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Anion Receptors

Bifunctional Indenyl-Derived Receptors for Fluoride Chelation and Detection

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Abstract: Anion receptors based on a [CpFe(indenyl)] scaffold offer the possibility for the incorporation of adjacent Lewis acidic functions onto a six-membered carbocyclic framework, while at the same time retaining the colorimetric/electrochemical reporter mechanisms available to synthetically simpler ferrocene systems. Thus, [CpFe(indenyl)] systems featuring mutually *ortho* $BMes_2$ and PPh_2Me^+ substituents (with either 4,5 or 5,6 regiochemistry) are accessible which are capable of cooperative fluoride ion fixation. Simultaneous binding at the borane and phosphonium centres can be established by spectroscopic, structural and computational approaches, and is responsible for the favourable thermodynamics associated with F^- uptake. Thus, in contrast to simple $BMes_2$ systems, the binding of fluoride is found to be more favourable than the uptake of cyanide (which interacts only with the borane Lewis acid). Moreover, in the case of a 4-($MePh_2P$)-5-(Mes_2B)-7-Me-indenyl derivative, fluoride chelation is signalled not only by a large cathodic shift in the Fe^{II}/Fe^{III} potential (>500 mV in THF), but also by a distinct colour change from green (for the free receptor) to maroon for the adduct.

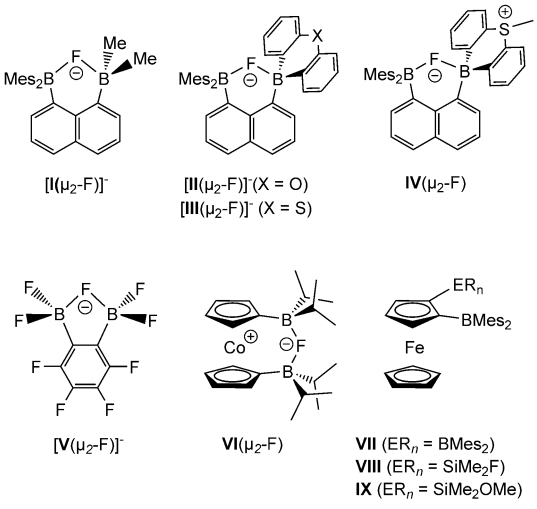
Introduction

The realisation of receptor design strategies for the selective binding of anions and neutral molecules is a critical step in the development of detection protocols for such analytes.[1] The detection, and ultimately sensing, of anions such as fluoride has clear-cut societal benefits derived, for example, from monitoring drinking water quality, and from the detection of certain classes of chemical warfare agent.[2] Within the field of receptor design, Lewis acid systems featuring the chemically robust $BMes_2$ binding domain have recently been the subject of significant research effort;[3] simple systems of this type, however, typically suffer from competing responses from other small, hard anions, such as cyanide.[3–6] To overcome such problems of selectivity, the development of pre-organised arrays featuring more than one binding site (with appropriate shape and size) could be perceived as being beneficial.

A number of bifunctional boranes capable of chelating the fluoride anion have been reported in the literature,[7–11] including the 1,8-naphthalenediyl systems **I**–**IV**$^+$,[7] developed originally by Katz and more recently by Gabbaï, and Piers' highly electron-deficient 1,2-diborylated benzene **V**,[8] together with organometallic systems such as the cobaltocenium bis-boryl complex **VI**, reported by Herberich and co-workers.[9]

Such an approach, however, cannot easily be realised for 1,2-ferrocenediyl systems;[12,13] the geometric constraints of the five-membered ring backbone in systems such as **VII** enforce a B–B separation (ca. 3.68 Å) that is too wide to accommodate fluoride in a bridging position.[12c,d] Given the value of the ferrocene unit as a robust electrochemical or colorimetric reporter of anion binding events,[14] strategies have therefore been developed to circumvent this problem, including the incorporation of secondary Lewis acids in the 2-position, which feature intrinsically longer E–F bonds, consistent with fluoride chelation (such as the silyl groups used in **VIII** and **IX**).[12d,15]

However, given the widespread versatility of systems based on a 1,2-disubstituted *benzene* backbone, in particular with respect to the variety of Lewis acid combinations which can



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readily be incorporated,[5j,16] a potentially more powerful strategy involves the combination of *ortho*-phenylene scaffolds of this type with a metallocene reporter. One way to accomplish this, which offers conjugated electronic communication between binding and reporter functions, is through the development of indenyl receptors functionalised at the 4–7 positions (Figure 1). Thus, herein we report strategies for the synthesis of systems of types **X** and **XI**, together with fluoride/cyanide binding studies of two such systems for which $ER_n = PPh_2Me^+$.[17]

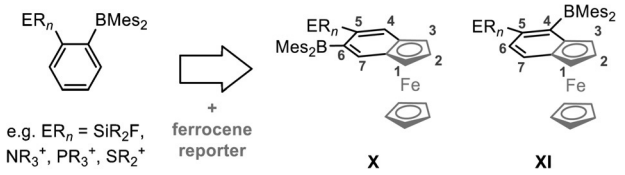


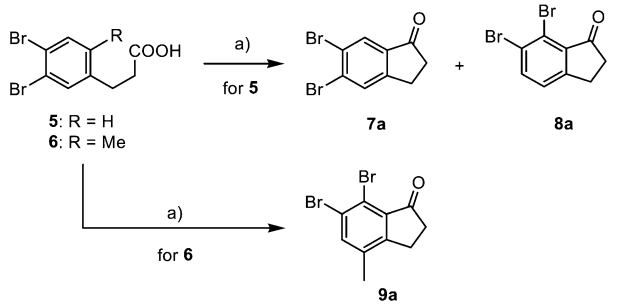
Figure 1. Molecular design strategies employed in the current study.

Results and Discussion

Syntheses of bifunctional indenyl-based receptors

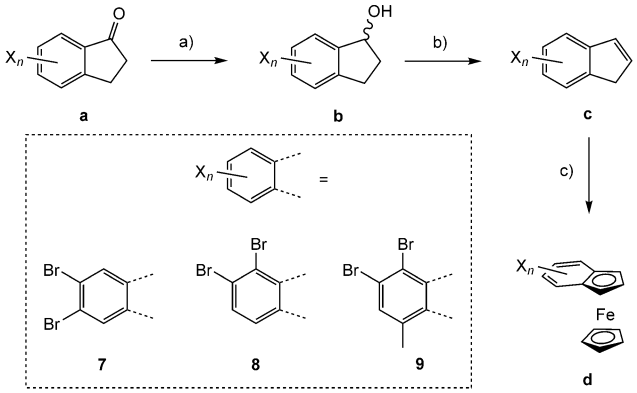
Initial attempts to synthesise *ortho*-disubstituted indenyl-based Lewis acids revolved around the use of 5,6- and 6,7-dichloro-1*H*-indenes (**1** and **2**)[18] and the corresponding (dichloroindenyl)cyclopentadienyliron(II) complexes (**3**: 5,6-dichloro; **4**: 4,5-dichloro; see the Supporting Information). Despite the relatively straightforward syntheses of both **3** and **4**, attempts to introduce the boryl function by the use of a lithiation/Mes_2BF electrophilic quench met with no success.[17] Previous reports on the generation of benzyne species from *ortho*-dichlorobenzenes, suggest that the elimination of lithium chloride from (lithio)chlorobenzenes is extremely facile (even at very low temperatures),[19] and this may account for the lack of success in borylating either **3** or **4**. With this in mind, and given the greater thermal robustness reported for *ortho*-(lithio)bromobenzenes,[20] attention was shifted to the corresponding dibromoindenyl precursors (Schemes 1, 2, and 3).

The syntheses of the requisite dibromo-1*H*-indene precursors can be achieved using a similar Friedel–Crafts acylation/reduction/dehydration protocol to that previously reported for the corresponding monofunctional 7-bromo-1*H*-indene (Schemes 1 and 2 and the Supporting Information).[17] The only issue encountered here is the lack of selectivity during the cyclisation of **5** using aluminium chloride (Scheme 1); this protocol generates the isomeric 5,6- and 6,7-dibromoindanones (**7a**[21] and **8a**) from which indenyl complexes **7d** and **8d** can be derived by subsequent reduction/dehydration/complexation (Scheme 2). In the case of **7a**, fractional crystallisation from the mixture of isomers **7a** and **8a** yields a spectroscopically pure material that can be used in subsequent steps. Recovery of **8a** from the supernatant solution proved much more difficult to achieve in usable yield and this route was therefore not viable for the bulk synthesis of the 4,5-dibromoindenyl complex **8d** for further studies (4% overall yield).



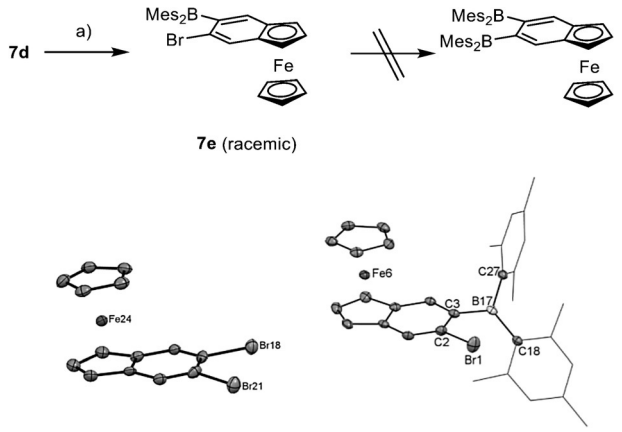
Scheme 1. Syntheses of dibromoindanone precursors **7a**–**9a**. Key reagents and conditions: a) Reflux in neat $SOCl_2$, followed by addition of $AlCl_3$ in dichloromethane.

With this in mind, the use of a precursor featuring a 'blocking' methyl group was targeted (e.g., **6**), with the aim of achieving selectivity in the Friedel–Crafts cyclisation leading to indanone intermediate **9a** (Scheme 1). Such chemistry can be successfully employed and the closely related 4,5-dibromo-7-methylindenyl complex **9d** subsequently synthesised on a 10–15 g scale (ca. 30% overall yield from **6**; Scheme 2).

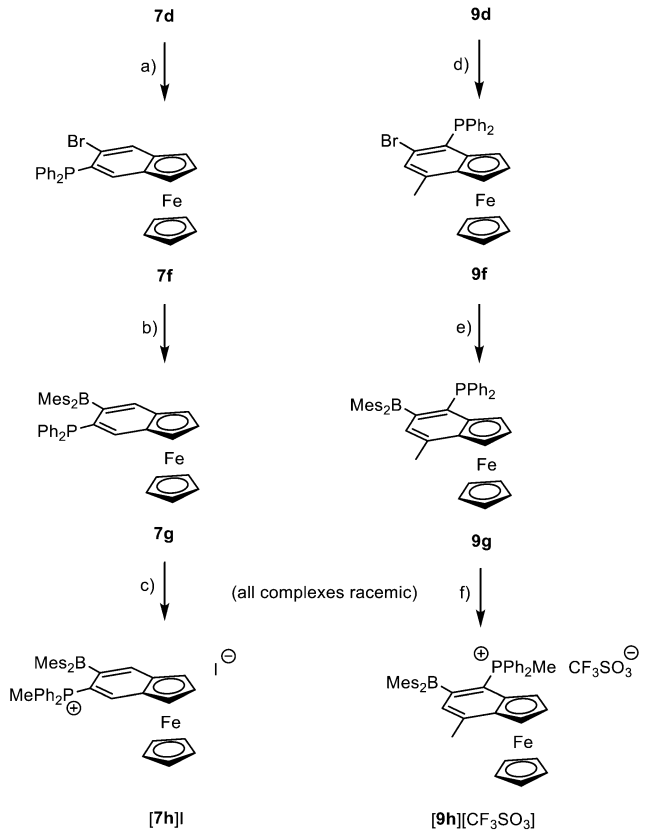


Scheme 2. Syntheses of the dibromoindenyl complexes **7d**–**9d** from the corresponding indanones **7a**–**9a**. Key reagents and conditions: a) $NaBH_4$ in MeOH/dichloromethane (1:1 v/v); b) 12 h at 125 °C in toluene with *p*-TsOH; c) KH then [FeCp(naphthalene)][PF_6] in THF.

All three dibromoindenyl complexes **7d**, **8d** and **9d** were isolated as dark purple crystalline materials and characterised both by standard spectroscopic methods and single crystal X-ray diffraction (Scheme 3 and the Supporting Information). From systems **7d** and **9d**, which are accessible in bulk quantities, introduction of boryl Lewis acid functions was attempted in stepwise fashion. Thus, treatment of **7d** with one equivalent of *n*BuLi at −120 °C followed by addition of Mes_2BF yields the corresponding 5-bromo-6-dimesitylborylindenyl complex **7e** (Scheme 3). The crude product can be purified by air-free column chromatography and obtained as a red solid in approximately 20% yield. The relatively low yield reflects—at least in part—the fact that Mes_2BF is a relatively bulky electrophile. Thus, as seen with related cyclopentadienyl nucleophiles, a major portion of the bromo(lithium)indenyl intermediate is



Scheme 3. Borylation of dibromoindenyl complex **7d** to give **7e**. Key reagents and conditions: a) *n*BuLi then Mes_2BF at −120 °C in THF/Et_2O (1:1 v/v). Molecular structures of **7d** (left) and **7e** (right) as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level; mesityl groups shown in wireframe format and H atoms omitted for clarity. Selected bond lengths [Å] and angles [°] for **7e**: B17–C18 1.571(3), B17–C27 1.581(3), B17–C3 1.566(3); C3-B17-C18 122.23(18), C3-B17-C27 115.81(18), C18-B17-C27 121.84(18), C2-C3-B17 126.73(19).



Scheme 4. Syntheses of bifunctional boryl/phosphonium Lewis acids $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$. Key reagents and conditions: a) *t*BuLi then PPh_2Cl in THF/Et_2O (1:1 v/v) at −120 °C; b) *t*BuLi then Mes_2BF in THF at 25 °C; c) excess MeI; d) *n*BuLi then Ph_2PCl in THF/Et_2O (1:1 v/v) at −120 °C; e) *n*BuLi then Mes_2BF in THF at −78 °C; f) excess CF_3SO_3Me.

not quenched when the temperature is raised, but protonated instead.[12c,d]

The formation of **7e** is implied by ^{11}B NMR spectroscopy, with a shift typical of a triarylborane being observed in $CDCl_3$ solution ($\delta_B = 77$ ppm).[3] Moreover, the structure of **7e** in the solid state was confirmed crystallographically, with a number of structural features implying that the steric hindrance around the boron centre is greater than that found in related compounds such as 1,2-fc($BMes_2$)Br. Thus, the mesityl rings in **7e** are aligned essentially perpendicular to the indenyl plane (**7e**: 88.7° and 87.4°, cf. 1,2-fc($BMes_2$)Br: 51.2° and 81.5°) and the C2-C3-B17 angle [126.7(2)°] is somewhat wider than expected in order to accommodate the large $BMes_2$ unit *ortho* to the bromine atom.[12c,d] Additional implications of this degree of steric hindrance become apparent in the next synthetic step. A range of reaction conditions was tested for the incorporation of the second $BMes_2$ unit, but in our hands these were unsuccessful. Moreover, the high degree of steric loading might in fact explain the absence of any 1,2-$(BMes_2)_2$ benzene derivatives in the literature, with 1,2-fc$(BMes_2)_2$ presumably being accessible due to the greater separation between *ortho* substituents enforced by a five (vs. six) membered carbocyclic backbone.[12c,d]

With this in mind, the incorporation of alternative secondary Lewis acid functions was targeted. Previous studies have shown that *ortho* boryl/silyl and boryl/phosphonium combinations (among others) can be incorporated onto a benzene skeleton,[16] and given the additional electrostatic component to anion binding implicit in the latter, we therefore targeted indenyl systems featuring $-BMes_2$ and $-PR_3^+$ functions with 4,5 and 5,6 regiochemistries. Moreover, given that Ph_2PCl has been shown to be a much more reactive electrophile towards aryllithium species than Mes_2BF,[12a] we hypothesised that sequential installation of phosphine/boryl functions, followed by methylation at phosphorus would be a viable synthetic strategy (Scheme 4).

Thus, as seen in the synthesis of related 1,2-boryl/phosphino benzenes,[16b] the reactions of Ph_2PCl with the lithiates generated in situ from *n*BuLi and either **7d** or **9d** at −120 °C, are shown to represent efficient and practical routes to **7f** and **9f** (in yields of 83% and 37%, respectively) and these (bromo)-phosphino indenyl derivatives can be purified without the need for column chromatography. In the case of **9f**, the apparent regioselectivity in the lithiation process is high, with no evidence being obtained for the formation of the alternative 5-phosphino derivative in anything other than trace amounts (as revealed by in situ ^1H NMR measurements). In a similar fashion, lithiation of **7f**/**9f** followed by reaction with Mes_2BF yields **7g**/**9g**, which can also be purified merely by washing/extraction procedures rather than necessitating chromatography. In the final step, $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$ can be synthesised by a simple methylation process; introduction of a large excess of methyl iodide or methyl trifluoromethanesulfonate generates the target boryl/phosphonium species [**7h**]I and [**9h**][CF_3SO_3] in almost quantitative yields.

At each step the intermediate species have been characterised by standard spectroscopic and analytical techniques, and by X-ray crystallography. Formation of indenylphosphine inter-

mediates **7f** and **9f** is signalled by the appearance of a resonance in the respective ^{31}P NMR spectra at $\delta_P = -4.14$ and -0.17 ppm (*cf.* PPh_3, $\delta_P = -6.0$ ppm) and the molecular structure of both compounds has been confirmed crystallographically (Figure 2). The subsequent step (lithiation/Mes_2BF quench) results in the appearance of broad signals at $\delta_B = 74$ and 76 ppm in the respective ^{11}B NMR spectra, consistent with the presence of an uncomplexed triarylborane function in **7g** and **9g**, respectively.[3] The incorporation of the Lewis acidic boryl function perturbs slightly the ^{31}P NMR signals, leading to an upfield shift in each case (e.g., **9f**: $\delta_P = -0.2$ ppm; **9g**: $\delta_P = -5.8$ ppm). Interestingly, compound **7g** features two distinct peaks in the solution-phase ^{31}P NMR spectrum at room temperature ($\delta_P = -6.5$, -9.5 ppm) in an approximate ratio of 1:2, which coalesce at approximately 85 °C. As is evident in the crystal structure of **7g**, the high steric bulk of the mutually *ortho*-orientated PPh_2 and $BMes_2$ substituents enforces a non-negligible torsion angle along the B-C-C-P chain. As a consequence, two limiting conformations are conceivable, in which either the PPh_2 or the $BMes_2$ function is displaced out of the indenyl plane on the face occupied by the CpFe unit (Figure 3). Of these, one (**A**) corresponds to the conformer seen in the solid state, with the other (**B**) presumably accessible through concerted rotation of the aryl groups associated with both the phosphine and borane components.[22] In the case of **9g**, only one ^{31}P signal is observed, which we associate with conformational 'locking' enforced by the closer proximity of the 4-PPh_2 group to the CpFe unit.

The structural characterisation of boryl phosphines **7g** and **9g** confirms the increased steric hindrance upon assimilation of the $BMes_2$ unit. For both systems, a propeller-like geometry is in evidence for the borane unit; in the case of **9g**, the mesityl rings are almost perpendicular to the indenyl ligand (83.1 and 89.2°) and the angle between the least-squares planes of the cyclopentadienyl and the indenyl unit deviates by approximately 5.6° from co-planarity. The P-C-C-B torsion angles in **7g** and **9g** differ somewhat (22.5° and 4.0° respectively), as do the intramolecular B–P distances (**7g**: 3.205 Å; **9g**: 3.063 Å), presumably as a result of the closer proximity of the metallocene and PPh_2 units in **9g**.

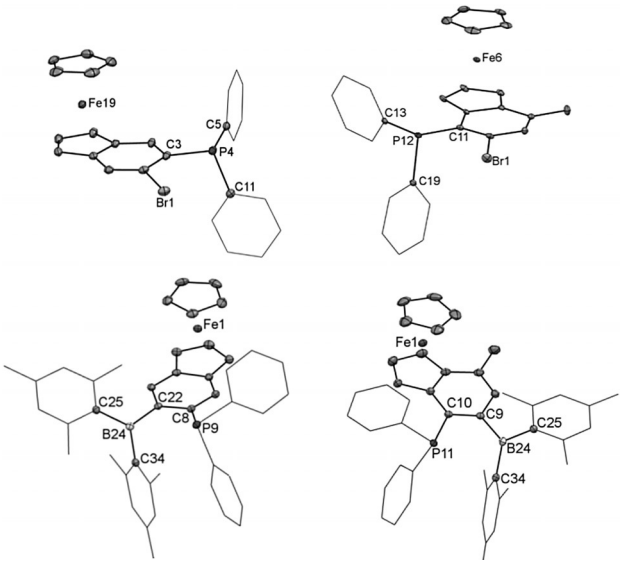


Figure 2. Molecular structures of **7f**/**9f** (upper) and **7g**/**9g** (lower) as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level; phenyl groups shown in wireframe format and H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: **7f**: C3–P4 1.839(2); C3-P4-C5 100.3(1), C3-P4-C11 103.3(1), C5-P4-C11 100.9(1); **9f**: C11–P12 1.841(2); C11-P12-C13 105.9(1), C11-P12-C19 102.9(1), C13-P12-C19 100.5(1). For key bond lengths and angles for **7g** and **9g**, see Table 1.

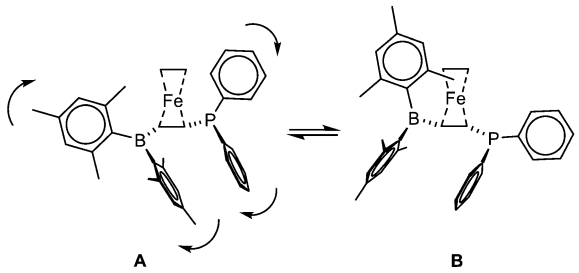


Figure 3. Fluxional interconversion between rotamers in **7g**.

In the final synthetic step, the target cations $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$ can be obtained by methylation of the phosphine function, a reaction which can be monitored by multinuclear NMR spectroscopy. The respective ^{31}P signals are shifted downfield (to $\delta_P = 23.4$ and 24.4 ppm for $[\mathbf{7h}]^+$ and $\delta_P = 17.5$ ppm for $[\mathbf{9h}]^+$) and both cations are also discerned in the corresponding positive ion ESI mass spectra. The presence of the $[CuI_4]^{2-}$ counter ion in the lattice of $[\mathbf{9h}]_2[CuI_4]$ can presumably be traced back to the iodomethane reagent which contains copper as a stabiliser.

The transformation of **7g** and **9g** into the respective phosphonium species leads to significant changes in the solid-state structures (Figure 4 and Table 1). The introduction of the methyl group leads to enhanced steric bulk in the P component, resulting in an increase in the intermolecular B–P distance (by 0.278 and 0.368 Å for **7g**/$[\mathbf{7h}]^+$ and **9g**/$[\mathbf{9h}]^+$ respectively) and widening of the C-C-P and C-C-B angles. The B–P separations are also very similar to that found in the *ortho*-phenylene derived system $[1,2\text{-}C_6H_4(BMes_2)(PPh_2Me)]^+$ ($[\mathbf{XII}]^+$, 3.494(3) Å).[16b] In each case, however, the boron centres

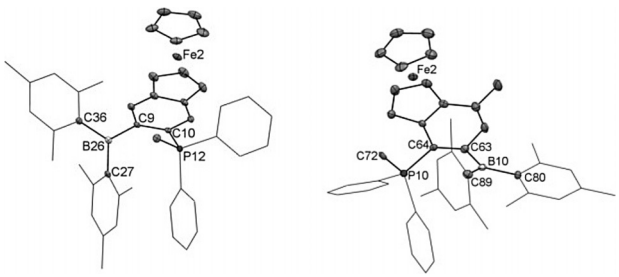


Figure 4. Molecular structures of the cationic components of $[\mathbf{7h}]I$ (left) and $[\mathbf{9h}]_2[CuI_4]$ (right) as determined by X-ray crystallography. Thermal ellipsoids set at the 50% probability level; mesityl and phenyl groups shown in wireframe format, and H atoms, counter anions and dichloromethane solvate molecules omitted for clarity. For key bond lengths and angles, see Table 1.

Table 1. Selected bond lengths (Å) and angles (°) for novel borylphosphine and borylphosphonium species, and the corresponding data for the related (known) system $[1,2\text{-}C_6H_4(BMes_2)(PPh_2Me)]^+$ ($[\mathbf{XII}]^+$).[16b]

Parameter	**7g**	$[\mathbf{7h}]^+$	**9g**	$[\mathbf{9h}]^+$	$[\mathbf{XII}]^+$
	1.577(2)	1.575(4)	1.584(3)	1.599(14)	1.562(4)
d(B–C_{aryl})	1.571(2)	1.581(5)	1.575(3)	1.587(15)	1.577(4)
	1.569(2)	1.572(4)	1.578(3)	1.550(15)	1.585(4)
$\Sigma\sphericalangle$CBC	359.95	359.2	359.62	359.7	359.7
d(B–P)	3.205	3.483	3.063	3.431	3.494(3)
B-C-C-P torsion	22.48	18.78	4.01	0.91	16.55
$\sphericalangle$P-C-C	116.1(1)	123.1(2)	114.8(1)	126.0(7)	124.4(2)
$\sphericalangle$B-C-C	123.2(1)	129.3(3)	124.2(2)	131.0(9)	130.1(3)

remain trigonal planar, (Σ_{CBC} = 359.2° and 359.7° for $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$, respectively), consistent with little, if any, interaction of the borane function with the counter anion.

Anion binding by bifunctional borane/phosphonium species

The scope for the indenyl systems outlined above to act as anion receptors has been probed by computational and electrochemical means. Thus, DFT calculations were carried out on **7g**, $[\mathbf{7h}]^+$, **9g** and $[\mathbf{9h}]^+$ in order to probe issues of electronic structure relating to their potential abilities as anion hosts. Moreover, to put these results in perspective, analogous calculations at the same level of theory were performed on $[\mathbf{XII}]^+$ and $[1,2\text{-fc}(BMes_2)(PPh_2Me)]^+$ ($[\mathbf{XIII}]^+$; see the Supporting Information).[16b] Not unexpectedly, the formation of the respective phosphonium cations by methylation of the phosphine function leads to significant stabilisation of the LUMO and LUMO + 1 (e.g., by ca. 3.0 eV for **9** and by ca. 2.7 eV for **7**); the absolute energies of these orbitals are also very similar to those calculated for $[\mathbf{XII}]^+$ and $[\mathbf{XIII}]^+$. In addition, whereas the parent neutral systems **7g** and **9g** feature Lewis acid character that is focused at the borane function, significant contributions to low lying orbitals are centred on the phosphonium function in both $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$. Thus, in the case of $[\mathbf{9h}]^+$, for example, the LUMO is still B-centred, but the LUMO + 1 features significant character centred on the P–Ph units (Figure 5). A similar orbital picture is found for the *ortho*-phenylene-based cation $[\mathbf{XII}]^+$ (see the Supporting Information).

Cyclic voltammetry measurements on **7g** and **9g** were also carried out (in THF solution), yielding values of +166 and +43 mV respectively for the iron-centred oxidation event (vs. Fc/Fc^+). In addition, an irreversible reduction wave centred at approximately −2300 mV is provisionally assigned the $B^{\cdot-}/B$ redox couple.[23] The corresponding redox events for $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$ (obtained for the trifluoromethylsulfonate salts rather than the parent iodide compounds to eliminate anion-centred electrochemical events) were measured in acetonitrile solution at +575/+576 mV and −1980/−1480 mV, respectively. The magnitudes of the shifts observed for each redox process on methylation are consistent with the formation of a cationic species,[5l] and with the corresponding changes in orbital energies (see the Supporting Information). Thus for **7g**/$[\mathbf{7h}]^+$ the respective HOMO energies are −3.98/−6.58 eV, and the corresponding LUMOs found at −2.40/−5.13 eV.

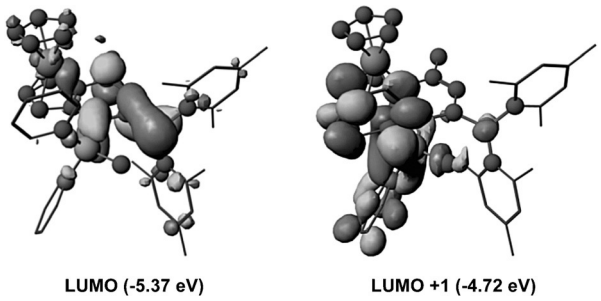


Figure 5. Contour plots of the LUMO and LUMO + 1 for $[\mathbf{9h}]^+$ (density isovalues = 0.03).

The binding capabilities of the receptors **7g**/**9g** and $[\mathbf{7h}]^+$/$[\mathbf{9h}]^+$ can be monitored by multinuclear NMR spectroscopy (^{11}B, ^{19}F and ^{31}P NMR). Thus, phosphine–borane receptors **7g** and **9g** were exposed to cyanide or fluoride in dry THF or chloroform, but only on addition of cyanide was a binding event detected. For both isomers, the ^{11}B NMR spectrum exhibits a new resonance at $\delta_B \approx -12$ ppm, characteristic of a dimesitylborane–cyanide adduct.[5l] Addition of a large excess of fluoride in dry chloroform (e.g., four equivalents of $[n\text{Bu}_4\text{N}]\text{F}\cdot 3\,\text{H}_2\text{O}$ or $[S(NMe_2)_3][Me_3SiF_2]$), however, does not seem to quaternize the Lewis acidic boron, and an ^{11}B NMR spectrum displaying a broad signal at $\delta_B \approx 77$ ppm is observed in each case, together with free fluoride in the ^{19}F NMR spectrum.[3] The absence of a peak envelope for the fluoride adduct detected by negative-ion ESI-MS further suggests that fluoride is not bound by either **7g** or **9g**, even in dry aprotic solvents. By contrast, the corresponding spectra obtained in the presence of cyanide display the molecular ion peak and expected isotopic distributions for both $[\mathbf{7g}\text{–CN}]^-$ and $[\mathbf{9g}\text{–CN}]^-$. This selectivity can be explained by the lower intrinsic Lewis basicity of fluoride in comparison to cyanide, in combination with the high steric loading provided by adjacent dimesitylborane and diphenylphosphine functions, which provides an enthalpic disincentive to the change in coordination number at boron from three to four. Consistent with such observations, recent studies have shown that the selective binding of cyanide over fluoride at $BMes_2$ receptors can be engineered by the incorporation of enhanced steric bulk adjacent to the borane binding site.[5d,17]

The molecular structures of $[n\text{Bu}_4\text{N}][\mathbf{7g}\text{–CN}]$ and $[n\text{Bu}_4\text{N}][\mathbf{9g}\text{–CN}]$ were determined by single X-ray crystallography (Figure 6). The binding of cyanide in each case is accompanied by pyramidalisation of the boron centre (Σ_{CBC} = 340.7° and 340.5° for $[\mathbf{7g}\text{–CN}]^-$ and $[\mathbf{9g}\text{–CN}]^-$ respectively), by elongation of the B–C bonds (by at least 0.09 Å), and by widening of the intramolecular B–P separation (Table 2). The B-CN bond length in each case falls within the range of previously reported cyanide adducts ($[\mathbf{7g}\text{–CN}]^-$: 1.625(2) Å; $[\mathbf{9g}\text{–CN}]^-$: 1.626(7) Å, cf. $[FcBMes_2\text{–CN}]^-$: 1.639(4) Å).[5f] The long contacts between phosphorus and the cyanide guest (3.102 Å for $[\mathbf{7g}\text{–CN}]^-$, 3.240 Å for $[\mathbf{9g}\text{–CN}]^-$), together with the marginal shifts in the respective ^{31}P NMR spectra on CN^- binding, argue however against any interaction between the phosphorus atom and the bound cyanide.

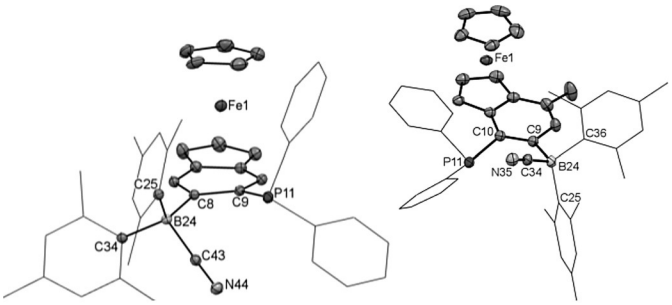


Figure 6. Molecular structures of the cationic components of [nBu$_4$N][**7g**–CN] (left) and of [nBu$_4$N][**9g**–CN] (right). Thermal ellipsoids set at the 50% probability level; mesityl and phenyl groups shown in wireframe format, and H atoms and tetrabutylammonium counter ions omitted for clarity. Selected bond lengths [Å] and angles [°]: [nBu$_4$N][**7g**–CN]: B24–C8 1.661(2), B24–C25 1.663(2), B24–C34 1.667(2), B24–C43 1.625(2); C8-B24-C25 119.62(13), C8-B24-C34 110.01(13), C25-B24-C34 111.04(13), C9-C8-B24 124.17(14), C8-C9-P11 119.15(12), B24-C43-N44 178.57(17), B24-P11 3.349(2), B24-C8-C9-P11 19.3; [nBu$_4$N][**9g**–CN]: B24–C9 1.677(6), B24–C25 1.669(7), B24–C36 1.678(7), B24–C34 1.626(7); C9-B24-C25 120.9(4), C9-B24-C36 106.5(3), C25-B24-C36 113.1(3), B24-C34-N35 174.9(4), C9-C10-P11 121.6(3), C10-C9-B24 128.9(4), B24-P11 3.456(5), B24-C9-C10-P11 21.0.

Table 2. Selected bond lengths (Å), angles (°) for anionic and zwitterionic cyanide/fluoride adducts.

	[**7g**–CN]$^-$	[**9g**–CN]$^-$	**7h**–CN	**9h**–CN	**7h**–F	**9h**–F
	1.661(2)	1.677(6)	1.663(2)	1.663(3)	1.657(3)	1.644(3)
d(B–C$_{aryl}$)	1.663(2)	1.669(7)	1.656(2)	1.666(3)	1.663(4)	1.652(3)
	1.667(2)	1.678(7)	1.663(2)	1.673(3)	1.649(3)	1.654(3)
$\Sigma\sphericalangle$CBC	340.7	340.5	341.29	340.32	341.15	340.09
d(B–P)	1.625(2)	1.626(7)	1.624(2)	1.626(3)	1.478(3)	1.477(2)
d(B–X)	3.349	3.455	3.559	3.529	3.335	3.295
B-C-C-P torsion	19.29	21.03	12.26	19.54	11.96	16.6
$\sphericalangle$P-C-C	119.2(1)	121.6(3)	126.5(1)	124.9(1)	123.4(2)	121.8(2)
$\sphericalangle$B-C-C	124.2(1)	128.9(4)	127.1(1)	129.9(2)	121.6(2)	124.2(2)

Binding studies were also conducted on the cationic receptors [**7h**]$^+$ and [**9h**]$^+$, revealing contrasting behaviour to the parent systems **7g**/**9g**. Addition of [nBu$_4$N][CN]·4H$_2$O can be monitored by ^{11}B NMR spectroscopy, which confirms the formation of a cyanide adduct, with a shift to $\delta_B = -13$ ppm being observed for both **7h**–CN and **9h**–CN. In contrast to the behaviour of the charge-neutral systems, however, treatment of receptors [**7h**]$^+$ and [**9h**]$^+$ with one equivalent of fluoride (as either [S(NMe$_2$)$_3$][Me$_3$SiF$_2$] or [nBu$_4$N]F·3H$_2$O) yields the respective fluoride adducts. Upfield shifts to $\delta_B \approx 7$ ppm are observed in each case, consistent with the formation of a fluoroborate,[3] and, additionally, broad new signals in the corresponding ^{19}F NMR spectra are also measured (at $\delta_F = -149.0$ and -145.1 ppm for **7h**–F and **9h**–F, respectively). Evidence for the chelation of the fluoride ion between borane and phosphonium Lewis acids is provided by ^{31}P NMR spectroscopy. In both cases, a downfield shift from $\delta_P \approx 24$ ppm to 29 ppm is accompanied by the splitting of the resonance into a doublet (^1J(F,P) = 26.0 and 22.9 Hz for **7h**–F and **9h**–F, respectively). A very similar coupling constant (24.3 Hz) was reported for the fluoride-chelated system **XII**–F.[16b]

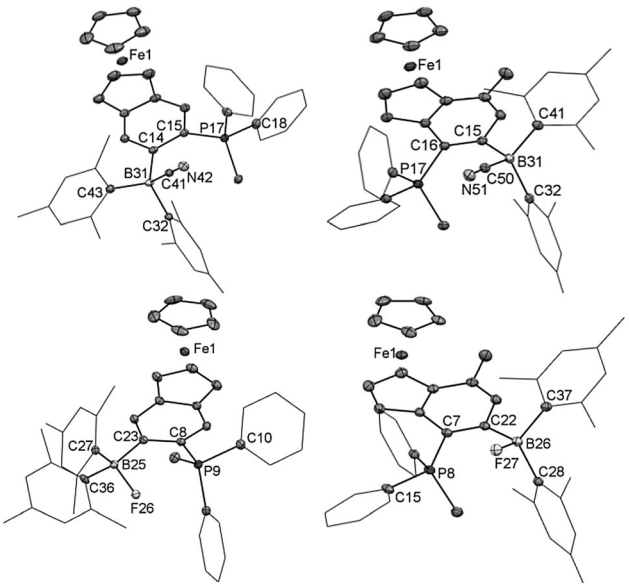


Figure 7. Molecular structures of **7h**–CN/**9h**–CN (upper) and **7h**–F/**9h**–F (lower). Thermal ellipsoids set at the 50% probability level; mesityl and phenyl groups shown in wireframe format, and H atoms and dichloromethane solvent molecules omitted for clarity. For key bond lengths and angles, see Table 2.

Single crystals suitable for X-ray crystallography were obtained for all four zwitterionic adducts **7h**–CN, **9h**–CN, **7h**–F and **9h**–F (Figure 7); selected bond lengths and angles are included in Table 2. The four structures each display a tetra-coordinate boron centre featuring either a bound cyanide or fluoride ion. Interestingly, for both receptors, the binding of cyanide increases the intramolecular B–P distance (e.g., from 3.483(4) to 3.5594(18) Å for [**7h**]$^+$, and from 3.430(12) to 3.529(2) Å for [**9h**]$^+$); by contrast, fixation of fluoride leads to a marked *decrease* in the B–P separation (to 3.335(3) and 3.295(2) Å for **7h**–F and **9h**–F, respectively). Moreover, both fluoride adducts show P–F distances [2.6756(15) and 2.6936(15) Å, respectively] which fall within the sum of the relevant Van der Waals radii (3.27 Å).[24] That these contacts are structurally significant is consistent with the observed contraction in the B–P distance in each case, and with the ^1J(F,P) coupling observed in the respective ^{31}P NMR spectra. Gabbaï and co-workers report a similar P–F contact [2.666(2) Å] for the fluoride adduct **XII**–F, together with a close-to-linear F-P-C$_{phenyl}$ angle [176.4(1)°] and a marked elongation of the P-Ph bond.[16b] Similar geometric features can also be discerned here, for example, $\sphericalangle$(F-P-C$_{phenyl}$) = 179.0, 172.3° for **7h**–F and **9h**–F, respectively. In the case of **XII**–F these spectroscopic/structural observations have been attributed to the presence of a lp(F)→σ*(C–Ph) interaction, and a similar scenario can be postulated for **7h**–F and **9h**–F. Consistently, AIM (atoms in molecules)[25] calculations reveal a bond path between P9 and F26 for **7h**–F (Figure 8), with an electron density, ρ(r), of 2.13×10^{-2} e bohr^{-3} at the bond critical point, very similar to that reported for **XII**–F (2.05×10^{-2} e bohr^{-3}).

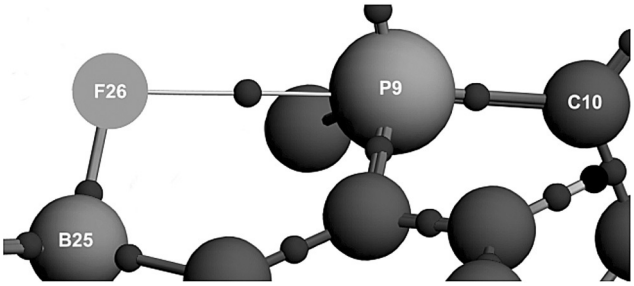


Figure 8. Atoms in molecules analysis of the B-F-P unit in **7h**–F, with key bond paths and critical points depicted.

Measurements of the binding affinities of **7g**/**9g** and $[\mathbf{7h}]^+$ /$[\mathbf{9h}]^+$ for both cyanide and fluoride were carried out by UV/Vis spectroscopy titration experiments. The neutral systems **7g** and **9g** were shown to have no affinity for fluoride on the basis of multinuclear NMR and mass spectroscopy. However, cyanide addition led to a change of colour from burgundy to pale red in each case, which in principle offers a basis for the spectroscopic determination of K_{CN}. However cyanide uptake appears to be kinetically very slow. Thus, on addition of one equivalent of the anion to solutions of either **7g** or **9g** in dry THF, equilibrium was still not reached even after 60 min (see the Supporting Information), thereby rendering accurate determination of binding constants extremely challenging. The slow kinetics of binding can be attributed to the increased steric loading provided by the diphenylphosphine unit *ortho* to the $BMes_2$ binding domain; a similar effect, in which positioning of a sterically bulky non-interacting substituent *ortho* to the primary Lewis acid has been shown to lead to slow anion uptake, has been reported for 1,2-fc$(BMes_2)_2$.[12c,d] By contrast, cationic receptors $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$ are much more labile towards the binding of either cyanide or fluoride, and sequential addition of alicquots of either anion can be monitored by UV/Vis spectroscopy. The resulting data can be fitted to a 1:1 binding isotherm (see the Supporting Information). The derived binding affinities are summarised in Table 3, along with the corresponding results for related monodentate receptors.

Consideration of the data outlined in Table 3 shows the following: i) In general, indenyl-derived systems show slightly greater fluoride *and* cyanide affinities than their cyclopentadienyl counterparts, presumably due to greater arene conjugation, and consequent lowering of the LUMO energy;[3,12d,17] ii) despite the cationic charge carried by both $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$, no uniform increase in cyanide affinity is seen over simple charge-neutral systems, presumably as a result of a compensatory steric disincentive to binding brought about by having the bulky phosphonium substituent *ortho* to the $BMes_2$ binding domain; iii) significant increases in fluoride ion affinity are seen for both $[\mathbf{7h}]^+$ and $[\mathbf{9h}]^+$ as a consequence of the accessibility of a pre-organised cooperative B/P binding geometry for the monatomic F^- ion.

From a detection perspective, the complexation of the fluoride or cyanide ion by $[\mathbf{9h}]^+$ can be monitored by using the electrochemical potential of the iron centre. Thus a large cathodic shift of −590 mV is observed between $[\mathbf{9h}]^+$ and **9h**–F in acetonitrile solution, reflecting the conversion of an electron-withdrawing borane function to a strongly electron-donating fluoroborate. Fixation by $[\mathbf{9h}]^+$ is also accompanied by a noticeable (and intuitive) colour change. Thus, for instance 'free' $[\mathbf{9h}]^+$ is green (λ_{max} = 596 nm), whereas the fluoride adduct is maroon (λ_{max} = 531 nm, Figure 9). $[\mathbf{7h}]^+$ also undergoes a colour change upon fixation of fluoride, although the change is not so marked; thus the free receptor is a dark brown (λ_{max} = 445 nm), whereas the adduct is pale red (λ_{max} ≈ 493 nm).

Table 3. Fluoride and cyanide binding affinities determined for $[\mathbf{7h}]^+$, $[\mathbf{9h}]^+$ and related receptors in THF solution.

Receptor	log *K*(F)	log *K*(CN)	Reference
$FcBMes_2$	6.06(0.06)	6.55(0.13)	[12d]
[CpFe{4-(Mes_2B)-indenyl}]	6.36(0.10)	7.01(0.21)	[17a]
[CpFe{5-(Mes_2B)-indenyl}]	6.28(0.03)	6.97(0.39)	[17b]
$[\mathbf{7h}]^+$	7.84(0.38)	7.28(0.13)	This work
$[\mathbf{9h}]^+$	8.09(0.26)	6.81(0.04)	This work

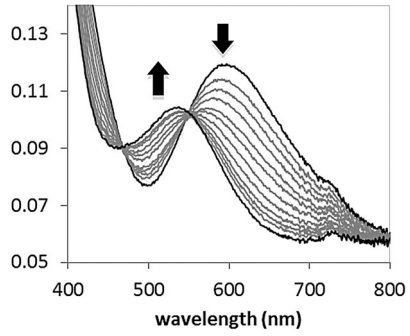


Figure 9. Changes in the absorption in the visible region of the spectrum on addition of fluoride to a solution of $[\mathbf{9h}][CF_3SO_3]$ in THF.

Conclusion

Indenyl-functionalised receptors offer the possibility for incorporation of adjacent Lewis acidic domains onto a six-membered carbocyclic framework, while retaining many of the advantages of synthetically simpler ferrocene systems in terms of available reporter mechanisms. Although the incorporation of adjacent $BMes_2$ groups has proven impossible in our hands, presumably on steric grounds, systems featuring mutually *ortho* $BMes_2$ and PPh_2Me^+ functions are accessible. These receptors are shown to be capable of cooperative fluoride ion fixation, involving simultaneous binding at the borane and phosphonium centres, and leading to enhanced thermodynamics for F^- uptake. Thus, in contrast to simple $BMes_2$-containing systems, F^- binding is found to be more favourable than that of cyanide (which interacts only with the borane Lewis acid). Moreover, in the case of the 4-($MePh_2P$)-5-(Mes_2B)-7-Me-indenyl derivative $[\mathbf{9h}]^+$, fluoride chelation is accompanied by a marked colour change from green for the free receptor to maroon for the adduct.

Experimental Section

General procedures

Manipulations of air-sensitive reagents were carried out in a glovebox, or by means of Schlenk-type techniques involving the use of a dry argon or a nitrogen atmosphere. HPLC grade solvents were purified, dried and degassed prior to use by a commercial available Braun Solvent-Purification System (SPS 500). NMR solvents $CDCl_3$ (vac transfer, stored over molecular sieves) $(CD_3)_2SO$ (distilled from CaH_2, stored over molecular sieves) and C_6D_5Br (distilled from CaH_2, stored over molecular sieves) were pre-dried before use. The known compounds [CpFe(naphthalene)][PF_6] and Mes_2BF were prepared according to literature procedures.[26] The syntheses of bromo precursors **7a–e**, **8a–d** and **9a–d**, together with dichloroindene and -indenyl systems **1–4** are given in the supporting information.[18] MeI, $MeSO_3CF_3$ and Ph_2PCl were used as supplied (Sigma Aldrich). ^1H and ^{13}C NMR spectra were measured on a Bruker AVII 500 FT-NMR or Varian Mercury VX-300 spectrometer; ^1H and ^{13}C NMR spectra were calibrated using the residual proton or natural abundance ^{13}C resonances of the solvent; ^{11}B and ^{19}F spectra were referenced with respect to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively. Mass spectra were measured by the EPSRC National Mass Spectrometry Service, Swansea University, and elemental microanalysis by London Metropolitan University.

Syntheses of new compounds

(4-Diphenylphosphino-5-bromo-7-methyl-indenyl)cyclopentadienyliron(II) (9f): To a solution of **9d** (0.24 g, 0.614 mmol) in a mixture of THF and Et_2O (20 mL, 1:1 v/v) at −120 °C was added a solution of *n*BuLi (4.02 mL of a 1.6 M solution in hexane, 6.43 mmol). The reaction mixture was stirred for 30 min at −120 °C, then a solution of PPh_2Cl (1.14 mL, 6.14 mmol) in a mixture of THF and Et_2O (10 mL, 1:1 v/v) at −78 °C added to the red solution. After stirring for a further 2 h at −120 °C and warming to room temperature over 12 h, volatiles were removed under reduced pressure. The crude solid was washed with hexane (3 × 10 mL) then extracted with dichloromethane (ca. 10 mL). The solution was concentrated and crystals suitable for X-ray crystallography were obtained on cooling to −25 °C (0.46 g, 37% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 2.50$ (d, $^3J(H,H) = 0.9$ Hz, 3H, Me), 3.59 (s, 5H, Cp), 3.89 (apparent t, $^3J(H,H) = 2.6$ Hz, 1H, C2H), 4.10 (dd, $^3J(H,H) = 2.6$ Hz, $^4J(H,H) = 0.9$ Hz, 1H, C1H), 4.80 (dd, $^3J(H,H) = 2.6$ Hz, $^4J(H,H) = 0.9$ Hz, 1H, C3H), 6.95 (d, $^4J(H,P) = 3.2$ Hz, 1H, C6H), 7.27 (m, 3H, CH of Ph), 7.48 (m, 5H, CH of Ph), 7.78 ppm (tt, $^3J(H,H) = 7.5$ Hz, $^4J(H,H) = 1.5$ Hz, 2H, *para*-CH of Ph); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 19.2$ (Me), 60.0 (C3), 64.7 (C1), 68.7 (Cp), 71.1 (C2), 86.2 (C9), 92.4 (C8), 126.9 (C6), 128.4 and 128.6 (CH of Ph), 128.9 (*meta*-CH of Ph), 129.3 (d, $^1J(C,P) = 36.0$ Hz, C4), 130.3 (C5), 133.1 (CH of Ph), 134.1 (*para*-CH Ph), 136.9 (CH of Ph), 144.6 ppm (C7); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): $\delta = -0.2$; elemental analysis (%) calcd for $C_{27}H_{22}BrFeP{\cdot}(CH_2Cl_2)_{0.2}$: C 61.62, H 4.26; found: C 61.78, H 4.66 (solvent content verified by NMR); MS (EI+): *m/z* (%): 512.0 (100), 514.0 (95); accurate mass calcd for $C_{27}H_{22}BrFeP$: 511.9994 (M^+, $^{56}Fe/^{79}Br$ isotopomer), 513.9976 (M^+, ^{81}Br isotopomer; meas.: 511.9986, 513.9961, isotopic pattern correct for $C_{27}H_{22}BrFeP$; crystallographic data: $C_{27}H_{22}BrFeP$; $M_r = 513.20$; triclinic; space group $P\bar{1}$; $a = 9.6042(3)$, $b = 10.5337(5)$, $c = 11.2465(4)$ Å; $\alpha = 92.027(3)$, $\beta = 95.965(3)$, $\gamma = 107.132(3)°$; $V = 1078.80(7)$ Å^3; $Z = 2$; $T = 150$ K; $\lambda = 1.54180$ Å. 12199 reflections collected; 4507 independent [R(int) = 0.026] used in all calculations, with 272 refined parameters; GOF on $F^2 = 1.0156$; $R_1 = 0.0310$; $wR_2 = 0.0842$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0312$; $wR_2 = 0.0844$ for all unique reflections; max. and min. residual electron densities 1.10 and −0.56 e Å^{-3}; CCDC reference: 1059132.

(4-Diphenylphosphino-5-dimesitylboryl-7-methyl-indenyl)cyclopenta-dienyliron(II) (9g): To a solution of **9f** (2.00 g, 3.90 mmol) in THF (20 mL) at −78 °C was slowly added a solution of *n*BuLi (4.1 mL of a 1.9 M solution in hexane, 7.79 mmol). The reaction mixture was stirred for 1 h at −78 °C, then a solution of Mes_2BF (2.09 g, 7.79 mmol) in THF (ca. 10 mL) was added, and the reaction mixture warmed to room temperature over 12 h. Volatiles were then removed under reduced pressure, and the crude solid washed with hexane (3 × 10 mL) and then extracted with dichloromethane (ca. 10 mL). The solution was concentrated and crystals suitable for X-ray crystallography were obtained on cooling to −25 °C (0.84 g, 31% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta =$ 1.99 and 2.16 (b s, each 6H, *ortho*-Me of Mes), 2.20 and 2.34 (s, each 3H, *para*-Me of Mes), 2.46 (s, 3H, Me), 3.52 (s, 5H, Cp), 4.00 (t, $^3J(H,H) = 2.3$ Hz, 1H, C2H), 4.45 (d, $^3J(H,H) = 1.5$ Hz, 1H, C1H), 4.89 (d, $^3J(H,H) = 1.5$ Hz, 1H, C3H), 6.64 (b s, 2H, *meta*-CH of Mes), 6.71 (s, 1H, C6H), 6.81 (s, 2H, *meta*-CH of Mes), 6.94–7.31 ppm (overlapping m, 10H, Ph); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 19.8$ (Me), 21.2 and 21.4 (*para*-Me of Mes), 23.7 (b s, *ortho*-Me of Mes), 59.6 (C3), 65.1 (C1), 67.9 (Cp), 70.9 (C2), 88.6 (C9), 91.8 (C8), 124.6 (C6), 127.1 and 127.6 (*meta*-CH of Ph), 127.9 and 128.0 (*para*-CH of Ph), 128.1 (C7), 128.2 (b s, *meta*-CH of Mes), 132.7 (d, $^2J(C,P) =$ 19.2 Hz, *ortho*-C Ph), 133.9 (d, $^2J(C,P) = 17.1$ Hz, *ortho*-CH Ph), 134.4 and 136.0 (*ipso*-quaternary C Ph), 138.9 (*para*-quaternary C of Mes), 140.9 (b s, *meta*-CH of Mes), 141.1 (C4), 147.0 (b s, C5), 159.5 ppm (*ipso*-quaternary C of Mes); $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 25 °C): $\boldsymbol{\delta = 76}$ ppm (b s); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): $\delta =$ −5.8 ppm (b s); MS (EI+): *m/z* (%): 667.2 ([M-CH_3]$^+$), isotopic pattern correct for $C_{44}H_{41}BFeP$; $E_{1/2} = +43$ mV (Fe^{II}/Fe^{III}) vs Fc/Fc^+ with 0.1 M [nBu$_4$N][PF_6] in THF; UV/Vis (THF): λ_{max} (ε, mol^{-1} L^{-1} cm^{-1}) = 351 (5560), 531 nm (1340); crystallographic data: $C_{45}H_{44}BFeP$; $M_r =$ 682.48; monoclinic; space group $P2_1/c$; $a = 20.2118(2)$, $b =$ 8.13040(10), $c = 22.8385(2)$ Å; $\beta = 108.4989(11)°$; $V = 3559.13(7)$ Å^3; $Z = 4$; $T = 150$ K; $\lambda = 1.54180$ Å. 20753 reflections collected; 7344 independent [R(int) = 0.042] used in all calculations, with 433 refined parameters; GOF on $F^2 = 0.9877$. $R_1 = 0.0435$; $wR_2 = 0.1119$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0483$; $wR_2 = 0.1166$ for all unique reflections; max. and min. residual electron densities 0.63 and −0.45 e Å^{-3}.

(4-Methyldiphenylphosphonium-5-dimesitylboryl-7-methylindenyl)cyclo-pentadienyliron(II) trifluoromethylsulfonate ([9h][CF_3SO_3]): To a solution of **9g** (0.50 g, 0.732 mmol) in chloroform (10 mL) was added excess CF_3SO_3Me (0.83 mL, 7.33 mmol), and the reaction mixture stirred at room temperature for 12 h. Volatiles were removed under reduced pressure, and single crystals suitable for X-ray crystallography were obtained from a solution in THF by layering with heptane (0.62 g, 97% yield). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.78$ (b s, 3H, *para*-Me of Mes), 1.95 (b s, 6H, *ortho*-Me of Mes), 2.19 (b s, 6H, *ortho*-Me of Mes), 2.32 (s, 3H, *para*-Me of Mes), 2.56 (s, 6H, PMe and Me of C7), 3.78 (s, 5H, Cp), 4.23 (s, 1H, C3H), 4.30 (t, $^3J(H,H) = 2.6$ Hz, 1H, C2H), 5.15 (s, 1H, C1H), 6.75, 6.77, 6.80 and 6.82 (b s, each 1H, *meta*-CH of Mes), 6.88 (d, $^4J(H,P) = 3.3$ Hz, 1H, C6H), 7.18 (dd, $^3J(H,P) = 13.1$ Hz, $^3J(H,H) =$ 7.4 Hz, 2H, *ortho*-CH of Ph#1), 7.44 (td, $^3J(H,H) = 8.1$ Hz, $^4J(H,P) =$ 3.7 Hz, 2H, *meta*-CH of Ph#1), 7.65 (td, $^3J(H,H) = 7.4$ Hz, $^5J(H,P) =$ 1.3 Hz, 1H, *para*-CH of Ph#1), 7.76 (td, $^3J(H,H) = 7.4$ Hz, $^4J(H,P) =$ 3.6 Hz, 2H, *meta*-CH of Ph#2), 7.85 ppm (m, 3H, para and *ortho*-CH of Ph#2); ^1H NMR (500 MHz, CD_2Cl_2, −80 °C, major isomer 55%): $\delta = 1.83$, 1.95 and 1.99 (s, each 3H, *ortho*-Me of Mes), 2.27 (s, 3H, *para*-Me of Mes), 2.42 (s, 3H, *ortho*-Me of Mes), 2.53 (d, $^2J(H,P) =$ 10.9 Hz, 3H, PMe), 2.55 (s, 3H, Me of C4), 3.76 (s, 5H, Cp), 4.01 (s,

1H, C3H), 4.23 (s, 1H, C2H), 5.17 (s, 1H, C1H), 6.68, 6.76 and 6.82 (s, 4H, *meta*-CH of Mes), 6.96 (s, 1H, C6H), 7.02 (dd, ^3J(H,P) = 12.9 Hz, ^3J(H,H) = 7.3 Hz, 2H, *ortho*-CH of Ph), 7.38 (t, ^3J(H,H) = 7.5 Hz, 2H, *meta*-CH of Ph), 7.58 (dd, ^3J(H,P) = 13.4 Hz, ^3J(H,H) = 7.3 Hz, 2H, *ortho*-CH of Ph), 7.72 (t, ^3J(H,H) = 7.5 Hz, 2H, *meta*-CH of Ph), 7.79 (m, 1H, *para*-CH of Ph), 7.88 ppm (t, ^3J(H,H) = 7.3 Hz, 1H, *para*-CH of Ph); ^{1}H NMR (500 MHz, CD_2Cl_2, −80 °C, minor isomer 45%): δ = 1.89, 1.90 and 2.05 (s, each 3H, *ortho*-Me of Mes), 2.27 (s, 3H, *para*-Me of Mes), 2.28 (d, ^2J(H,P) = 11.0 Hz, 3H, PMe), 2.31 (s, 3H, *ortho*-Me of Mes), 2.50 (s, 3H, Me of C4), 3.71 (s, 5H, Cp), 4.18 (s, 1H, C3H), 4.29 (s, 1H, C2H), 5.15 (s, 1H, C1H), 6.60 (s, 1H, *meta*-CH of Mes), 6.82 (s, 1H, C6H), 6.86 (s, 1H, *meta*-CH of Mes), 7.13 (dd, ^3J(H,P) = 12.6 Hz, ^3J(H,H) = 8.0 Hz, 2H, *ortho*-CH of Ph), 7.49 (t, ^3J(H,H) = 7.5 Hz, 2H, *meta*-CH of Ph), 7.69 (t, ^3J(H,H) = 7.5 Hz, 2H, *meta*-CH of Ph), 7.77 (m, 1H, *para*-CH of Ph), 7.82 (dd, ^3J(H,P) = 13.9 Hz, ^3J(H,H) = 7.8 Hz, 2H, *ortho*-CH of Ph), 7.90 ppm (t, ^3J(H,H) = 7.3 Hz, 1H, *para*-CH of Ph); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ = 15.0 (^1J(C,P) = 57 Hz, PMe), 20.4 (Me), 21.1, 21.3, 23.9 and 24.2 (Me of Mes), 61.0 (C1), 64.5 (C3), 68.4 (Cp), 74.2 (C2), 87.9 (C9), 92.4 (C8), 114.2 (d, ^1J(C,P) = 90.0 Hz, C4), 119.2 (CF_3SO_3), 119.6 (d, ^1J(C,P) = 50.0 Hz, *ipso*-quaternary C of Ph), 126.0 (C6), 129.4 (*ortho*-quaternary C of Mes), 130.0 and 130.1 (*meta*-CH of Mes), 130.2 (*meta*-CH of Ph), 130.3 (*meta*-CH of Mes), 130.4 (*meta*-CH of Ph), 132.2 (b s, *ortho*-CH of Ph), 132.6 (d, ^2J(C,P) = 11.0 Hz, *ortho*-CH of Ph), 134.2 and 134.5 (d, ^4J(C,P) = 2.8 Hz, *para*-CH of Ph), 141.3 and 142.4 (each *para*-quaternary C of Mes), 150.2 (C7), 160.2 ppm (b s, *ipso*-quaternary C of Mes), C5 bound to the boron atom not found; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 25 °C): δ = 75 ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 17.5 ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = −77.8 ppm; MS (ESI+): *m/z* (%): 697.3 (100%), 698.3 (48%); accurate mass calc. for $[C_{47}H_{50}BFeP]^+$: 697.2861 (M^+, ^{11}B/^{56}Fe isotopomer); meas.: 697.2876, isotopic pattern correct for $[C_{47}H_{50}BFeP]^+$; $E_{1/2}$ = −1302 mV ($B^{\bullet-}$/B) vs Fc/Fc^+ with 0.1 M $[nBu_4N][PF_6]$ in THF, +576 mV (Fe^{II}/Fe^{III}) and −1479 mV ($B^{\bullet-}$/B) vs Fc/Fc^+ with 0.1 M $[nBu_4N][PF_6]$ in acetonitrile; UV/Vis (THF): λ_{max} (ε, $mol^{-1}\,L^{-1}\,cm^{-1}$) = 340 (24250), 596 nm (1070); although [**9h**][CF_3SO_3] could not be obtained as single crystals suitable for X-ray diffraction, crystals of the corresponding $[CuI_4]^{2-}$ salt could be obtained from the corresponding reaction with methyl iodide in the presence of adventitious copper (present as a stabiliser in the MeI); crystallographic data: $C_{92}H_{94}B_2CuFe_2I_4P_2$; M_r = 1966.18; monoclinic; space group $P2_1/c$; a = 12.9526(3), b = 44.3256(11), c = 16.6123(3) Å; β = 106.822(2)°; V = 9129.5(4) Å^3; Z = 4; T = 150 K; λ = 1.54180 Å; 18770 reflections collected; 18770 independent [R(int) = 0.081] used in all calculations, with 928 refined parameters; GOF on F^2 = 1.0007. R_1 = 0.0898; wR_2 = 0.2204 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.1127; wR_2 = 0.2353 for all unique reflections; max. and min. residual electron densities 3.13 and −2.47 e Å^{-3}.

[*n*Bu$_4$N][9g−CN]: A solution of **9g** (0.25 g, 0.366 mmol) in THF (10 mL) was stirred with $[nBu_4N][CN]\cdot 4H_2O$ (0.11 g, 0.403 mmol) for 24 h at room temperature. Volatiles were removed from the resulting red solution under reduced pressure and the residue extracted with diethyl ether (ca. 10 mL). After removal of the solvent under reduced pressure, crystals suitable for X-ray crystallography were obtained from a solution in chloroform by layering with heptane (0.10 g, 28% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.94 (t, ^3J(H,H) = 7.2 Hz, 12H, CH_3 of [nBu$_4$N]), 1.27 (b sextet, ^3J(H,H) = 7.1 Hz, 8H, CH_2 of [nBu$_4$N]), 1.44 (m, 8H, CH_2 of [nBu$_4$N]), 1.98 (s, 3H, Me bound to C7), 2.08 (s, 6H, *ortho*-Me of Mes), 2.14 (s, 6H, *para*-CH_3 of Mes), 2.28 (s, 6H, *ortho*-Me of Mes), 2.94 (t, ^3J(H,H) = 7.9 Hz, 8H, NCH_2 of [nBu$_4$N]), 3.42 (s, 5H, Cp), 3.68 (s, 1H, C2H), 4.27 (s, 1H, C1H), 4.62 (s, 1H, C3H), 6.36 and 6.69 (s, each 2H, *meta*-CH of Mes), 6.91 (s, 1H, C6H), 7.00 and 7.05 (d, ^3J(H,H) = 5.8 Hz, each 2H, *ortho*-CH of Ph), 7.21 and 7.31 (t, ^3J(H,H) = 7.3 Hz, each 2H, *meta*-CH of Ph), 7.91 ppm (t, ^3J(H,H) = 6.1 Hz, 2H, *para*-CH of Ph); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ = 13.6 (CH_3 of [nBu$_4$N]), 19.5 (CH_2 of [nBu$_4$N]), 20.7 and 20.8 (*ortho*-Me of Mes), 23.9 (CH_2 of [nBu$_4$N]), 26.2 (*para*-Me of Mes), 26.4 (Me bound to C4), 57.5 (C3), 58.2 (NCH_2 of [nBu$_4$N]), 65.1 (C1), 67.6 (C2), 67.8 (Cp), 86.1 (C9), 95.1 (d, ^2J(C,P) = 5.4 Hz, C8), 125.8 (d, ^1J(C,P) = 27.0 Hz, quaternary C of Ph), 126.6 (d, ^4J(C,P) = 4.5 Hz, *para*-CH of Ph), 127.3 (d, ^4J(C,P) = 4.2 Hz, *para*-CH of Ph), 128.4 (C7), 128.5 (*meta*-CH of Mes), 131.1 (*para*-quaternary C of Mes), 133.4 (d, ^2J(C,P) = 18.3 Hz, *ortho*-CH of Ph), 133.2 (d, ^2J(C,P) = 18.2 Hz, *ortho*-CH of Ph), 134.2 (d, ^3J(C,P) = 16.7 Hz, *meta*-CH of Ph), 135.5 (C6), 138.1 (d, ^3J(C,P) = 16.9 Hz, *meta*-CH of Ph), 142.1 (d, ^1J(C,P) = 25.3 Hz, C4), 142.9 and 143.3 (*ortho*-quaternary C of Mes), 147.4 (b s, CN bound to B), 152.1 ppm (b s, *ipso*-quaternary C of Mes), 169.8 ppm (b s, C5); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 25 °C): δ = −13 ppm; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = −12.3 ppm; MS (ESI−): *m/z* (%): 708.3 (100%); accurate mass calcd for $[C_{46}H_{44}BFeNP]^-$: 708.2657 (M^-, ^{11}B/^{56}Fe isotopomer); meas.: 708.3428, isotopic pattern correct for $[C_{46}H_{44}BFeNP]^-$; elemental analysis (%) calcd for $C_{62}H_{80}BFeN_2P\cdot(CH_2Cl_2)_{0.4}$: C 76.09, H 8.27; found: C 75.75, H 8.66 (solvent content verified by NMR); UV/Vis (THF): $\lambda_{max,}$ (ε, $mol^{-1}\,L^{-1}\,cm^{-1}$) = 531 nm (1060); crystallographic data: $C_{62}H_{80}BFeN_2P$; M_r = 950.96; monoclinic; space group $P2_1$; a = 11.3694(1), b = 19.0026(1), c = 12.1698(1) Å; β = 90.0233(6)°; V = 2629.26(3) Å^3; Z = 2; T = 150 K; λ = 1.54180 Å; 26989 reflections collected; 10492 independent [R(int) = 0.027] used in all calculations, with 604 refined parameters; GOF on F^2 = 1.0009; R_1 = 0.0787; wR_2 = 0.1880 for observed unique reflections [$I > 2\sigma(I)$] and R_1 = 0.0799; wR_2 = 0.1891 for all unique reflections; max. and min. residual electron

9h−F: A solution of [**9h**][CF_3SO_3] (250 mg, 0.374 mmol) in THF (5 mL) was stirred with $[nBu_4N]F\cdot 3H_2O$ (113 mg, 0.411 mmol) for 6 h at room temperature. Volatiles were removed from the resulting red solution under reduced pressure and the residue extracted with diethyl ether (ca. 5 mL). The volatiles were removed under reduced pressure and the byproduct [nBu$_4$N][CF_3SO_3] was then precipitated from dichloromethane by the addition of diethyl ether at −25 °C. Crystals of **9h**−F suitable for X-ray crystallography were then obtained from solution in THF by layering with heptane (47 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.67 (b s, 3H, *ortho*-Me of Mes), 1.90 (b s, 9H, *ortho*-Me of Mes), 2.16 (s, 6H, *para*-Me of Mes), 2.18 (d, ^2J(H,P) = 14.6 Hz, 3H, PMe), 2.41 (s, 3H, Me of C7), 3.77 (s, 5H, Cp), 3.82 (s, 2H, C2H and C3H), 4.82 (s, 1H, C1H), 6.49, 6.57 and 6.62 (each s, 4H, *meta*-CH of Mes), 7.12 (s, 1H, C6H), 7.15 (b s, 2H, *ortho*-CH of Ph#1), 7.36 (t, ^3J(H,H) = 6.5 Hz, 2H, *meta*-CH of Ph#1), 7.52 (t, ^3J(H,H) = 6.8 Hz, 1H, *para*-CH of Ph#1), 7.72 (t, ^3J(H,H) = 7.7 Hz, 1H, *para*-CH of Ph#2), 7.76 (t, ^3J(H,H) = 7.2 Hz, 2H, *meta*-CH of Ph#2), 7.81 ppm (d, ^3J(H,H) = 7.2 Hz, 2H, *ortho*-CH of Ph#2); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ = 18.5 (dd, ^1J(C,P) = 64.4 Hz, ^2J(C,F) = 19.2 Hz, PMe), 20.0 (s, Me of C7), 20.9 (s, *para*-Me of Mes), 24.2 and 24.9 (b s, *ortho*-Me of Mes), 59.7 (C1), 63.9 (C2), 68.9 (Cp), 69.5 (b s, C3), 86.3 (d, ^3J(C,P) = 8.5 Hz, C9), 94.3 (d, ^2J(C,P) = 18.8 Hz, C8), 108.5 (d, ^1J(C,P) = 97.2 Hz, C4), 116.8 (d, ^1J(C,P) = 101.5 Hz, *ipso*-quaternary C of Ph), 128.6, 128.7, 129.1 and 129.3 (*meta*-CH of Mes), 129.5 (d, ^3J(C,P) = 11.2 Hz, *meta*-CH of Ph#1), 129.6 (d, ^3J(C,P) = 12.5 Hz, *meta*-CH of Ph#2), 132.0 (d, ^2J(C,P) = 9.2 Hz, *ortho*-CH of Ph#2), 132.5 (d, ^3J(C,P) = 8.0 Hz, C6), 132.6 and 132.7 (d, J(C,P) = 7.6 Hz, *para*-CH of Ph of #1 and #2, 133.0 and 133.2 (*para*-quaternary C of Mes), 133.3 (d, ^2J(C,P) = 11.5 Hz, *ortho*-CH of Ph#1), 140.8 and 142.9 (b s, *ortho*-quaternary C of Mes), 143.7 (C7), 153.1 (b s, *ipso*-quaternary C of Mes), 183.8 ppm (b s, C5); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 25 °C): δ =

6.0 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): $\delta = 21.3$ ppm ($^1J(F,P) = 22.9$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta_F = -145.1$ ppm (b s); $E_{1/2} = -13$ mV (Fe^{II}/Fe^{III}) vs Fc/Fc^+ with 0.1 M [nBu$_4$N][PF_6] in acetonitrile; UV/Vis (THF): λ_{max} (ε, $mol^{-1}\,L^{-1}\,cm^{-1}$) = 531 nm (1185); crystallographic data: $C_{46}H_{47}BFFeP$; $M_r = 716.51$; monoclinic, space group $P2_1/n$; $a = 17.1968(2)$, $b = 12.0044(1)$, $c = 18.0916(2)$ Å; $\beta = 101.5347(12)°$; $V = 3659.35(7)$ Å^3; $Z = 4$; $T = 150$ K; $\lambda = 1.54180$ Å. 21019 reflections collected; 7549 independent [R(int) = 0.067] used in all calculations, with 497 refined parameters; GOF on $F^2 = 0.9907$. $R_1 = 0.0550$; $wR_2 = 0.1422$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0599$; $wR_2 = 0.1496$ for all unique reflections; max. and min. residual electron densities 0.85 and −0.89 e Å^{-3}. CCDC reference: 1059120.

9h−CN: A solution of [**9h**][CF_3SO_3] (250 mg, 0.732 mmol) in THF (5 mL) was stirred with [nBu$_4$N]F·3H$_2$O (243 mg, 0.878 mmol) for 6 h at room temperature. Volatiles were removed from the resulting red solution under reduced pressure and the residue extracted with diethyl ether (ca. 5 mL). After removal of the solvent under reduced pressure, crystals suitable for X-ray crystallography were obtained from solution in THF by layering with heptane (154 mg, 29% yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 1.71$, 1.87, 1.93, 2.08, 2.09 and 2.17 (b s, each 3H, Me of Mes), 2.22 (d, $^2J(H,P) = 11.2$ Hz, 3H, PMe), 2.30 (s, 3H, Me of C7), 3.74 (b s, 1H, C2H), 3.77 (s, 5H, Cp), 3.92 (s, 1H, C3H), 4.72 (s, 1H, C1H), 6.62, 6.66, 6.70 and 6.73 (b s, each 1H, *meta*-CH of Mes), 7.20 (s, 1H, C6H), 7.23 (b s, 2H, *ortho*-CH of Ph), 7.36 (m, 2H, *meta*-CH of Ph), 7.43 (t, $^3J(H,H) = 8.1$ Hz, 1H, *para*-CH of Ph), 7.63 (td, $^3J(H,H) = 7.9$ Hz, $^5J(H,P) = 1.8$ Hz, 1H, *para*-CH of Ph) 7.78 ppm (overlapping m, 4H, ortho and *meta*-CH of Ph); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 18.6$ (d, $^1J(C,P) = 55.0$ Hz, PMe), 19.7 (Me), 20.6, 20.8, 23.3, 25.1, 26.6, and 27.5 (Me of Mes), 58.5 (C1), 64.7 (C3), 68.5 (Cp), 69.4 (C2), 85.5 (C9), 95.7 (C8), 109.2 (C4), 119.3 and 121.8 (*ipso*-quaternary C of Ph), 126.9 and 128.3 (*meta*-CH of Mes), 128.5 (*meta*-CH of Ph), 129.2 (*meta*-CH of Mes), 129.4 (*ortho*-CH of Ph), 130.8 (d, $^4J(C,P) = 9.5$ Hz, *para*-CH of Ph), 132.2 (CH of Ph), 133.6 (*para*-CH of Ph), 135.2 (d, $^3J(C,P) = 20.0$ Hz, C6), 137.7 and 138.8 (*para*-quaternary C of Mes), 141.7 and 142.5 (*ortho*-quaternary C of Mes), 144.3 (C7), 145.9 and 150.0 (b s, *ipso*-quaternary C of Mes), 179.4 ppm (C5), C of the cyanide bound to the boron atom was not found; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 25 °C): $\delta = -13$; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): $\delta = 21.5$ ppm; elemental analysis (%) calcd for $C_{47}H_{47}BFeNP$·THF: C 76.99, H 6.97; found: C 77.17, H 6.94 (solvent content verified by NMR); UV/Vis (THF): λ_{max} (ε, $mol^{-1}\,L^{-1}\,cm^{-1}$) = 532 nm (1650); crystallographic data: $C_{47}H_{47}BFeNP$; $M_r = 723.53$; monoclinic; space group $C2/c$; $a = 18.4347(2)$, $b = 12.65370(10)$, $c = 36.2152(3)$ Å; $\beta = 97.0569(9)°$; $V = 8383.82(13)$ Å^3; $Z = 8$; $T = 150$ K; $\lambda = 1.54180$ Å; 8735 reflections collected; 8735 independent [R(int) = 0.053] used in all calculations, with 460 refined parameters; GOF on $F^2 = 1.0162$. $R_1 = 0.0427$; $wR_2 = 0.1061$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0466$; $wR_2 = 0.1086$ for all unique reflections; max. and min. residual electron densities 0.39 and −0.60 e Å^{-3}. CCDC reference: 1059119.

Crystallography

Diffraction data were collected using a Nonius Kappa CCD or Oxford Diffraction (Agilent) SuperNova diffractometer at 150 K; data were reduced using either DENZO, SCALEPACK or CrysAlisPro, and the structures were solved with either SIR92 or SuperFlip and refined with full-matrix least squares within CRYSTALS as described in the CIF.[27]

Determination of binding constants

Binding constants were determined by titration using UV/Vis spectra measured in tetrahydrofuran solution. A stock solution of the receptor was prepared (typically 20 mg in 20 mL THF), from which exactly 3 mL was transferred to a UV cuvette. A first absorption spectrum of the free receptor was measured and then aliquots of a solution of [nBu$_4$N]F·3H$_2$O or [nBu$_4$N][CN]·4H$_2$O were added. Further alicquots of these solutions were added until a total of at least 2.5 equivalents was reached. The binding constants were typically fitted to a 1:1 binding isotherm taking dilution into account, using the REACTLAB software package.[28]

Electrochemical measurements

Electrochemical measurements were performed within a Saffron Omega Scientific glovebox under anhydrous nitrogen on a PARAMETEK VersaSTAT3 potentiostat. Cyclic voltammetry (CV) measurements were carried out using a silver quasi-reference electrode, a glassy-carbon working electrode and a platinum auxiliary electrode. The supporting electrolyte was a 0.1 M solution of [nBu$_4$N][PF_6] in THF. The quasi-reference electrode was immersed in the electrolyte solution for 48 h prior to the experiment and the $NiCp_2$/$NiCp_2^+$ couple was used as an internal reference. Redox potentials were subsequently re-calibrated to Fc/Fc^+ ($\Delta E = -379$ mV).[29] CV experiments were typically performed at three different scan rates of 0.05, 0.1 and 1.0 V s^{-1}.

Supporting information for this article is available on the WWW under http://www.chemeurj.org/or from the author (complete synthetic/characterisation data, details of DFT calculations and CIFs for all crystal structures; CCDC 1059115–1059133 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Keywords: anions · boranes · fluorides · iron · Lewis acids

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