{-1}(CO). $\mathrm{C_{16}H_{32}BClFeGeO_2Si_3}$ (515.38): found C 37.08, H 6.12; requires C 37.29, H 6.26%.

[Chloro{pentakis(trimethylsilyl)disilyl}boryl]dicarbonyl(η^5-cyclopentadienyl)iron (9e). As described for **9a**, Na[(η^5-$\mathrm{C_5H_5}$)-Fe(CO)$_2$] (0.40 g, 2.00 mmol) was treated with **6** (1.00 g, 2.00 mmol). After decantation all volatiles were removed under vacuum and almost pure **9e** (0.42 g, 35%) was obtained as a brown, extremely air and moisture sensitive oil, which has to be stored at −30 °C for longer periods. ^{1}H-NMR: δ = 0.38 (m, br, 45 H, $\mathrm{Si(CH_3)_3}$), 4.18 (s, br, 5 H, $\mathrm{C_5H_5}$); ^{11}B-NMR: δ = 141.2; ^{13}C-NMR: δ = 4.02 ($\mathrm{Si\{Si(CH_3)_3\}_2}$), 4.24 ($\mathrm{Si\{Si(CH_3)_3\}_3}$), 85.67 ($\mathrm{C_5H_5}$), 214.25 (CO). IR (toluene): ν = 2007, 1956 cm^{-1} (CO). $\mathrm{C_{22}H_{50}BClFeO_2Si_7}$ (645.35): found C 39.88, H 7.12; requires C 40.95, H 7.81%.

[Chloro{tris(trimethylsilyl)silyl}boryl]dicarbonyl(η^5-methylcyclopentadienyl)hydrido-manganese (10a). K[(η^5-$\mathrm{C_5H_4Me}$)Mn-(CO)$_2$H] (0.86 g, 3.74 mmol) was suspended in 20 ml of toluene at 0 °C. A solution of **3** (1.23 g, 3.74 mmol) in 5 ml of toluene was added in one gush to the yellow suspension; after that the colour changed spontaneously from yellow to dark red. After stirring for 5 min at 0 °C all volatiles were removed under vacuum, the red, oily residue was suspended in 25 ml of hexane and centrifuged. The red solution was decanted from the lightly yellow solid and concentrated under vacuum to 10 ml. After storage at −80 °C for 7 d pure **10a** (1.21 g, 67%) was obtained as red, air and moisture sensitive crystals, which can be stored at −30 °C. ^{1}H-NMR: δ = −15.32 (br. s, 1 H, Mn-H), 0.48 (s, 27 H, $\mathrm{Si\{Si(CH_3)_3\}_3}$), 1.37 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 4.04–4.17 (m, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$); ^{11}B-NMR: δ = 105.2 (br. s); ^{13}C-NMR: δ = 2.01 ($\mathrm{Si\{Si(CH_3)_3\}_3}$), 12.76 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$), 87.5–87.7 ($\mathit{C}_5\mathrm{H_4CH_3}$), 105.82 (ipso-C, $\mathit{C}_5\mathrm{H_4CH_3}$), 211.73 (CO). IR (toluene): ν = 1978, 1913 cm^{-1} (CO). $\mathrm{C_{17}H_{35}BClMnO_2Si_4}$ (485.01): found C 40.97, H 7.56; requires C 42.10, H 7.24%.

[Chloro{tris(trimethylsilyl)germyl}boryl]dicarbonyl(η^5-methylcyclopentadienyl)hydrido-manganese (10b). As described for **10a**, K[(η^5-$\mathrm{C_5H_4Me}$)Mn(CO)$_2$H] (0.35 g, 1.52 mmol) was treated with **4** (0.57 g, 1.52 mmol). After storage at −80 °C for 2 d pure **10b** (0.31 g, 38%) was obtained as red crystals, which deliquesce above −30 °C into a red, extremely air and moisture sensitive oil. ^{1}H-NMR: δ = −15.03 (br. s, 1 H, Mn-H), 0.51 (s, 27 H, $\mathrm{Ge\{Si(CH_3)_3\}_3}$), 1.39 (s, 3 H, $\mathrm{C_5H_4C}\mathit{H}_3$), 4.05–4.16 (kB, 4 H, $\mathrm{C_5}\mathit{H}_4\mathrm{CH_3}$); ^{11}B-NMR: δ = 105.8 (br. s); ^{13}C-NMR: δ = 3.37 ($\mathrm{Ge\{Si(CH_3)_3\}_3}$), 12.76 ($\mathrm{C_5H_4}\mathit{C}\mathrm{H_3}$), 87.29–87.52 ($\mathit{C}_5\mathrm{H_4CH_3}$), 105.54 (ipso-C, $\mathit{C}_5\mathrm{H_4CH_3}$). IR (toluene): ν = 1975, 1914 cm^{-1} (CO). $\mathrm{C_{17}H_{35}BClGeMnO_2Si_3}$ (529.51): found C 37.97, H 6.48; requires C 38.56, H 6.66%.

[Fluoro{tris(trimethylsilyl)silyl}boryl]dicarbonyl(η^5-cyclopentadienyl)iron (11). **9a** (1.87 g, 3.97 mmol) was dissolved in 30 ml of $\mathrm{CH_2Cl_2}$ and TlF (1.33 g, 5.96 mmol, 50% excess) were added at ambient temperature. The reaction mixture was stirred for 24 h and all volatiles were removed under vacuum. The brown–red residue was suspended in 30 ml of hexane, centrifuged and the brown–red solution was decanted from the light brown solid. After reducing to 5 ml under vacuum 5 ml of perfluorohexane were added and the two phase mixture was stored at −80 °C for 4 d. **11** (0.83 g, 46%) was obtained as yellow, extremely air and moisture sensitive crystals growing at the interface of the two solvents. ^{1}H-NMR: δ = 0.39 (s, 27 H, $\mathrm{Si(CH_3)_3}$), 4.15 (s, 5 H, $\mathrm{C_5H_5}$); ^{11}B-NMR: δ = 113.2 (d, $^1J_{\mathrm{BF}}$ = 232 Hz); ^{13}C-NMR: δ = 2.93 ($\mathrm{Si(CH_3)_3}$), 84.35 ($\mathrm{C_5H_5}$), 214.19 (CO). IR (toluene): ν = 2001, 1946 cm^{-1} (CO). MS m/z = 454 (M$^+$, 2%), 426 (M$^+$ − CO, 26%), 398 (M$^+$ − 2CO, <1%), 325 (M$^+$ − $\mathrm{SiMe_3}$–CO, 8%), 277 ($\mathrm{FBSi\{SiMe_3\}_3}$, 18%), 121 (CpFe, 38%), 73 ($\mathrm{SiMe_3}$, 71%). $\mathrm{C_{16}H_{32}BFFeO_2Si_4}$ (454.43): found C 42.01, H 6.90; requires C 42.29, H 7.10%.

X-Ray crystallography

Geometry and intensity data were collected on an ENRAF Nonius CAD4 diffractometer using Mo-K$_\alpha$ radiation (λ = 0.7107 Å). Crystal data, data collection parameters, and convergence results are compiled in Table 1. All crystals studied were platelets sensitive to air and moisture and showed relatively broad reflections. In the case of **9d** crystal faces were difficult to index and an empirical absorption correction[16] was applied. For the remaining crystals absorption corrections were based on Gaussian integration.[17] The structures were solved by direct methods[18] and refined on F^2[19] with hydrogen atoms in calculated positions. For **10a** only the Mn, Cl, and Si atoms have been refined anisotropically. Displacement ellipsoid plots were obtained with PLATON94.[20]

CCDC reference numbers 178620–178623.

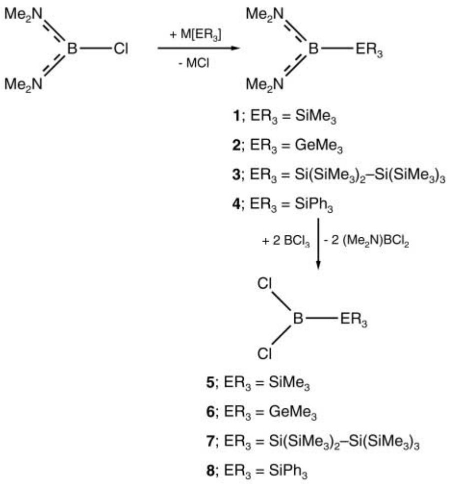
See http://www.rsc.org/suppdata/dt/b2/b201100j/ for crystallographic data in CIF or other electronic format.

Results and discussion

(Dichloro)silyl- and -germylboranes

In view of the synthesis of boryl complexes *via* salt elimination reactions from anionic transition metal complexes and haloboranes, the use of borane precursors of the type $\mathrm{R_3E\text{-}BCl_2}$ (E = Si, Ge) appears to be advantageous. Silyl and germyl substituents do not compensate for the electron deficiency of the boron atom, thus providing a strongly electrophilic centre for the addition of an anionic transition metal species. Besides, extremely bulky groups such as $\mathrm{Si(SiMe_3)_3}$ and $\mathrm{Ge(SiMe_3)_3}$ should provide sufficient sterical shielding to stabilise the target boryl complexes.

As attempts to obtain the compounds $\mathrm{R_3E\text{-}BCl_2}$ (E = Si, Ge) in useful yields and on a sufficient scale by direct reaction of M[ER$_3$] (M = Li, K) with $\mathrm{BCl_3}$ failed, we applied the stepwise procedure outlined in Scheme 1.



Scheme 1

Similar to the reported preparation of $\mathrm{(Me_2N)_2B\text{–}Si(SiMe_3)_3}$ (**1**)[9] and $\mathrm{(Me_2N)_2B\text{–}SiPh_3}$(**3**)[13] the bis(dimethylamino) boranes $\mathrm{(Me_2N)_2B\text{–}Ge(SiMe_3)_3}$ (**2**) and $\mathrm{(Me_2N)_2B\text{–}Si(SiMe_3)_2\text{–}Si(SiMe_3)_3}$ (**4**) were obtained from the reaction of M[ER$_3$] with $\mathrm{(Me_2N)_2B\text{–}Cl}$. The boranes **1**–**4** were subsequently treated with two equivalents of $\mathrm{BCl_3}$, thus affording the corresponding dichloroboranes $\mathrm{Cl_2B\text{–}ER_3}$ (**5**, ER$_3$ = $\mathrm{Si(SiMe_3)_3}$; **6**, ER$_3$ = Ge-

Table 1 Crystal data for **9a**, **9d**, **10a** and **11**

	9a	**9d**	**10a**	**11**
Empirical formula	$C_{16}H_{32}BClFeO_2Si_4$	$C_{16}H_{32}BClFeGeO_2Si_3$	$C_{17}H_{35}BClMnO_2Si_4$	$C_{16}H_{32}BFFeO_2Si_4$
M	470.89	515.39	485.01	454.43
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (14)	$P2_1/c$ (14)	$C2/c$ (15)	$C2/c$ (15)
a/Å	17.262(5)	17.320(4)	34.35(2)	16.782(5)
b/Å	9.403(2)	9.425(2)	9.268(9)	9.611(3)
c/Å	16.525(5)	16.572(3)	17.00(2)	31.15(1)
a/°	90	90	90	90
β/°	106.72(2)	106.53(2)	100.94(5)	94.84(3)
γ/°	90	90	90	90
V/Å^3	2569(1)	2594(1)	5312(9)	5006(3)
Z	4	4	8	8
μ/mm^{-1}	0.882	1.950	0.765	0.803
Reflections measured	14960	12034	11192	10134
Independent reflections	5031	5105	4687	4894
Final $R1$ [$I > 2\sigma(I)$]	0.0793	0.0851	0.1145	0.0940
$wR2$ (all data)	0.1649	0.1925	0.2245	0.1981
GOF	0.905	0.969	0.894	1.134

$(SiMe_3)_3$; **7**, ER_3 = $Si(SiMe_3)_2$–$Si(SiMe_3)_3$; **8**, ER_3 = $SiPh_3$) in useful yields after removal of the accompanying two equivalents of $(Me_2N)BCl_2$ under high vacuum.

The new germyl borane $(Me_2N)_2B$–$Ge(SiMe_3)_3$ (**2**) was obtained in almost quantitative yield (>97%) as a bright yellow solid after filtration and evaporation of the reaction mixture. In the case of $(Me_2N)_2B$–$Si(SiMe_3)_2$–$Si(SiMe_3)_3$ (**4**), however, the crude solid material being obtained after removal of all volatile materials under high vacuum, had to be recrystallised from hexane at −80 °C giving 53% of the product as a colourless solid.

Both compounds were characterised in solution by multinuclear NMR spectroscopy and displayed the expected shifts such as ^{11}B NMR resonances at δ = 39.3 (**2**) and 38.9 (**4**).

The dichloroboranes **5** and **6** were obtained in high yields of 90–97% as colourless solids, while **7** was isolated as a colourless, viscous oil in a similarly good yield of 94%. Due to its higher volatility with respect to those of **5**–**7**, the phenyl derivative Cl_2B–$SiPh_3$ (**8**) had to be separated by fractionated distillation at elevated temperatures from the accompanying $(Me_2N)BCl_2$, thus accounting for a lower yield of 48%. All dichloroboranes, and the triphenylsilyl derivative **8** in particular, proved to be extremely sensitive towards air and moisture and thermally rather labile, but can be stored neat or in solution at temperatures below −30 °C for prolonged periods of time without decomposition.

The multinuclear NMR data of **5**–**8** in solution meet the expectations, showing for example considerably deshielded ^{11}B NMR resonances with respect to those of the aminoborane precursors at δ = 79.2 (**5**), 80.0 (**6**), 79.7 (**7**) and at δ = 55.5 (**8**). The smaller boranes **5**, **6**, and **8** display single sets of signals for the ER_3-ligand in the ^1H and ^{13}C NMR spectra, thus proving free rotation with respect to the B–E bond in solution. Cl_2B–$Si(SiMe_3)_2$–$Si(SiMe_3)_3$ (**7**) shows the expected two sets of signals in a 2 : 3 ratio for the two different sets of $SiMe_3$-ligands in the ^1H, ^{13}C, and ^{29}Si NMR spectra.

Silyl- and germylboryl complexes of iron and manganese

Synthesis. A range of new iron boryl complexes was obtained from the reaction of the boranes **5**–**7** with the strongly nucleophilic anionic iron complexes $Na[(\eta^5\text{-}C_5R_4R')Fe(CO)_2]$ (R, R′ = H, Me) in toluene at 0 °C according to Scheme 2 *via* salt elimination. The compounds $[(\eta^5\text{-}C_5R_4R')(OC)_2Fe$–$B(Cl)Si(SiMe_3)_3]$ (**9a**, R = R′ = H; **9b**, R = H, R′ = Me; **9c**, R = R′ = Me), $[(\eta^5\text{-}C_5H_5)(OC)_2Fe$–$B(Cl)Ge(SiMe_3)_3]$ (**9d**), and $[(\eta^5\text{-}C_5H_5)(OC)_2Fe$–$B(Cl)Si(SiMe_3)_2$–$Si(SiMe_3)_3]$ (**9e**) were afforded in yields between 35–69% as yellow or brown crystals in the case of **9a**, **c**, **d** or viscous liquids in the case of **9b**, **e**. All complexes readily dissolve in all common aliphatic and aromatic hydrocarbons, are moderately air and moisture sensitive, and can be stored at temperatures below −30 °C without significant decomposition.

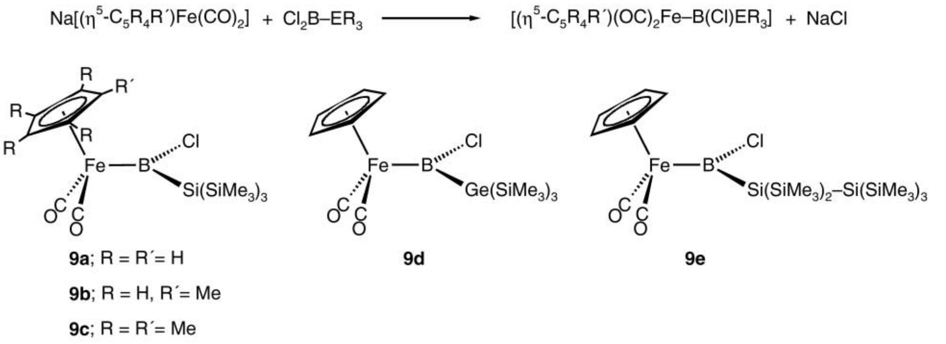
A corresponding reaction of the anionic manganese complex $K[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]$ with Cl_2B–$Si(SiMe_3)_3$ (**5**) and Cl_2B–$Ge(SiMe_3)_3$ (**6**) in a 1 : 1 ratio at 0 °C in toluene afforded the silyl- and germylboryl complexes $[(\eta^5\text{-}C_5H_4Me)(OC)_2(H)Mn$–$B(Cl)Si(SiMe_3)_3]$ (**10a**) and $[(\eta^5\text{-}C_5H_4Me)(OC)_2(H)Mn$–$B(Cl)Ge(SiMe_3)_3]$ (**10b**) in yields of 67% and 38%, respectively, according to Scheme 3.

The products **10a**, **b** were obtained as dark red, air and moisture sensitive crystals from hexane solutions at −30 °C, which in the case of **10b** melt into a red oil above this temperature. Both complexes are stable under nitrogen and can be stored at −30 °C without degradation. In the case of Cl_2B–$Si(SiMe_3)_2$–$Si(SiMe_3)_3$ (**7**) no reaction was observed with $K[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]$ – obviously due to the increased sterical shielding of the borane and the decreased nucleophilicity of the manganese complex with respect to its iron analogue. Attempts to obtain the corresponding (triphenylsilyl)boryl complexes from the reactions of Cl_2B–$SiPh_3$ (**8**) with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ or $K[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]$ under identical conditions resulted in the formation of intractable, viscous liquids, which are extremely sensitive towards air and moisture, and readily decompose in hexane or toluene solution. The presence of the target molecules $[(\eta^5\text{-}(C_5H_5)(OC)_2Fe$–$B(Cl)SiPh_3]$ (**9f**) and $[(\eta^5\text{-}C_5H_4Me)(OC)_2(H)Mn$–$B(Cl)SiPh_3]$ (**10c**), however, can be deduced from characteristic spectroscopic data (*vide infra*) such as the deshielded ^{11}B NMR shifts at δ = 109.2 (**9f**) and 81.3 (**10c**), and the shielded ^1H NMR resonance for the manganese bound hydrogen atom at δ = −15.9 in the case of the latter. The enhanced sensitivity of Cl_2B–$SiPh_3$ (**8**) and the boryl complexes **9f** and **10c** with respect to all other compounds discussed here, is supposed to be solely due to the lesser sterical shielding by the phenyl groups. The presence of β-silyl groups in the boranes **1**–**4**, **5**–**8** and the complexes **9a**–**e**, **10a**, **b** could also account for their increased stability with respect to that of the corresponding phenyl derivatives **8**, **9f**, and **10c**, as a β-silyl effect is well known to stabilise electron deficient boron centres by formation of non-classical three-centre two-electron bonds (hyperconjugation) with adjacent silyl groups – there is, however, no indication of the characteristic spectroscopical and structural features of this effect (*vide infra*).[21]

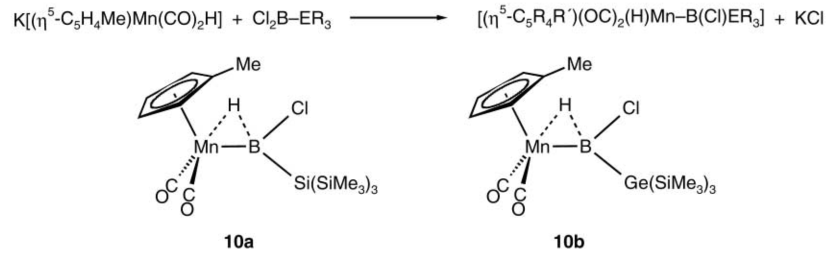
Structure. *Iron complexes.* The structure of the boryl iron complexes **9a**–**e** in solution was derived from multinuclear NMR and IR data (Table 2). All complexes show significantly deshielded ^{11}B NMR signals ranging from δ = 138.9 to 141.2. The observed resonances are low-field shifted by approximately

Table 2 Selected spectroscopic and structural data for **9a**–**e**, **10a**, **b** and **11**

	9a	**9b**	**9c**	**9d**	**9e**	**10a**	**10b**	**11**
δ^{11}B	141.2	140.1	138.9	139.0	141.2	105.2	105.8	113.2
νCO/cm^{-1}	2009, 1956	2008, 1957	1990, 1939	2009, 1956	2007, 1956	1978, 1913	1975, 1914	2001, 1946
d_{M-B}/Å	1.964(8)	—	—	1.985(11)	—	2.138(16)	—	1.983(9)
d_{B-E}/Å	2.030(8)			2.063(12)		2.052(16)		2.046(10)



Scheme 2



Scheme 3

20 ppm with respect to the diphenylboryl complex [(η^5-C$_5$H$_5$)(OC)$_2$Fe–BPh$_2$][22] and by even 80 ppm with respect to aminoboryl complexes of the type [(η^5-(C$_5$H$_5$)(OC)$_2$Fe–B(X)-NR$_2$],[4,5,6] thus being in the expected range for a metal coordinated boryl ligand without π-donating substituents. The ^{1}H- and ^{13}C NMR spectra are unobtrusive and exhibit the expected signals for the SiMe$_3$ groups and η^5-C$_5$R$_5$ ligands. All complexes show two CO stretching frequencies in the IR spectra, which in the case of **9a**, **b**, **d**, **e** were found at 2008–9 cm^{-1} and 1956–7 cm^{-1}, thus being in the range of corresponding aminoboryl (ν = 2000–2005, 1940–1946 cm^{-1})[4,5,6] and alkyl iron complexes (ν = 1999–2005, 1938–1944 cm^{-1},[23] but red shifted with respect to the related catecholboryl complex [(η^5-C$_5$H$_5$)-(OC)$_2$FeBCat] (ν = 2024, 1971 cm^{-1}), for which an albeit weak iron–boron π-bond was established.[22] The permethylated cyclopentadienyl ligand in **9c** causes the expected redshift with respect to **9a**, **b**, **d**, **e** and the CO stretching frequencies at ν = 1990 cm^{-1} and 1939 cm^{-1} match those of its amino counterpart [η^5-C$_5$Me$_5$(OC)$_2$Fe–B(Cl)NMe$_2$] (ν = 1988 cm^{-1}, 1928 cm^{-1}).[4] These findings clearly indicate the absence of any iron–boron π-backdonation in solution.[1]

In the case of **9a** and **d** suitable crystals for X-ray structure analyses were obtained from hexane solutions at −30 °C within several days. The compounds are isostructural, crystallise in the monoclinic space group $P2_1/c$, and the molecules adopt C_1-symmetry in the solid state (Fig. 1). In both cases the plane defined by Si(1)–B–Cl and Ge–B–Cl is almost orthogonal with respect to the plane defined by Fe–B–Cp$_m$ (Cp$_m$ = centre point of the cyclopentadienyl ring). This particular conformation in the crystal has been already established for [(η^5-(C$_5$H$_5$)(OC)$_2$-Fe–BPh$_2$][22] and complexes of the type [(η^5-(C$_5$H$_5$)(OC)$_2$Fe–B(X)-NR$_2$],[4,5,6] and does not allow for π-backdonation from the metal-like a″ symmetrical HOMO into the vacant p$_z$-orbital at boron (Fig. 2).

The iron–boron distances were found to be 196.4(8) pm (**9a**) and 198.5(11) pm (**9d**), thus being somewhat smaller than in the amino boryl complex [(η^5-C$_5$Me$_5$)(OC)$_2$Fe–B(Cl)NMe$_2$] (202.7(5) pm),[4] but still close to the sum of the covalent radii for iron and boron.

A structural indication for the presence of a stabilising β-silyl or hyperconjugative effect would be a significant distortion *i.e.* reduction of the B–E–Si angles.[21] In the case of **9a**, **d**, however, all corresponding angles range from 107 to 119°, and the overall geometry of the E(SiMe$_3$)$_3$ moieties resembles that of the Si(SiMe$_3$)$_3$ ligand in [(OC)$_5$Cr=B–Si(SiMe$_3$)$_3$] for which a hyperconjugation was ruled out on the basis of DFT calculations.[8]

Manganese complexes

The manganese boryl complexes [(η^5-C$_5$H$_4$Me)(OC)$_2$(H)Mn–B(Cl)Si(SiMe$_3$)$_3$] (**10a**) and [(η^5-C$_5$H$_4$Me)(OC)$_2$(H)Mn–B(Cl)-Ge(SiMe$_3$)$_3$] (**10b**) were characterised in solution by multinuclear NMR and IR spectroscopy (Table 2). The CO stretching frequencies at 1975–8 cm^{-1} and 1913–4 cm^{-1} match those of the corresponding dihydride complex [(η^5-C$_5$H$_5$)(OC)$_2$Mn(H)$_2$] (1972, 1910 cm^{-1}),[24] thus indicating a manganese–boron σ-bond without π-contribution. The SiMe$_3$ groups and η^5-C$_5$R$_5$ ligands show the expected signals in the ^{1}H- and ^{13}C NMR spectra, and for the metal coordinated boron centres deshielded resonances at δ = 105.2 (**10a**) and 105.8 (**10b**) are detected in the ^{11}B NMR spectra. Although these signals are fairly low-field shifted the effect of deshielding is less pronounced than in the corresponding iron complexes **9a**–**e**, thus indicating the presence of a Mn–H–B bridge in solution and an increased coordination number of the boron atoms. A corresponding Mn–H–Si bridge is known for the corresponding silyl hydride complexes [(η^5-C$_5$H$_5$)(OC)$_2$(H)MnSiR$_3$].[25] Similar interactions

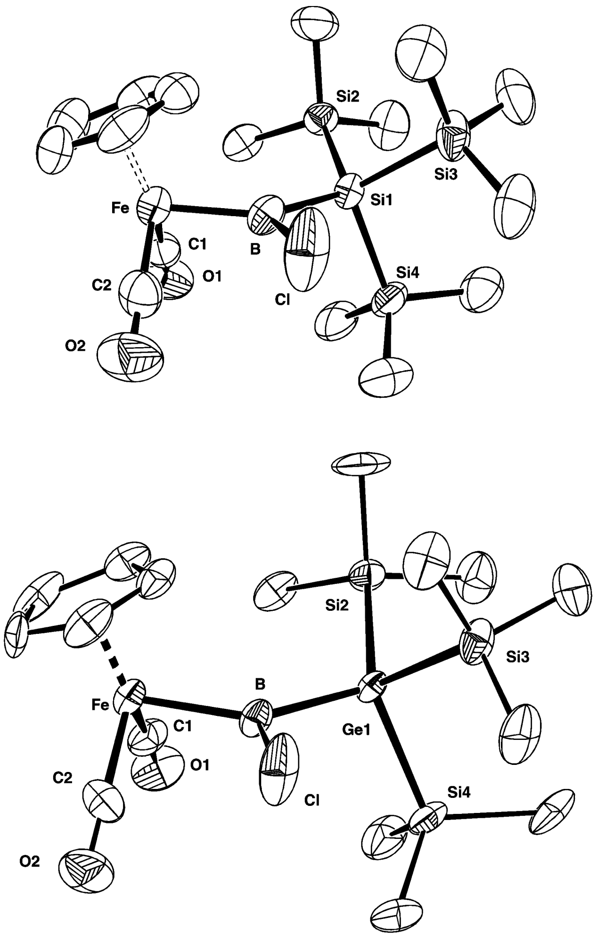


Fig. 1 X-Ray crystal structure of **9a** (left) and **9d** (right). Selected bond lengths (Å) and angles (°): **9a**: Fe–B 1.964(8), B–Si(1) 2.030(8), Si(1)–Si(2) 2.342(3), Si(1)–Si(3) 2.355(3), Si(1)–Si(4) 2.356(3), B–Si(1)–Si(2) 118.6(2), B–Si(1)–Si(3) 107.2(2), B–Si(1)–Si(4) 107.7(2); **9d**: Fe–B 1.985(11), B–Ge(1) 2.063(12), Ge(1)–Si(3) 2.389(3), Ge(1)–Si(2) 2.378(3), Ge–Si(4) 2.384(3), B–Ge(1)–Si(3) 106.9(3), B–Ge(1)–Si(2) 118.5(3), B–Ge(1)–Si(4) 107.8(3).

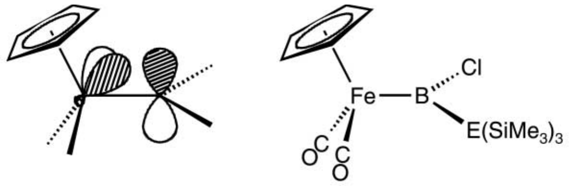


Fig. 2 Orbital mismatch in boryl iron complexes [(η^5-C_5H_5)$(OC)_2$Fe–B(Cl)E$(SiMe_3)_3$] (E = Si, Ge) (**9a**, **d**): possible orbital interaction (left) and schematic structure (right).

between boron and hydrogen co-ligands were reported for boryl complexes of early transition metals such as [(η^5-C_5H_5)$_2$NbH_2-(BR_2)] and are known to be more pronounced in cases of electron poor boron atoms *i.e.* boryl groups without π-donating substituents.[26] The presence of a Mn–H–B bridge in solution is also indicated by the different line widths of the Mn–H resonance at $\delta = -15.3$ in the ^{1}H- and ^{1}H{^{11}B}-NMR spectra (Fig. 3), which were determined to be 15 and 5 Hz, respectively. In the proton coupled ^{11}B NMR spectra only broad singlets rather than the expected doublets were observed, which is, however, in accordance with earlier spectroscopic findings for related boryl complexes.[26]

Suitable crystals of **10a** for a X-ray structure analysis were obtained after several days from hexane solution at −30 °C. The complex crystallises in the monoclinic space group C_2/c and the molecule adopts C_1-symmetry in the crystal (Fig. 4).

The two planes being defined by Si(1)–B–Cl and B–Mn–Cp$_m$ slightly deviate by 9.2° from the coplanar arrangement. The manganese–boron distance of 213.8(16) pm is considerably greater than that of a related catecholboryl manganese complex [$(OC)_5$Mn–BCat][27] (210.8(6) pm) and those in the bridged borylene complex [μ-B(NMe_2){(η^5-C_5H_4Me)Mn$(CO)_2$}$_2$][28] (203(1) pm), both of which are described as manganese–boron σ-bonds.

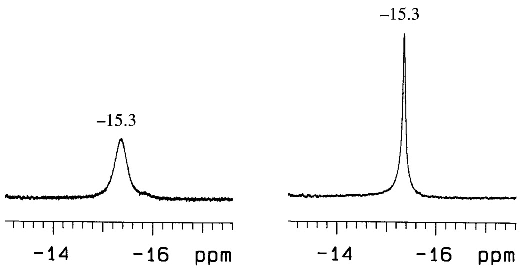


Fig. 3 Mn–*H* resonance of **10a** in boron coupled (^{1}H-) and boron decoupled (^{1}H{^{11}B}-) NMR spectra.

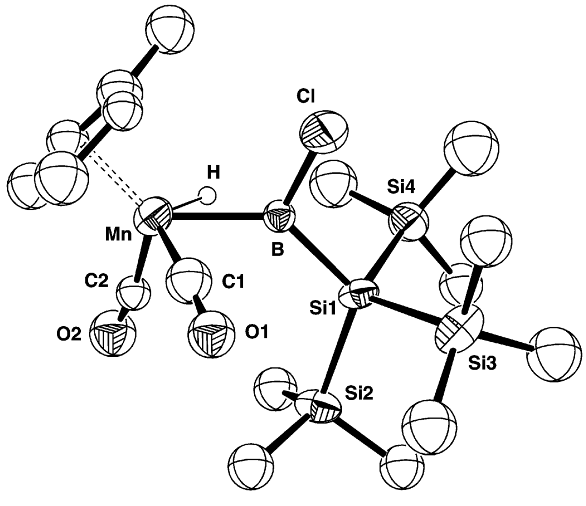


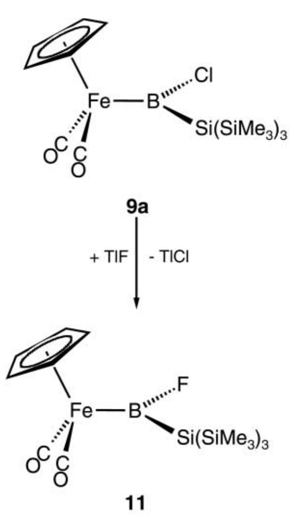
Fig. 4 X-Ray crystal structure of **10a** with idealised position of the manganese bound hydrogen atom. Selected bond lengths (Å): Mn–B 2.138(16), B–Si(1) 2.052(16).

The elongated metal–boron bond indicates the presence of the Mn–H–B bridge in the crystal, too. However, due to broad, particularly overlapping reflexes of the crystals, the quality of the results and especially of the refinement is significantly reduced, and hence, the exact position of the hydrogen atom could not be determined from the X-ray structure analysis.

Reactivity. Both experimental and theoretical investigations have shown that the strength of a metal–boron bond in boryl complexes with respect to homolytic dissociation may well exceed that of a metal–carbon bond in alkyl complexes.[29] Despite their thermodynamic stability, however, boryl complexes tend to react with facile cleavage of the metal–boron bond, thus giving evidence for their kinetic lability.[1] As a consequence, there is only limited information on substitution reactions at boryl centres with retention of the metal–boron bond.[30]

The reaction of the silylboryl complex [(η^5-C_5H_5)$(OC)_2$-Fe–B(Cl)Si$(SiMe_3)_3$] (**9a**) with a 50% excess of TlF in CH_2Cl_2 at ambient temperature afforded the fluorinated silylboryl complex [(η^5-C_5H_5)$(OC)_2$Fe–B(F)Si$(SiMe_3)_3$] (**11**) according to Scheme 4. As monitored by ^{11}B NMR spectroscopy, the trans-halogenation was completed after 24 h and not accompanied by formation of any other boron-containing side products. Complex **11** was isolated from a 1 : 1 mixture of hexane–perfluorohexane at −80 °C as a yellow, crystalline material in 46% yield.

Neither the corresponding germylboryl complex **9d** nor the silylboryl manganese complex **10a** displayed a comparable



Scheme 4

reactivity towards TlF: **9d** undergoes complete decomposition within 2 h, while no reaction is observed in the case of **10d**.

[(η^5-C_5H_5)(OC)$_2$Fe–B(F)Si(SiMe$_3$)$_3$] (**11**) was characterised in solution and shows the expected IR and multinuclear NMR data (Table 2). Introduction of the strong π-donor fluorine to the boron centre results in a ^{11}B NMR signal at $\delta = 113.2$, which is considerably high-field shifted with respect to that of the starting material and shows the expected doublet splitting and a $^1J_{B-F}$ coupling of 232 Hz. The CO stretching frequencies in the IR spectrum at 2001 and 1946 cm^{-1} closely resemble those of **9a**–**e**, thus giving no evidence for an iron–boron π-backbonding in solution.

Single crystals of **11** suitable for a X-ray structure analysis were grown at −80 °C at the interface of a hexane–perfluorohexane mixture. The complex crystallises in the monoclinic space group C_2/c and the molecule adopts C_1-symmetry in the crystal (Fig. 5).

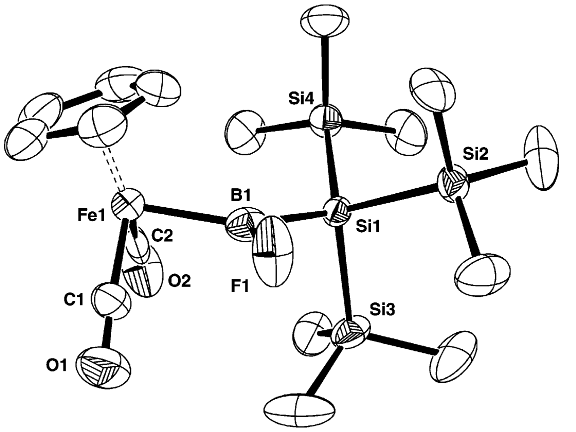


Fig. 5 X-Ray crystal structure of **11**. Selected bond lengths (Å) and angles (°): Fe–B 1.983(9), B–Si(1) 2.046(10), B–F 1.342(9), Si(1)–Si(2) 2.355(3), Si(1)–Si(3) 2.356(3), Si(1)–Si(4) 2.344(3), B–Si(1)–Si(2) 102.8(3), B–Si(1)–Si(3) 105.1(3), B–Si(1)–Si(4) 119.4(3).

The overall geometry of **11** in the crystal bears a close resemblance to that of the corresponding chloro derivative [(η^5-C_5H_5)(OC)$_2$Fe–B(Cl)Si(SiMe$_3$)$_3$] (**9a**). The dihedral angle between the Si(1)–B–F and B–Fe–Cp$_m$ planes is 83.5° and the iron–boron distance was found to be 198.3(9) pm, which again provides no indication for a π-contribution to the metal–boron bond. The boron–fluorine distance of 134.2(9) pm is considerably smaller than the sum of the covalent radii of fluorine and boron, thus reflecting the expected multiple bond character and matching the corresponding distance in *cis*-[(Ph$_3$P)$_2$Pt(BF$_2$)$_2$], which is the only other structurally authentic fluoroboryl complex.[31]

Conclusion

The present study is concerned with a series of new silyl- and germylboranes and provides insight into their reactivity towards transition metal complexes of the type Na[(η^5-C_5R_4R')Fe(CO)$_2$] (R, R′ = H, Me) and K[(η^5-C_5H_4Me)Mn(CO)$_2$H]. The synthesis of [(η^5-C_5R_4R')(OC)$_2$Fe–B(Cl)E(SiMe$_3$)$_3$] (E = Si, Ge; **9a**–**d**), [(η^5-C_5R_4R')(OC)$_2$Fe–B(Cl)Si(SiMe$_3$)$_2$Si(SiMe$_3$)$_3$] (**9e**) and [(η^5-C_5H_4Me)(OC)$_2$(H)Mn–B(Cl)E(SiMe$_3$)$_3$] (**10a**, **b**) proves them to be versatile starting materials for the preparation of the first silyl- and germylboryl complexes *via* salt elimination reactions. The silyl- and germylsubstituents do not relieve the electron deficiency at the three coordinate boron centre by π-interaction or hyperconjugation. However, the spectroscopic and structural findings for the iron complexes **9a**–**e** give no indication that this electron deficiency is compensated for by metal–boron π-backdonation. In the case of the corresponding manganese complexes **10a** and **b** spectroscopic and structural data prove a similar situation as far as the absence of metal-to-boron π-donation is concerned. However, the electron deficiency of the boron atom enables the formation of a Mn–H–B bridge incorporating the manganese bound hydrogen co-ligand. The first transhalogenation at a metal coordinated boryl centre was carried out by reacting [(η^5-C_5R_4R')(OC)$_2$Fe–B(Cl)Si(SiMe$_3$)$_3$] (**9a**) with TlF yielding the fluoroboryl complex [(η^5-C_5R_4R')(OC)$_2$Fe–B(F)Si(SiMe$_3$)$_3$] (**11**), which shows similar spectroscopic and structural features as its precursor.

Acknowledgements

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