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Iminoborylene complexes: evaluation of synthetic routes towards BN-allenylidenes and unexpected reactivity towards carbodiimides†‡

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The synthetic and reaction chemistries of cationic iminoborylene complexes $[L_nM{=}B{=}N{=}CR_2]^+$, which feature a unique heterocumulene structure, have been systematically investigated. Precursors of the type $CpFe(CO)_2B(Cl)NCAr_2$ (Ar = *p*-Tol/Mes, **5c**/**d**) have been generated by B-centred substitution chemistry using $CpFe(CO)_2BCl_2$ and suitable lithiated ketimines – a reaction which is found to be highly sensitive to the steric bulk at both the metal fragment and the ketimino group. Carbonyl/phosphine exchange (using PCy_3 or PPh_3), followed by halide abstraction allows for the generation of the cationic iminoborylenes $[CpFe(PR_3)(CO)(BNCAr_2)]^+[BAr^X{}_4]^-$ (R = Cy, Ar = *p*-Tol/Mes, **12c**/**d**; R = Ph, Ar = Mes, **13d**; Ar^X = 3,5-$X_2C_6H_3$ where X = Cl, CF_3) which have been characterized spectroscopically and by X-ray crystallography. The reactivity of these iminoborylene systems towards a range of nucleophiles and unsaturated substrates has been investigated. The latter includes the first examples of M=B metathesis reactivity with a carbodiimide, and results in Fe=B cleavage and formation of the isonitrile complexes $[CpFe(PCy_3)(CO)(CNR)]^+[BAr^{Cl}{}_4]^-$ (R = ^iPr/Cy, **16**/**17**).

Introduction

The investigation of boron-transition metal complexes has attracted widespread attention in recent years. A number of novel classes of compounds featuring conventional 2-centre 2-electron metal–boron bonds have been studied, not only with respect to their structural and bonding properties, but also with a view to targeting new modes of reaction chemistry.[1] Within this area, boryl complexes, $L_nM(BX_2)$, featuring a di-substituted boron-fragment coordinated at M were the first to be discovered,[2] and have subsequently been implicated in a number of unprecedented transformations, such as the borylation of unactivated hydrocarbon substrates.[3]

More recently, reliable synthetic routes to subvalent transition metal borylene complexes, $(L_nM)_x(BX)$, have also been developed.[4] These species feature a mono-substituted boron fragment, and are of particular interest due to their close relationship with archetypal organometallic complexes.[5] Along these lines, fluoroborylene (L_nMBF) and aminoborylene (L_nMBNR_2) species have been have been synthesized, representing isolobal analogues of classical carbonyl (L_nMCO)[6] and vinylidene (L_nMCCR_2) complexes.[7,8]

Reactivity-wise the chemistry of many borylene complexes is dominated by the electrophilicity of the boron centre, which underpins their use in C–H activation[9] or cycloaddition reactions.[7a,10] One possibility, with precedent in organometallic systems, to further broaden the scope of reactivity of transition-metal boron complexes is by the introduction of further elements of unsaturation into the boron ligand. Thus, for example, Braunschweig and co-workers have achieved this by use of boryl ligands containing B–X double or triple bonds (X = NR, O or CR_2, Scheme 1).[11] Taking this idea further, we have recently communicated[12] the first examples of cationic iminoborylene complexes $[L_nM{=}B{=}N{=}CR_2]^+$ featuring an extended array of unsaturated bonds (Scheme 1).[13] Such complexes can be viewed as hetero-analogues of well-known allenylidene complexes,[14] which show a highly versatile reaction chemistry resulting from their dual α, γ-electrophilicity and β-nucleophilicity. With this in mind, we set out to uncover new patterns of reactivity for iminoborylene complexes which are otherwise inaccessible to known alkyl- or aminoborylene systems.[4,7]

Herein, we now report in full on synthetic approaches towards iminoborylene systems, and their reaction chemistry

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† Dedicated to the memory of Professor Ken Wade FRS.

‡ Electronic Supplementary Information (ESI) available: Synthetic details and analytical data for all compounds. CCDC 1037786 and 1037787 (crystallographic data for **6** and **16**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00131e

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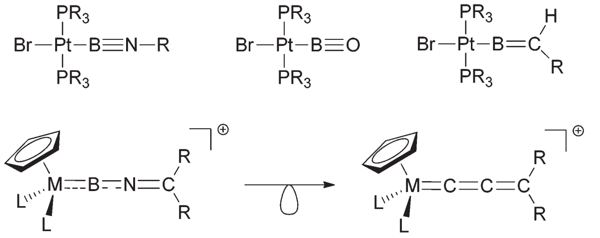


Scheme 1 Highly unsaturated metal–boron complexes featuring iminoboryl, oxoboryl, alkylideneboryl (top) and iminoborylene ligands (bottom, also showing the isolobal relationship with allenylidenes).

both with respect to anionic nucleophiles and unsaturated substrates. A key finding is the discovery of novel metathesis-type reactivity towards carbodiimides, RNCNR.

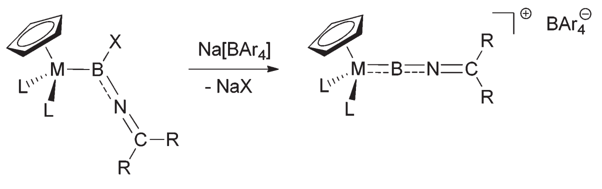
Results and discussion

The synthesis of terminal borylene complexes has been achieved using a variety of different approaches, including double salt elimination,[4f,g] metal-to-metal borylene transfer,[15] and dehydrogenation of σ-borane complexes.[16] Moreover, halide abstraction from haloboryl complexes has been shown to give access to *cationic* borylenes in a reliable fashion.[17] Based on this approach, we envisaged the use of suitable imino-functionalized haloboryl complexes as precursors, which upon halide abstraction with sodium tetra-arylborates would give the desired cationic iminoborylenes (Scheme 2).

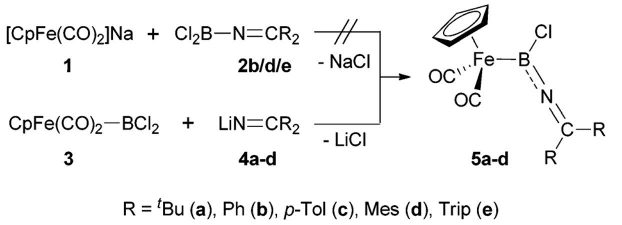
Synthesis of iminoboryl complexes

In order to put our synthetic efforts towards imino-substituted systems on a comparable basis to known complexes, we initially decided to target the [CpFe(CO)$_2$] unit as the metal fragment, given its successful use for the generation of related cationic aminoborylenes.[7a,b] For the construction of precursors featuring the necessary array of consecutive Fe–B–N–C bonds, we evaluated two synthetic approaches, differing in the order of formation of the relevant bonds to the boron centre (Scheme 3).

Mirroring existing synthetic routes to [CpFe(CO)$_2$] boryl complexes,[17c] we initially attempted the generation of complexes of type **5** by reaction of the anionic [CpFe(CO)$_2$]$^-$ reagent **1** (as the sodium salt) with the corresponding dichloro-(imino)boranes **2**, thus establishing the B–N connectivity prior to the formation of the Fe–B bond (Scheme 3, upper). While Cl$_2$B(N=CPh$_2$), **2a**, was readily synthesized according to Wade's original procedure,[18] it showed no reactivity towards ferrate **1**. Assuming that the dimeric nature of **2a** (indicated by its ^{11}B NMR shift of $\delta_B = -7$ ppm) is responsible for its low reactivity, we attempted to generate monomeric dichloro-(imino)boranes by the use of bulkier ketimino substituents (*e.g.* R = Mes or Trip). These syntheses were initially frustrated by a ligand redistribution reaction which apparently occurs on exposure to continuous vacuum [yielding ClB(N=CR$_2$)$_2$], and which prevents isolation of the pure dichloro(ketimino)-boranes.[19] This problem could be circumvented by *in situ* generation (see ESI‡), which generates the corresponding monomeric compounds Cl$_2$B(N=CR$_2$) (R = Mes/Trip (**2d**/**e**), δ_B = 26/27 ppm). However, these systems do not show clean reactivity towards **1**, with the starting borane being the predominant species in the reaction mixtures even under forcing conditions.



Scheme 2 Target synthesis of iminoborylene complexes by halide abstraction from halo(imino)boryl complexes.



Scheme 3 Synthesis of iminoboryl complexes **5** *via* dichloro-iminoboranes (top) or dichloroboryl iron precursors (bottom).

For this reason, we shifted our synthetic strategy towards a reversed order of bond formation reactions at boron, employing the known reaction of **1** with BCl$_3$ to generate the iron dichloroboryl complex **3** *in situ* (δ_B = 91 ppm).[20] Complex **3** was then treated with a series of ketiminolithium reagents LiN=CR$_2$ [R = ^{t}Bu/Ph/*p*-Tol/Mes/Trip (**4a–e**)],[21] to install the B–N linkage (Scheme 3, lower). Accordingly, the reactions with less bulky lithium salts (*e.g.* **4a–d**) lead to clean formation of the desired iminoboryl complexes **5a–d** (as judged by ^{1}H and ^{11}B NMR spectroscopy), which could be purified by precipitation from hexane in case of the *p*-tolyl- and mesityl-substituted complexes (**5c**/**d**, 38–52%); the high solubility of complexes **5a**/**b**, on the other hand, prevented their isolation as pure compounds. By contrast, the reaction of the lithium salt LiN=CTrip$_2$ (**4e**) with **3** gives a different type of boron-containing product, with the high field ^{11}B chemical shift (δ_B = 27 ppm) arguing against Fe–B bond formation. The product is tentatively assigned as borane **2e**, resulting from the nucleophilic displacement of the [CpFe(CO)$_2$]$^-$ anion (rather than chloride) from precursor **3**. Such a transformation has recent precedent,[22] and is presumably induced by the large steric bulk of the bis(triisopropylphenyl)ketimino group.

Complexes **5c**/**d** have been characterized spectroscopically, showing the expected NMR resonances for the [CpFe(CO$_2$)] fragment (Cp: δ_H = 4.26/4.30 ppm, δ_C = 84.4/84.6 ppm, CO: δ_C = 215.3/215.3 ppm) and [B–N=C] fragments (δ_C = 150.7/153.1 ppm, δ_B = 50/47 ppm). Additionally, in the case of **5c** structural authentication could be achieved by X-ray crystallography (Fig. 2). In the solid state, **5c** exhibits a near-linear arrangement of the B–C–N unit [∠ B(11)–N(13)–C(14) = 175.6(3)°], consistent with a significant degree of N → B π-donation, a finding also reflected in the short B–N [1.349(4) Å] and relatively long Fe–B bond lengths [2.016(4) Å].

Having established a viable synthetic route for the generation of complexes of type **5** by boron-centred substitution chemistry, and with the steric constraints of the ketimino nucleophile now apparent, we set out to investigate the scope of this approach by variation of the metal fragment. Thus, we generated the previously described tungsten dichloroboryl complex **6** (δ_B = 91 ppm) alongside its bromo analogue **7** (δ_B = 84 ppm) by reaction of the tungstate Na[CpW(CO$_3$)] with the respective trihaloboranes.[23]

Although **6** has previously been reported by Schmid and Nöth, it has not been structurally characterized, and given the dearth of structural data available for dihaloboryl systems we sought to investigate it crystallographically. Accordingly, the solid-state structure of **6** (Fig. 1) features a W–B bond [2.22(2) Å] which is considerably longer than in the corresponding CpFe(CO)$_2$BCl$_2$ complex **3** [1.942(3) Å] (even taking into account the larger van der Waals radius of tungsten *vs.* iron: 2.10 *vs.* 2.05 Å),[20a,24] while the B–Cl bonds are in the expected range [*e.g.* 1.78(1) and 1.79(1) Å for **6**, *cf.* 1.781(6) and 1.783(4) Å for **3**].[20a] Due to the presence of three carbonyl co-ligands, complex **6** is sterically rather congested when compared to **3**, as can be seen from the close B–CO contacts [B(13)–C(11) 2.37(2), B(13)–C(2) 2.53(2) Å, *cf.* B–C(1) 2.574(5), B–C(2) 2.638(6) Å for **3**], a factor which presumably also leads to the (near parallel) orientation of the BCl$_2$ unit with respect to the Cp(centroid)-W-B plane [∠ Cp(centroid)–W(1)–B(13)–Cl(14) = 9.5(9)°, *cf.* ∠ Cp(centroid)–Fe–B–Cl(1) = 100.7(2)° for **3**].

While **6** could be structurally characterized, its reactivity – in terms of boron-centred substitution processes – proves to be much less facile than the corresponding chemistry for **3**. Thus, in contrast to the clean reactivity observed in the iron case, no M-B containing products could be observed upon reaction of the representative ketiminolithium salts **4a**/**d** with either of the dihaloboryl-tungsten complexes **6** or **7**. As judged by ^{11}B NMR spectroscopy, breakage of the W–B bond and extrusion of the [CpW(CO)$_3$]$^-$ unit generates instead the corresponding dihalo(ketimino)boranes **2a**/**d** (δ_B = 21/26 ppm) (Scheme 4).

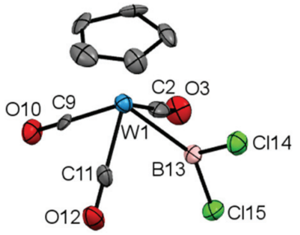
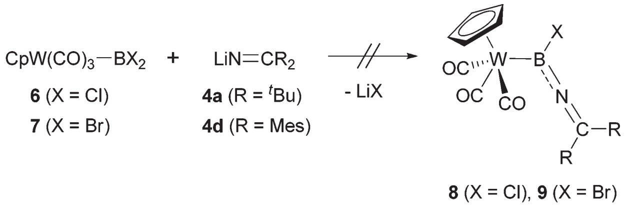


Fig. 1 Molecular structure of **6** in the solid state, hydrogen atoms omitted for clarity and thermal ellipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: W(1)–B(13) 2.22(2), B(13)–Cl(14) 1.78(1), B(13)–Cl(15) 1.79(1), Cl(14)–B(13)–Cl(15) 110.5(7).

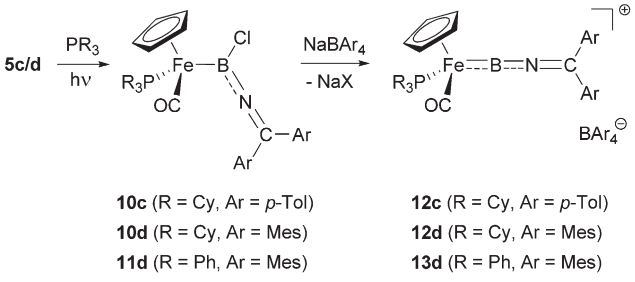


Scheme 4 Attempted synthesis of tungsten iminoboryl complexes.

These results further suggest that the boron-centred substitution reaction using a metal dihaloboryl complex is very sensitive to the steric bulk of the substituents both on the metal fragment and on the incoming nucleophile, with the partnership of the less sterically demanding iron boryl complex **3** and the less bulky iminolithium salts **4a–d** uniquely bringing about substitution at boron without breakage of the metal–boron bond.

Synthesis of iminoborylene complexes

With the iminoboryl-complexes **5c**/**d** in hand, we next attempted the synthesis of the corresponding borylene complexes by halide abstraction. Reaction of **5d** with Na[BAr$^f_4$] [Ar^f = 3,5-(CF$_3$)$_2$C$_6$H$_3$] leads to the formation of the corresponding cationic borylene [CpFe(CO$_2$)(BNCMes$_2$)]$^+$, as indicated by a downfield shift in the ^{11}B NMR signal (δ_B = 75 ppm, *cf.* 47 ppm for **5d**). While this borylene complex could be shown to be stable at −30 °C in solution over a period of several days, it decomposes rapidly at room temperature. This led us to investigate the use of more electron-rich metal fragments in order to generate borylene species stabilized by more efficient M → B π-backbonding. Thus, we attempted the photolytic displacement of the π-acidic carbonyl-ligands in **5c**/**d** by strong σ-donor phosphine ligands. While attempts to substitute both carbonyl ligands by reaction with chelating bis-phosphines (dppe/dmpe for example) failed to yield the desired products,[25] reaction of **5c**/**d** with monodentate donors cleanly gave the corresponding mixed phosphine/carbonyl complexes (Scheme 5).[26] Assuming that bulky trialkylphosphines would lead to an additional kinetic stabilization of the corresponding borylene complexes, we first used PCy$_3$ in this substitution chemistry, leading to the formation of the desired complexes **10c**/**d** in moderate yields (48–60%). In order to further investi-



Scheme 5 Synthesis of phosphine-substituted iminoboryl complexes **10** and **11** and halide abstraction to give borylenes **12** and **13**.

gate the influence of the steric/electronic properties of the phosphine ligands, we also employed PPh_3 in the reaction with **5d**, giving the triphenylphosphine-substituted boryl complex **11d** (43%).

Spectroscopic characterization of **10c**/**d** and **11d** clearly signals the successful introduction of the phosphine co-ligands *via* ^{31}P NMR spectroscopy (δ_P = 77.1/75.0/78.8 ppm for **10c**/**10d**/**11d**), while little change is observed in the respective ^{11}B spectra (δ_B = 47/50/51 ppm). In addition, diastereotopic splitting is observed for the aryl substituents of the axially prochiral ketimino fragments, brought about by the formation of a chiral metal centre (*e.g.* p-CH_3 groups in **10c**/**10d**/**11c**: δ_H = 2.09, 2.06/2.11, 2.09/2.12, 2.11 ppm). In addition, the formation of a more electron-rich metal centre leads to the expected red-shift of the C═O stretches in the respective IR-spectra [ν(CO) = 1902/1905/1909 cm^{-1} for **10c**/**10d**/**11d**, *cf.* ν(CO) = 2002, 1922/2005, 1937 cm^{-1} for **5c**/**d**].

Crystallographically, complexes **10c**/**d** (Fig. 2) feature a piano-stool geometry around the central metal atom in the solid state, with the M–C(O) distances reflecting a higher degree of π-backbonding compared to **5c** [1.716(2)/1.716(3) Å for **10c**/**d**, *cf.* 1.758(3), 1.753(3) Å for **5c**]. Interestingly (and in contrast to dicarbonyl-ligated **5c**), complex **10c** features a non-linear arrangement of the B–N–C unit [∠ B–N–C = 144.8(2)°], implying a reduced degree of N → B donation. Consistently, **10c** features a relatively long B–N [1.396(4) Å], with the accompanying shortening of the Fe–B bond [1.980(4) Å] presumably reflecting augmented Fe → B donation. This balance of competing π-donation to boron is clearly a fine one, however, as the closely related *dimesityl* system **10d** features a linear B–N–C arrangement [∠ B–N–C = 174.7(2)°] and bond lengths consistent with dominant N → B donation [B–N 1.368(3) Å, Fe–B 2.015(2) Å].

Utilising the monophosphine boryl complexes **10c**/**d** and **11d** as precursors, halide abstraction with $Na[BAr^{Cl}_4]$ (Ar^{Cl} = 3,5-$Cl_2C_6H_3$) leads to the clean formation of the desired borylene complexes **12c**/**d** and **13** in yields of 55–77% (Scheme 5). In comparison with their dicarbonyl-supported analogues, these complexes are more stable at room temperature, at least when handled under inert atmosphere conditions. Borylene formation can be followed by the downfield shifts in the respective ^{11}B signals (δ_B = 82/85/85 ppm for **12c**/**12d**/**13d**), while the shifts of the ^{31}P resonances are less informative (δ_P = 84.9/75.0/69.3 ppm). In the ^1H and ^{13}C NMR spectra, the two sets of distinct signals for the ketimino aryl substituents merge to give a single set of resonances, indicating fast rotation of the $BNCAr_2$ unit (*e.g.* δ_H = 2.48/2.31/2.34 ppm for the p-CH_3 signal in **12c**/**12d**/**13c**), which is not frozen out even at low temperatures (down to −75 °C). The IR spectra of these new compounds are also informative. These feature not only a BNC stretch consistent with the analogous mode observed for allenylidenes [ν(BNC) = 1763/1753/1779 cm^{-1}], but also blue-shifted carbonyl stretching frequencies in comparison with their chloroboryl precursors [ν(CO) = 1962/1969/1984 cm^{-1} for **12c**/**12d**/**13c**] consistent with weaker Fe → CO π-backbonding in the cationic systems.

Attempts to obtain crystals of complexes **12c** and **13d** revealed instead the tendency of each complex to slowly decompose over several days to $[CpFe(PR_3)(CO)_2]^+[BAr^{Cl}_4]^-$ (R = Cy, Ph, respectively); the combined steric bulk of the mesityl and tricyclohexyl substituents, however, render complex **12d** stable enough to be characterized by both X-ray crystallography and by positive-ion ESI-MS, the latter being consistent with the presence of the $[CpFe(PCy_3)(CO)_2(BNCMes_2)]^+$ cation (ESI‡). Moreover, the solid state structure (Fig. 2) reveals two crystallographically independent species with almost identical structural features. The cationic borylene component features a cumulene-type linear arrangement of the Fe–B–N–C unit [∠ Fe(1)–B(28)–N(29) = 170.9(5)°, ∠ B(28)–N(36)–C(37) = 175.3(2)°]. In the solid state at least, the ketimino-group is orientated near-parallel to the Cp(centroid)–Fe–B plane [∠ Cp(centroid)–Fe(1)–C(30)–C(40) = 7.1°], and the Fe–B bond [1.835(6) Å] is noticeably shorter than in the precursor **10d** [2.015(2) Å], being comparable to that observed in monophosphine-substituted aminoborylene-complexes (*e.g.* 1.821(4) Å in $[CpFe(CO)(PMe_3)(BNCy_2)]^+$).[26] However, the observed B–N distance is rather short and the N–C distance is long [B–N 1.314(6) Å, N–C 1.292(6) Å, *cf.* 1.368(3) Å and 1.263(3) Å for **10d**], consistent with a significant contribution from a resonance form containing a Fe–B≡N–$CMes_2^+$ unit. Such a contribution is also con-

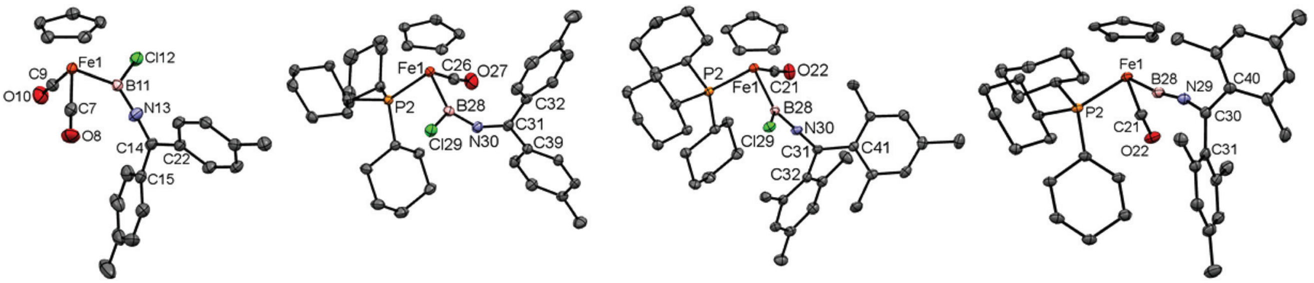


Fig. 2 Molecular structures of **5c**, **10c**, **10d** and **12d** in the solid state. Hydrogen atoms and counter-ion omitted for clarity and thermal ellipsoids set at the 40% probability level (20% for **12d**). Key bond lengths [Å] and angles [°]: (for **5c**) Fe(1)–B(11) 2.016(4), B(11)–N(13) 1.349(4), N(13)–C(14) 1.277(4), Fe(1)–B(11)–N(13) 126.0(2), B(11)–N(13)–C(14) 175.6(3); (for **10c**/**d**) Fe(1)–B(28) 1.980(4)/2.015(2), B(28)–N(30) 1.397(4)/1.368(3), N(30)–C(31) 1.269(3)/1.263(3), B(28)–N(30)–C(31) 144.8(2)/174.7(2); (for **12d**) Fe(1)–B(28) 1.835(6), B(28)–N(29) 1.302(8), N(29)–C(30) 1.287(7), Fe(1)–B(28)–N(29) 170.9(5), B(28)–N(36)–C(37) 175.3(2).

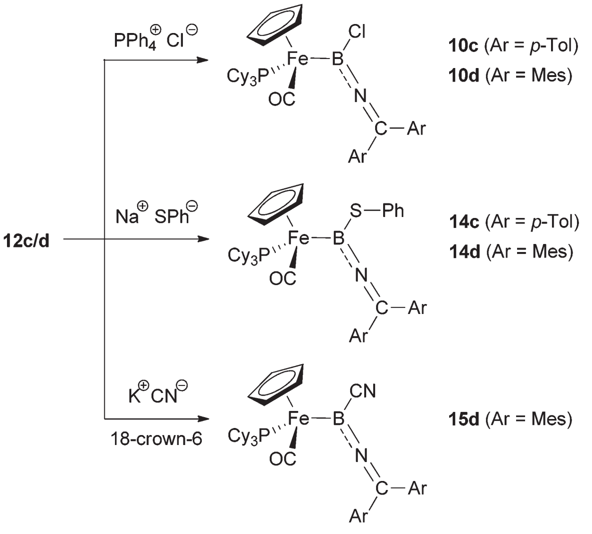
sistent with the low-field shift of the ketimino-carbon ^{13}C resonance, a feature also characteristic of allenylidene complexes (δ_C = 187.0 ppm, *cf.* δ_C = 150.2 ppm for **10d**).

Reactivity of the iminoborylene complexes

With the crystallographic and spectroscopic analysis of iminoborylene complex **12d** hinting at a partial contribution from a carbo-cationic resonance form, we set out to determine experimentally whether selectivity for nucleophilic addition at either the α- or γ-position would be observed. With this in mind, we further sought to compare the addition chemistry of both the mesityl- and *p*-tolyl substituted systems (**12c**/**d**, Scheme 6) in order to investigate the influence of the steric loading at the ketimino group.

In the first instance, we investigated whether reactions with a chloride source (*e.g.* [PPh_4]Cl) could be used to generate products of the type $CpFe(CO)(PCy_3)\{BNC(Cl)Mes_2\}$, thus allowing a formal α, γ-isomerization of the precursors **10c**/**d** *via* iminoborylene intermediates (*i.e.* a formal reversal of the conversion of $[L_nM{=}C{=}C{-}CR_2OH]^+$ to $[L_nM{=}C(OH)C{=}CR_2]^+$ *via* the corresponding allenylidene[27]). However, exclusive α-attack led to the re-formation of the precursors **10c**/**d**. In similar fashion, the reaction of **12c**/**d** with sodium thiophenolate leads to the products of boron-centred nucleophilic attack, exclusively giving the B(SPh) complexes **14**, independent of the steric bulk at the ketimino group. The syntheses of the thiolate-functionalized boryl complexes **14c**/**d** could also be achieved directly by reaction of **10c**/**d** with NaSPh in a boron-centred substitution reaction, thus providing independent verification of compound identity.

The situation is slightly different, however, when using cyanide (KCN, 18-crown-6) as a nucleophile. In this case, boryl precursors **10c**/**d** are completely resistant towards substitution at boron, so we investigated the reactivity of the corresponding borylenes **12c**/**d** towards CN^-. On mixing KCN and 18-crown-6 with **12c**/**d** generated *in situ* by the reaction of **10c**/**d** with Na[BAr^{Cl}_4], re-formation of the chloroboryls **10c**/**d** is observed. This suggests that in the presence of NaCl (from the initial salt metathesis) and KCN, in conjunction with 18-crown-6 as a solubilizing agent, the addition of chloride is preferred over the addition of cyanide. Presumably such an observation reflects thermodynamic control due the more favourable B–Cl bond enthalpy (*ca.* 128 *vs.* 107 kcal mol^{-1}).[28] The reaction of the pure complex **12d** with KCN does, however, lead to addition of cyanide to the borylene. Once again, α-selectivity is observed, yielding the corresponding cyano-substituted boryl-complex **15d**. Unfortunately, reaction of KCN with the less sterically encumbered borylene **12c** gives only decomposition products, so that the influence of the aryl substituents on the regio-selectivity could not be fully investigated in this case.



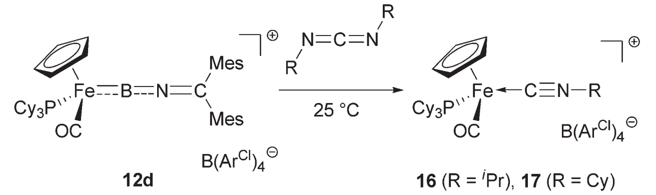
Scheme 6 Reactivity of the borylene-complexes **12c**/**d** towards anionic nucleophiles.

Complexes **14c**/**d** and **15d** were fully characterized by spectroscopic, mass spectrometric and, in case of **14d**, by crystallographic methods.[12] The ^{11}B and ^{31}P resonances (δ_B = 56/52/41 ppm, δ_P = 76.3/74.1/73.3 ppm for **14c**/**14d**/**15d**) are similar to those of the corresponding chloroboryl complexes (δ_B = 47/50 ppm, δ_P = 77.1/75.0 ppm for **10c**/**10d**), which together with the C=N ketimino-resonances (δ_C = 147.7/149.9/150.5 ppm) verify the postulated structures resulting from α-attack at boron. The observed high α-selectivity is presumably brought about by the high electrophilicity of the boron centre in each case, bearing in mind the fact that γ-selectivity has been observed in the addition of a variety of nucleophiles (including thiolate and cyanide) to cationic allenylidene complexes.[14,29]

Hoping to uncover more diverse patterns of reactivity, we targeted a study of the reactivity of the iminoborylenes towards unsaturated substrates. It has been shown that neutral borylene complexes undergo borylene transfer reactions with alkynes,[10] insertion reactions with isonitriles and carbodiimides,[30] and metathesis-type reactions with ketones,[30] while cationic borylenes oftentimes show contrasting reactivity, displaying hydride transfer reactivity towards ketones,[31] insertion reactions with carbodiimides,[32] and metathesis-type reactivity with isocyanates and phosphine sulfides.[7b]

In order to investigate the reactivity of our iminoborylene complexes towards unsaturated substrates, we used the mesityl-substituted complex **12d** which shows the highest resistance towards undesired hydrolysis and decomposition reactions. Mixing of **12d** with non-polar substrates such as 2,3-dimethyl-butadiene and trimethylsilyl-acetylene in dichloromethane leads to no conversion, even at 40 °C, and over prolonged periods of time. While this result is consistent with the fact that other cationic borylenes show little affinity for alkenes or alkynes, we were surprised to find that mixing of **12d** with isopropyl-isocyanate also did not lead to any conversion (as judged from *in situ* ^{1}H and ^{11}B NMR measurements). This contrasts with the chemistry of cationic aminoborylenes, which react with isocyanates, RNCO, cleanly and under mild conditions to give the corresponding isonitrile complexes $[CpFe(CO)_2(NCR)]^+$ *via* a metathesis-type reaction.[26]

By contrast, the reaction of **12d** with an excess of either diisopropyl- or dicyclohexylcarbodiimide (RN=C=NR,



Scheme 7 Reaction of iminoborylene complex **12d** with carbodiimides to give isonitrile complexes **16**/**17**.

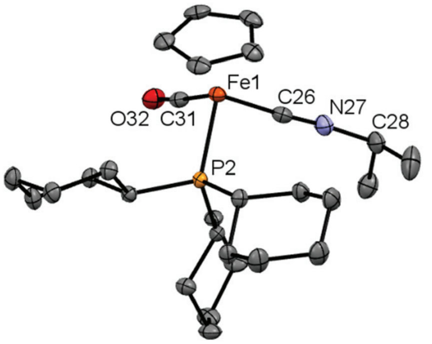


Fig. 3 Molecular structure of **16** in the solid state, hydrogen atoms and counter-ion omitted for clarity and thermal ellipsoids set at the 40% probability level. Key bond lengths [Å] and angles [°]: Fe(1)–C(26) 1.850(2), C(26)–N(27) 1.163(3), N(27)–C(28) 1.461(3), Fe(1)–C(26)–N(27) 176.7(2), C(26)–N(27)–C(28) 175.0(2).

R = ^{i}Pr/Cy) gives clean conversion within hours at room temperature, to a single ^{31}P containing species (δ_P = 76.4/76.5 ppm, respectively) and a compound giving rise to a ^{11}B signal at δ_B = 29/30 ppm. Rather than the carbodiimide insertion products found for related aminoborylene complexes[30,32] and organic boranes,[33] *in situ* spectroscopic analysis of the reaction mixture in this case supports an alternative pathway. Thus, as opposed to a characteristic low-field carbene ^{13}C resonance seen for either a mono- or a bis-carbodiimide insertion product (*e.g.* $[\mathrm{CpFe(CO)_2{=}C(NCy)_2BNCy_2}]^+$, δ_C = 251.5 ppm or $[\mathrm{CpFe(CO)_2 = C(NCy)_2B(NCy)_2CNCy_2}]^+$, δ_C = 224.0 ppm),[32b] we observe the corresponding quaternary carbon resonance at δ_C = 153.6/153.8 ppm (for R = ^{i}Pr/Cy). This observation suggests the formation of the isonitrile complexes $[\mathrm{CpFe(CO)(PCy_3)(NCR)}]^+[\mathrm{BAr^{Cl}{}_4}]^-$ (**16**/**17**, R = ^{i}Pr/Cy, Scheme 7), which could also be detected by positive-ion ESI MS (SI).

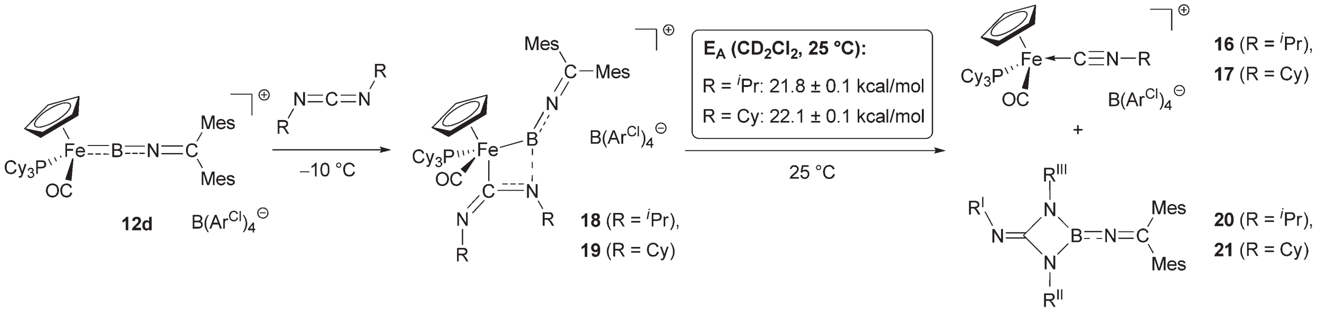
In case of **16**, we were also able to isolate the metal-containing species by crystallization and unambiguously confirm its structure by X-ray crystallography (Fig. 3). In the solid state, complex **16** shows a piano-stool geometry, with the isonitrile unit featuring a linear geometry [∠ C(26)–N(27)–C(28) = 175.0(2)°], brought about by the presence of the C–N triple bond [C(26)–N(27) 1.163(3) Å]. In solution, complexes **16** and **17** show very similar spectroscopic features, *e.g.* resonances in the ^{1}H and ^{13}C NMR spectra for the Cp (δ_H = 4.92/4.92 ppm, δ_C = 84.2/84.3 ppm for **16**/**17**) and $\mathrm{C{\equiv}N{-}CHR_2}$ units (CH: δ_H = 4.08/3.85 ppm, δ_C = 51.3/57.3 ppm for **16**/**17**).

This chemistry represents, to our knowledge, the first example of metathesis-type reactivity of a borylene complex towards a carbodiimide, and we therefore performed further investigations in order to better understand the reaction mechanism and to probe the fate of the boron-containing $[\mathrm{B{=}N{=}CMes_2}]$ heterocumulene fragment.

Upon mixing of the **12d** with the respective carbodiimide $\mathrm{RN{=}C{=}NR}$ at −60 °C in $\mathrm{CD_2Cl_2}$, we observe the immediate formation of an intermediate (**18**/**19** for R = ^{i}Pr/Cy), which is stable at temperatures below 0 °C. Accordingly, we were able to characterize these species by multinuclear NMR spectroscopy. In the ^{1}H and ^{13}C NMR spectra we observe a splitting of the resonances for the ketimino aryl substituents (*e.g.* mesityl *p*-$\mathrm{CH_3}$ in **18**/**19**: δ_H = 2.30, 2.25/2.31, 2.25 ppm), as is also seen for the boryl precursor **10d**. In addition, we also observe two sets of resonances for the carbodiimide ^{i}Pr/Cy substituents (*e.g.* for the N–C*H*R$_2$ protons in **18**/**19**: δ_H = 3.73, 3.01/3.24, 2.54 ppm), consistent with desymmetrization of the RNCNR unit. These spectroscopic features are consistent with the formation of either a Lewis acid–base adduct between the electrophilic boron and one of the carbodiimide nitrogens,[32a,b,33b] or with the formation of a [2 + 2]-cycloaddition product,[30a] both of which have been observed as intermediates in the reactions of carbodiimides with borylene complexes.

Somewhat unexpectedly, the ^{11}B and ^{31}P NMR resonances for **18**/**19** are shifted *downfield* in comparison to those observed for the free borylene (δ_B = 91/91 ppm, δ_P = 80.8/80.4 ppm for **18**/**19**, *cf.* δ_B = 85 ppm, δ_P = 75.0 ppm for **12d**). While these shifts imply retention of the Fe–B linkage at this stage in the reaction, they appear counter-intuitive for the formation of either a B-bound Lewis acid–base adduct or a [2 + 2]-cycloaddition product, both of which would be expected to lead to an upfield shift in the ^{11}B NMR resonance. Thus, adducts of $[\mathrm{CpFe(CO)_2(BNR_2)}]^+$ (δ_B = 94 ppm) with carbodiimides or imines (adducts: δ_B = 71/54 ppm)[7b,32b] and the [2 + 2] cyclo-addition product of $\mathrm{CpMn(CO)_2(B^tBu)}$ (δ_B = 144 ppm) with carbodiimide (product: δ_B = 62 ppm) show upfield shifts in the ^{11}B signal, consistent with an increased coordination number at boron.[30c] To an even greater extent, the ^{11}B resonances measured for **18** and **19** contrast with those observed for the Fe=B insertion products formed in the reaction of the same carbodiimides with cationic iron *amino*borylene complexes (*e.g.* δ_B = 25 ppm for $[\mathrm{CpFe(CO)_2\{C(NCy)_2BNCy_2\}}]^+$).[32b]

In the ^{13}C spectra the downfield shifts observed for the carbodiimide quaternary carbons (δ_C = 168.8/168.3 ppm for **18**/**19**, *cf.* δ_C = 140.2/139.9 ppm for free $\mathrm{RN{=}C{=}NR}$ with R = ^{i}Pr/Cy)[34] are consistent with the formation of a direct metal-carbon interaction [*cf.* δ_C = 151.0, 162.0 for $\mathrm{CpMn(CO)_2\{\kappa^2\text{-}B(^tBu)N(Cy)CNCy\}}$ and $\mathrm{CpMn(CO)_2\{\kappa^2\text{-}B(^tBu)OCPh_2\}}$, respectively], although not with complete insertion into the Fe=B bond (*cf.* δ_C = 251.0 ppm for $[\mathrm{CpFe(CO)_2\{C(NCy)_2BNCy_2\}}]^+$, which features partial Fe=C carbenoid character). Moreover, the observation of resonances at $\delta_c \approx 180$ ppm for the γ-carbons of the FeBNC units (along with the downfield ^{11}B shifts for **18**/**19**), suggests retention of a substantial degree of delocalization along the hetero-cumulene framework. With this in mind, we



Scheme 8 Pathway of the reaction of borylene complex **12d** with carbodiimides. Formation of the intermediates **18**/**19** and subsequent reaction to give the final products **16**/**17** and **20**/**21** (tentative structures).

suggest the formation of an unsymmetrical [2 + 2]-cycloaddition product featuring a strong interaction between the metal and the central carbodiimide carbon and a relatively weak N → B interaction (Scheme 8).

Repeated attempts to obtain structural information on **18**/**19** by crystallization at low temperatures failed to give crystals suitable for X-ray analysis, and in contrast to the [2 + 2] cycloaddition products of carbodiimides with $CpMn(CO)_2(B^tBu)$,[30c] solutions of **18**/**19** are labile, yielding isonitrile complexes **16**/**17** within a few hours at room temperature. The activation barriers for this step could be determined in each case by following of the intensity of the cyclopentadienyl ^1H signals as a function of time. Values of 21.8 ± 0.1 kcal mol^{-1} and 22.1 ± 0.1 kcal mol^{-1} (at T = 25 °C) are thus obtained for **18** and **19**, respectively (Scheme 8).

Finally, we sought to establish the fate of the boron-containing fragment in the final reaction mixture. When the reaction is performed with a stoichiometric amount of either carbodiimide, the ^1H NMR spectra show the isonitrile complexes **16**/**17**, together with a number of products containing mesityl- or isopropyl/cyclohexyl groups, respectively. Only in the presence of an excess of carbodiimide, could well-defined boron-containing products be isolated. The ^{11}B resonances (δ_B = 29/30 ppm for R = ^{i}Pr/Cy) indicate a three-coordinate boron centre without any metal–boron interaction, while the ^1H NMR spectra show the presence of three inequivalent ^{i}Pr- or Cy-groups [*e.g.* CHR_2-units: δ_H = 3.90/3.39/3.61 for ^{i}Pr-(I/II/III), 3.04/2.96/3.45 for Cy-(I/II/III), (for numbering see Scheme 8)]. The ^{13}C-NMR and GHMBC-data indicate that all three alkylamino-substituents are bound to a central quaternary carbon (δ_C = 152.4/ 155.9 ppm), with two of the alkyl-groups (I and III, respectively) being in close proximity as seen from NOE difference spectra. Taken together, these observations suggest that in the presence of excess carbodiimide, $R^{II}N{=}C{=}NR^{III}$, coordinative trapping of the initial metathesis product [$R^IN{=}B{=}N{=}CMes_2$] leads to the formation of a trialkyl-guanidinate, which is bound to the B=N=CMes heterocumulene fragment. The resulting triaminoboranes of the type $RN{=}C(NR)_2BNCMes_2$ [with R = ^{i}Pr (**20**) and R = Cy (**21**), Scheme 8] thus resemble the metalla-amidinates $[CpFe(CO)_2\{C(NCy)_2BNCy_2\}]^+$ formed by mono-carbodiimide insertion in the case of aminoborylene systems.[32]

Conclusions

Our investigation of the possible synthetic routes to iminoborylene complexes (**12**/**13**) has given insight into the scope of metal-fragments, ketimino substituents and ancillary ligands which allow for successful formation of the desired cationic heterocumulenes. For the synthesis of the iminoboryl-precursors, it is found that an optimal level of overall steric bulk, in combination with the correct order of bond formation (Fe–B prior to B–N bond formation), is required for the generation of the boryl complexes $CpFe(CO)_2\{B(Cl)NCAr_2\}$ (Ar = *p*-Tol/Mes, **5c**/**d**). The use of reagents with increased steric bulk on either the metal [$CpW(CO)_3$ *vs.* $CpFe(CO)_2$] or the ketimino side (Trip *vs.* Mes) leads primarily to products resulting from M–B bond breakage, illustrating the sensitivity of the boron-centred substitution reaction to steric factors.

While direct halide abstraction from complexes **5c**/**d** leads to thermally unstable borylene species, the substitution of one carbonyl ligand for a tertiary phosphine drastically increases complex stability, leading to the isolation of the cationic heteroallenylidenes $[CpFe(PR_3)(CO)(BNCAr_2)]^+$ as borate salts (**12c**/**d**, **13d**). The reactivity of these complexes towards nucleophilic substrates is dominated by the high electrophilicity of the boron centre, leading exclusively to α-attack, while the reactivity towards unsaturated substrates leads to unprecedented transformations. While no reactivity is observed towards isocyanates, we observe clean metathesis-type reactivity with carbodiimides. This contrasts with the insertion-type reactivity of closely related amino- and alkylborylene complexes towards the same substrates. Spectroscopic analysis of the reaction mixtures leads to identification of the boron-containing reaction products as the coordinatively trapped heteroallenes (**20**/**21**), with the metal-containing products being unambiguously identified as the isonitrile complexes (**16**/**17**). This reactivity is unprecedented and represents the first example of a productive metathesis-type reaction of a borylene compound with a carbodiimide.

Experimental

General considerations

All reactions involving air- or moisture-sensitive compounds were carried out under an inert atmosphere by using Schlenk-type glassware or in a glovebox. UV photolysis experiments were carried out using a Spectral Energy mercury arc lamp (1 kW) with samples contained within quartz Schlenk vessels. Solvents were dried using an MBraun SPS800 prior to use. NMR-solvents were dried over molecular sieves and degassed before use when necessary. Solid starting materials were dried on high vacuum before use when necessary. Unless otherwise noted, all starting materials were commercially available and were used without further purification. The following compounds were synthesized according to literature procedures (for references see ESI‡): $Na[B(3,5\text{-}Cl_2C_6H_3)_4]$, $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, $Na[CpW(CO)_3]$, $Na[CpFe(CO)_2]$ (**1**), $(Ph_2CNBCl_2)_2$ (**2b**), $CpFe(CO)_2BCl_2$ (**3**), ketimino lithium salts **4a/b/c/d**, boryl complexes **5c/d**, **10c/d**, **14c/d** and **15d**, borylene complexes **12c/d**. For the synthesis of **4e** see ESI.‡

The following instruments were used for physical characterization of novel compounds: IR: Nicolet Magna-IR 560; NMR: Bruker AVC500 (^{1}H: 500 MHz; ^{13}C: 125 MHz); Bruker DRX500 (^{11}B: 160 MHz), Varian Unity500 (^{1}H: 500 MHz; ^{13}C: 125 MHz, ^{11}B: 160 MHz), Varian Mercury VX-300 (^{31}P: 122 MHz, ^{19}F: 282 MHz, ^{11}B: 96 MHz). Mass spectra of compounds **12d**, **16** and **17** were recorded on a Bruker Microtof mass-spectrometer. All other mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, Swansea University. For all crystallographic studies, diffraction data were collected at 150 K using an Enraf Nonius Kappa CCD diffractometer or an Oxford Diffraction/Agilent Technologies SuperNova instrument. For complete analytical data (including 2D-NMR data) and for details concerning the determination of the activation energies, see the ESI.‡

Syntheses

$CpW(CO)_3BCl_2$ (6).[23] $Na[CpW(CO)_3]$ (250 mg, 0.702 mmol, 1 equiv.) was suspended in hexanes (20 mL) and boron trichloride (0.70 mL of a 1 M solution in hexanes, 0.702 mmol, 1 equiv.) was added at −78 °C. The mixture was stirred at −78 °C for 30 min, warmed to room temperature and stirred for another 4 h. The mixture was filtered and the filtrate cooled to −30 °C. After storage for 24 h, the supernatant was removed by filtration to give to product as a white powder (35 mg, 0.084 mmol, 12%). Storage of the mother liquor at −30 °C for another 24 h gave crystals suitable for X-ray crystallography. ^{1}H NMR (300 MHz, [D$_8$]toluene, 248 K): $\delta = 4.38$ (s, 5 H, Cp); ^{13}C NMR (75 MHz, [D$_8$]toluene, 248 K): $\delta = 218.1$ (CO), 215.7 (CO), 94.1 (Cp); ^{11}B NMR (96 MHz, [D$_8$]toluene, 248 K): $\delta = 91$ ($\nu_{1/2} = 940$ Hz); Crystallographic data: $C_8H_5BCl_2O_3W$, M_r 414.69, monoclinic, $P2_1/n$, $a = 7.8866(4)$, $b = 11.0772(5)$, $c = 12.3944(6)$ Å, $\beta = 97.450(2)°$, $V = 1073.65(9)$ Å^3, $Z = 4$ $\rho_c = 2.565$ Mg m^{-3}, $T = 150$ K, $\lambda = 0.71073$ Å. 11 681 reflections collected, 2427 independent [R(int) = 0.0069], which were used in all calculations. $R_1 = 0.0578$, w$R_2 = 0.1389$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0834$, w$R_2 = 0.1558$ for all unique reflections. Max. and min. residual electron densities 3.87 and −4.01 e Å^{-3}. CSD reference: 1037787.

$CpFe(PPh_3)(CO)\{B(Cl)NCMes_2\}$ (11d). **5d** (250 mg, 0.512 mmol, 1 equiv.) and triphenylphosphine (148 mg, 0.564 mmol, 1.1 equiv.) were dissolved in toluene (20 mL) in a quartz Schlenk tube. The mixture was irradiated (UV-lamp) and the reaction was monitored by ^{1}H NMR. After complete consumption of the starting material (*ca.* 4 h), the mixture was filtered and the solvent was removed. The residue was dried *in vacuo* overnight (thorough drying important!) and then suspended in pentane (20 mL). The mixture was stirred vigorously for 30 min, the resulting solid isolated by filtration, washed with pentane (2 × 20 mL) and dried *in vacuo*. The product **11d** was isolated as a beige solid (160 mg, 0.222 mmol, 43.3%). ^{1}H NMR (500 MHz, [D$_6$]benzene, 298 K): $\delta = 7.56$ (m, 6 H, *o*-Ph), 6.99 (m, 3 H, *p*-Ph), 6.90 (m, 6 H, *m*-Ph), 6.70 (s, 2 H, *m*-Mes^A), 6.66 (s, 2 H, *m*-Mes^B), 4.42 (d, ^3J(P,H) = 1.0 Hz, 5 H, Cp), 2.40 (s, 6 H, *o*-CH$_3^A$), 2.27 (s, 6 H, *o*-CH$_3^B$), 2.12 (s, 3 H, *p*-CH$_3^B$), 2.11 (s, 3 H, *p*-CH$_3^A$); ^{13}C NMR (126 MHz, [D$_6$]benzene, 298 K): $\delta = 221.8$ (d, ^2J(P,C) = 29.7 Hz, CO), 150.1 (CN), 138.3 (d, ^1J(P,C) = 41.9 Hz, i-Ph), 137.9 (*o*-Mes^B), 137.8 (*p*-Mes^A), 137.7 (i-Mes^B), 137.6 (i-Mes^A), 137.4 (*p*-Mes^B), 136.6 (*o*-Mes^A), 133.6 (d, ^2J(P,C) = 9.9 Hz, *o*-Ph), 130.2, 130.1 (*m*-Mes$^{A/B}$), 129.4 (d, ^4J(P,C) = 1.8 Hz, *p*-Ph), 127.8 (*m*-Ph), 84.5 (Cp), 21.9 (*o*-CH$_3^B$), 21.6 (*o*-CH$_3^A$), 20.92, 20.89 (*p*-CH$_3^{A/B}$); ^{11}B NMR (160 MHz, [D$_6$]benzene, 298 K): $\delta = 51$ ($\nu_{1/2} = 1150$ Hz);.^{31}P NMR (122 MHz, [D$_6$]benzene, 298 K): $\delta = 78.8$; IR (KBr): ν bar = 3059 (w), 2976 (w), 2923 (w), 2857 (w), 1909 (s, CO), 1769 (m), 1747 (m), 1609 (w), 1479 (w), 1438 (m), 1261 (w), 1161 (w), 1092 (w), 1073 (w), 1029 (w), 877 (w), 851 (m), 824 (w) cm^{-1}; HR-MS (EI): *m*/*z*: 692.2216, calcd for $(C_{42}\ H_{42}\ {}^{10}B\ Cl\ Fe\ N\ P)^+$ = 692.2217 [(M − CO)$^+$]; elemental microanalysis: (calcd for $C_{43}H_{42}BClFeNOP$) C 71.53, H 5.86, N 1.94; (measd) C 71.16, H 5.66, N 2.10.

$[CpFe(PPh_3)(CO)(BNCMes_2)]^+[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ (13d). **11d** (30.0 mg, 0.0416 mmol, 1 equiv.) and $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (36.9 mg, 0.0416 mmol, 1 equiv.) were dissolved in fluorobenzene (2 mL) and the mixture was stirred for five min. The solution was filtered (glovebox) and the solvent was removed to give the product as a dark-red solid (49.4 mg, 0.0319 mmol, 76.6%). ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 298 K): δ = 7.74 (bs, 8 H, *o*-Ar^F), 7.56 (s, 4 H, *p*-Ar^F), 7.43 (m, 3 H, *p*-Ph), 7.29 (m, 6 H, *m*-Ph), 7.26 (m, 6 H, *o*-Ph), 6.96 (s, 4 H, *m*-Mes), 4.95 (s, 5 H, Cp), 2.34 (s, 6 H, *p*-CH$_3$), 2.03 (s, 12 H, *o*-CH$_3$); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 298 K): $\delta = 213.4$ (d, ^2J(P,C) = 25.8 Hz, CO), 188.3 (CN), 162.1 (q, ^1J(B,C) = 50.0 Hz, i-Ar^F), 144.1 (*p*-Mes), 139.5 (i-Mes), 138.8 (*o*-Mes), 135.2 (b, *o*-Ar^F), 134.4 (d, ^1J(P,C) = 50.6 Hz, i-Ph), 132.8 (d, ^2J(P,C) = 10.3 Hz, *o*-Ph), 131.7 (d, ^4J(P,C) = 2.4 Hz, *p*-Ph), 131.4 (*m*-Mes), 129.3 (d, ^3J(P,C) = 10.7 Hz, *m*-Ph), 129.2 (qq, ^2J(F,C) = 31.5 Hz, ^3J(B,C) = 2.9 Hz, *m*-Ar^F), 124.9 (q, ^1J(F,C) = 272.6 Hz, CF$_3$), 117.8 (sept, ^3J(F,C) = 3.8 Hz, *p*-Ar^F), 86.0 (Cp), 21.6 (*o*-CH$_3$), 21.5 (*p*-CH$_3$); ^{11}B NMR (96 MHz, [D$_2$]dichloromethane, 298 K): $\delta = 85$ ($\nu_{1/2} = 820$ Hz), −6 ($\nu_{1/2} = 6$ Hz); ^{19}F NMR (282 MHz, [D$_2$]dichloromethane, 298 K): −62.8; ^{31}P NMR (122 MHz, [D$_2$]dichloromethane, 298 K): $\delta = 69.3$ (b, ($\nu_{1/2} = 10$ Hz); IR (KBr): ν bar = 2963 (w), 1984 (s, CO), 1779 (m), 1608 (s), 1482 (w), 1435 (m), 1355 (s), 1275 (s), 1141 (m), 1017 (w), 889 (w), 855 (s), 839 (m), 803 (m), 745 (m), 713 (m) cm^{-1}. Attempts to obtain reproducible microanalytical data for **11d** were frustrated by its ready decomposition in solution during recrystallization.

[CpFe(PCy$_3$)(CO)(CN^{i}Pr)]$^+$[B(3,5-Cl$_2$-C$_6$H$_3$)$_4$]$^-$ (16). **10d** (126 mg, 0.170 mmol, 1 equiv.) and Na[B(3,5-Cl$_2$C$_6$H$_3$)$_4$] (105 mg, 0.170 mmol, 1 equiv.) were dissolved in fluorobenzene (5 mL). The mixture was stirred for five minutes and diisopropylcarbodiimide (26.5 µl, 21.5 mg, 0.170 mmol, 1 equiv.) was added. The mixture was stirred overnight, filtered into a layering Schlenk and layered with hexanes. After 7 d, the supernatant was removed and the product was isolated as yellow crystals suitable for X-ray crystallography (55.0 mg, 0.0503 mmol, 29.6%). ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 298 K): δ = 7.03 (m, 8 H, o-Ar^{Cl}), 7.00 (m, 4 H, p-Ar^{Cl}), 4.92 (d, ^3J(P,H) = 0.7 Hz, 5 H, Cp), 4.08 (sept, ^3J(H,H) = 6.6 Hz, 1 H, CH), 1.95 (m, 3 H, H-1), 1.89 (m, 12 H, H-2$^{A/B}$, H-3$^{A/B}$), 1.79 (m, 3 H, H-4), 1.39 (d, ^3J(H,H) = 6.6 Hz, 6 H, CH$_3$, CH$_3$′), 1.34 (m, 6 H, H-3$^{A\prime/B\prime}$), 1.29 (m, 9 H, H-2$^{A\prime/B\prime}$, H-4′); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 298 K): δ = 215.7 (d, ^2J(P,C) = 24.7 Hz, CO), 165.0 (q, ^1J(B,C) = 49.4 Hz, i-Ar^{Cl}), 153.6 (b, CN), 133.4 (m-Ar^{Cl}), 133.2 (q, ^2J(B,C) = 4.2 Hz, o-Ar^{Cl}), 123.4 (p-Ar^{Cl}), 84.2 (Cp), 51.3 (CH), 38.7 (d, ^1J(P,C) = 20.3 Hz, C-1), 30.8 (d, ^3J(P,C) = 1.2 Hz, C-3$^{A/B}$), 30.7 (d, ^3J(P,C) = 3.2 Hz, C-3$^{A/B}$), 27.9 (d, ^2J(P,C) = 10.8 Hz, C-2$^{A/B}$), 27.8 (d, ^2J(P,C) = 9.9 Hz, C-2$^{A/B}$), 26.4 (C-4), 23.29, 23.27 (CH$_3$, CH$_3$′); ^{11}B NMR (96 MHz, [D$_2$]dichloromethane, 298 K): δ = −7 ($\nu_{1/2}$ = 21 Hz); ^{31}P NMR (122 MHz, [D$_2$]dichloromethane, 298 K): δ = 76.4; IR (KBr): ν bar = 2961 (m), 2935 (m), 2854 (m), 2164 (s, CN), 1991 (s, CO), 1566 (m), 1544 (s), 1446 (m), 1421 (m), 1390 (m), 1369 (m), 1262 (s), 1139 (m), 846 (m), 800 (s), 783 (s), 710 (m), 703 (m) cm^{-1}; HR-MS (EI): m/z: 498.2545, calcd for (C$_{24}$ H$_{45}$ Fe N O P)$^+$ = 498.2583 [(M-B(C$_6$H$_3$Cl$_2$)$_4$)$^+$]; elemental microanalysis: (calcd for C$_{52}$H$_{57}$BCl$_8$FeNOP) C 57.12, H 5.25, N 1.28; (measd) C 56.88, H 4.99, N 1.30.

Crystallographic data. C$_{52}$H$_{57}$BCl$_8$FeNOP, M_r 1093.28, monoclinic, $P2_1/n$, a = 13.0423(1), b = 24.8523(2), c = 17.0945(1) Å, β = 108.2053(4)°, V = 5263.50(7) Å^3, Z = 4 ρ_c = 1.380 Mg m^{-3}, T = 150 K, λ = 0.71073 Å. 23 500 reflections collected, 11 969 independent [R(int) = 0.000], which were used in all calculations. R_1 = 0.0384, wR_2 = 0.0905 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0590, wR_2 = 0.0982 for all unique reflections. Max. and min. residual electron densities 0.97 and −0.65 e Å^{-3}. CSD reference: 1037786.

[CpFe(PCy$_3$)(CO)(CNCy)]$^+$[B(3,5-Cl$_2$-C$_6$H$_3$)$_4$]$^-$ (17). **12d** (20.0 mg, 0.0154 mmol, 1 equiv.) and dicyclohexylcarbodiimide (7.0 mg, 0.0339 mmol, 2.2 equiv.) were dissolved in [D$_2$]dichloromethane in an NMR tube at −78 °C. The NMR tube was warmed to room temperature and allowed to stand for 4 h. The mixture, containing complex **17** and adduct **21** (resonances not listed), was analyzed by NMR spectroscopy and mass spectrometry. ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 293 K): δ = 7.04 (m, 8 H, o-Ar^{Cl}), 7.01 (m, 4 H, p-Ar^{Cl}), 4.92 (d, ^3J(P,H) = 0.9 Hz, 5 H, Cp), 3.85 (m, 1 H, Cy-1), 1.96, 1.69, 1.57, 1.36 (each m, 10 H, Cy-2, Cy-3, Cy-4), 1.94 (m, 3 H, H-1), 1.88 (m, 12 H, H-2$^{A/B}$, H-3$^{A/B}$), 1.74 (m, 3 H, H-4), 1.32 (m, 6 H, H-3$^{A\prime/B\prime}$), 1.27 (m, 9 H, H-2$^{A\prime/B\prime}$, H-4′); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 293 K): δ = 215.8 (d, ^2J(P,C) = 25.7 Hz, CO), 165.0 (q, ^1J(B,C) = 49.1 Hz, i-Ar^{Cl}), 153.8 (CN), 133.5 (m-Ar^{Cl}), 133.3 (q, ^2J(B,C) = 4.2 Hz, o-Ar^{Cl}), 123.4 (p-Ar^{Cl}), 84.3 (Cp), 57.3 (Cy-1), 38.8 (d, ^1J(P,C) = 19.8 Hz, C-1), 30.9 (C-3$^{A/B}$), 30.7 (d, ^3J(P,C) = 2.3 Hz, C-3$^{A/B}$), 28.0 (d, ^2J(P,C) = 10.8 Hz, C-2$^{A/B}$), 27.9 (d, ^2J(P,C) = 9.8 Hz, C–2$^{A/B}$), 26.4 (C-4); ^{11}B NMR (96 MHz, [D$_2$]dichloromethane, 293 K): δ = −7 ($\nu_{1/2}$ = 16 Hz); ^{31}P NMR (122 MHz, [D$_2$]dichloromethane, 293 K): δ = 76.5; HR-MS (EI): m/z: 538.2876, calcd for (C$_{31}$ H$_{49}$ Fe N O P)$^+$ = 538.2896 [(M-B(C$_6$H$_3$Cl$_2$)$_4$)$^+$].

Intermediate 18. **12d** (41.7 mg, 0.0321 mmol, 1 equiv.) was dissolved in [D$_2$]dichloromethane in an NMR tube and the solution was cooled to −78 °C. Diisopropylcarbodiimide (5.0 µl, 4.05 mg, 0.0321 mmol, 1 equiv.) was added and the NMR tube transferred to the precooled NMR spectrometer. NMR spectra for intermediate **18** were measured at 263 K. ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 263 K): δ = 7.03 (m, 8 H, o-Ar^{Cl}), 7.00 (m, 4 H, p-Ar^{Cl}), 6.99 (bs, 2 H, m-Mes^A), 6.93 (bs, 2 H, m-Mes^B), 4.70 (s, 5 H, Cp), 3.73 (sept, ^3J(H,H) = 6.6 Hz, 1 H, CH(I)), 3.01 (sept, ^3J(H,H) = 6.8 Hz, 1 H, CH(II)), 2.30 (s, 3 H, p-CH$_3$^{A}), 2.25 (s, 3 H, p-CH$_3$^{B}), 2.11 (bs, 6 H, o-CH$_3$^{A}), 2.05 (bs, 6 H, o-CH$_3$^{B}), 1.82 (m, 9 H, H-1, H-3$^{A/B}$), 1.79 (m, 6 H, H-2$^{A/B}$), 1.71 (m, 3 H, H-4), 1.35 (d, ^3J(H,H) = 6.6 Hz, 3 H, CH$_3$(I)), 1.32 (m, 6 H, H-3$^{A\prime/B\prime}$), 1.31 (d, ^3J(H,H) = 6.6 Hz, 3 H, CH$_3$(I)′), 1.18 (m, 6 H, H-2$^{A\prime/B\prime}$), 1.17 (m, 3 H, H-4′), 1.13 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH$_3$(II)), 0.52 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH$_3$(II)′); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 263 K): δ = 220.9 (d, ^2J(P,C) = 27.5 Hz, CO), 180.9 (CN), 168.8 (NCN), 164.7 (q, ^1J(B,C) = 49.5 Hz, i-Ar^{Cl}), 143.6 (p-Mes^A), 143.2 (p-Mes^B), 138.8 (o-Mes^A), 137.0 (o-Mes^B), 136.0 (i-Mes^B), 135.0 (i-Mes^A), 133.1 (m-Ar^{Cl}), 133.0 (q, ^2J(B,C) = 4.0 Hz, o-Ar^{Cl}), 131.4 (m-Mes^A), 130.9 (m-Mes^B), 123.1 (p-Ar^{Cl}), 81.2 (Cp), 46.7 (CH(I)), 46.0 (CH(II)), 39.5 (d, ^1J(P,C) = 19.6 Hz, C-1), 29.9 (2 × C-3$^{A/B}$), 27.9 (d, ^2J(P,C) = 10.8 Hz, C-2$^{A/B}$), 27.6 (d, ^2J(P,C) = 8.6 Hz, C-2$^{A/B}$), 26.2 (C-4), 23.8 (CH$_3$(I)′), 22.5 (CH$_3$(II)), 21.8 (o-CH$_3$^{A}, CH$_3$(I)), 21.7 (o-CH$_3$^{B}), 21.3 (CH$_3$(II)′), 21.2 (p-CH$_3$^{A}), 21.1 (p-CH$_3$^{B}); ^{11}B NMR (160 MHz, [D$_2$]dichloromethane, 263 K): δ = 91 ($\nu_{1/2}$ = 1470 Hz), −7 ($\nu_{1/2}$ = 11 Hz); ^{31}P NMR (122 MHz, [D$_2$]dichloromethane, 263 K): δ = 80.8 ($\nu_{1/2}$ = 5 Hz).

Intermediate 19. **12d** (20.0 mg, 0.0154 mmol, 1 equiv.), was dissolved in [D$_2$]dichloromethane in an NMR tube and the solution cooled to −78 °C. Dicyclohexylcarbodiimide (3.5 mg, 0.0170 mmol, 1.1 equiv.) was added and the NMR tube transferred to the precooled NMR spectrometer. The NMR-spectra for intermediate **19** were measured at 263 K. ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 263 K): δ = 7.03 (m, 8 H, o-Ar^{Cl}), 7.00 (m, 4 H, p-Ar^{Cl}), 6.99 (bs, 2 H, m-Mes^A), 6.93 (bs, 2 H, m-Mes^B), 4.68 (s, 5 H, Cp), 3.24 (m, 1 H, Cy(I)-1), 2.54 (m, 1 H, Cy(II)-1), 2.31 (s, 3 H, p-CH$_3$^{A}), 2.25 (s, 3 H, p-CH$_3$^{B}), 2.10 (bs, 6 H, o-CH$_3$^{A}), 2.06 (bs, 6 H, o-CH$_3$^{B}), 1.90 (m, 1 H, Cy(I)-2^B), 1.86 (m, 6 H, H-3$^{A/B}$), 1.85 (m, 1 H, Cy(II)-2^A), 1.84 (m, 4 H, Cy(I)-2^A, H-1), 1.83 (m, 6 H, H-2$^{A/B}$), 1.82 (m, 2 H, 2 × Cy-3^A), 1.72 (m, 3 H, H-4), 1.71 (m, 1 H, Cy(I)-2$^{B\prime}$), 1.60 (m, 1 H, Cy(I)-2$^{A\prime}$), 1.58 (m, 1 H, Cy-4), 1.55 (m, 1 H, Cy(II)-2^B), 1.49 (m, 1 H, Cy-4), 1.46 (m, 1 H, Cy-3^B), 1.43 (m, 1 H, Cy-3^B), 1.34 (m, 6 H, H-3$^{A\prime/B\prime}$), 1.31 (m, 1 H, Cy(II)-2$^{A\prime}$), 1.23 (m, 8 H, 2 × Cy-3$^{A\prime}$, H-2$^{A\prime/B\prime}$), 1.22 (m, 3 H, H-4′), 1.04 (m, 1 H, Cy-4′), 0.95 (m, 1 H, Cy-3$^{B\prime}$), 0.94 (m, 1 H, Cy-3$^{B\prime}$), 0.70 (m, 1 H, Cy-4′), 0.12 (m, 1 H, Cy(II)-2$^{B\prime}$); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 263 K):

δ = 221.0 (d, ^2J(P,C) = 27.6 Hz, CO), 180.8 (CN), 168.3 (NCN), 164.7 (q, ^1J(B,C) = 49.2 Hz, i-Ar^{Cl}), 143.6 (*p*-Mes^A), 143.1 (*p*-Mes^B), 138.8 (*o*-Mes^A), 136.8 (*o*-Mes^B), 136.0 (*i*-Mes^B), 135.0 (i-Mes^A), 133.2 (*m*-Ar^{Cl}), 133.0 (q, ^2J(B,C) = 4.2 Hz, *o*-Ar^{Cl}), 131.5 (*m*-Mes^A), 131.1 (*m*-Mes^B), 123.1 (*p*-Ar^{Cl}), 81.2 (Cp), 55.5 (Cy(I)-1), 53.5 (Cy(II)-1), 39.7 (d, ^1J(P,C) = 17.0 Hz, C-1), 34.5 (Cy(I)-2^A), 32.7 (Cy(II)-2^A), 32.5 (Cy(I)-2^B), 31.6 (Cy(II)-2^B), 30.0 (2 × C-3$^{A/B}$), 28.0 (d, ^2J(P,C) = 10.9 Hz, C-2$^{A/B}$), 27.7 (d, ^2J(P,C) = 8.8 Hz, C-2$^{A/B}$), 26.62 (Cy-3^A), 26.57 (Cy-3^A), 26.3 (Cy-3^B), 26.2 (C-4), 26.0 (Cy-4), 25.0 (Cy-4), 24.4 (Cy-3^B), 22.2 (*o*-CH$_3$^{B}), 22.0 (*o*-CH$_3$^{A}), 21.3 (*p*-CH$_3$^{A}), 21.0 (*p*-CH$_3$^{B}); ^{11}B NMR (160 MHz, [D$_2$]dichloromethane, 263 K): δ = 91 ($\nu_{1/2}$ = 1430 Hz), −7 ($\nu_{1/2}$ = 17 Hz); ^{31}P NMR (122 MHz, [D$_2$]dichloromethane, 263 K): δ = 80.4 ($\nu_{1/2}$ = 4 Hz).

Boron-containing product 20. 12d (10 mg, 0.0077 mmol, 1 equiv.) was dissolved in [D$_2$]dichloromethane in an NMR tube and the solution was cooled to −78 °C. Diisopropylcarbodiimide (5.0 µl, 4.05 mg, 0.0321 mmol, 4.2 equiv.) was added and the NMR-tube was transferred to a precooled NMR spectrometer. After full conversion (*ca.* 3 h at room temperature), the mixture was analyzed by NMR spectroscopy in order to identify the boron-containing product. The spectra showed the presence of complex **16** (resonances not listed) and one other species, which was tentatively assigned as compound **20**. ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 298 K): δ = 6.84 (s, 4 H, *m*-Mes), 3.90 (sept, ^3J(H,H) = 6.2 Hz, CH(I)), 3.61 (sept, ^3J(H,H) = 6.6 Hz, CH(III)), 3.39 (sept, ^3J(H,H) = 6.4 Hz, CH(II)), 2.27 (s, 6 H, *p*-CH$_3$), 2.15 (s, 12 H, *o*-CH$_3$), 1.10 (d, 6 H, ^3J(H,H) = 6.2 Hz, CH$_3$(I)), 0.93 (d, 6 H, ^3J(H,H) = 6.6 Hz, CH$_3$(III)), 0.82 (d, 6 H, ^3J(H,H) = 6.4 Hz, CH$_3$(II)); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 298 K): δ = 171.8 (BN=C), 152.4 (N=C(NR$_2$)), 139.4 (*p-Mes*), 139.1 (i-*Mes*), 136.4 (*o*-Mes), 130.1 (*m*-Mes), 46.3 (CH-(III)), 46.2 (CH(I)), 42.9 (CH(II)), 25.5 (CH$_3$(I)), 23.2 (CH$_3$(III)), 22.3 (CH$_3$(II)), 21.5 (*o*-CH$_3$), 21.0 (*p*-CH$_3$); ^{11}B NMR (96 MHz, [D$_2$]dichloromethane, 298 K): δ = 29 ($\nu_{1/2}$ = 390 Hz).

Boron-containing product 21. 12d (20.0 mg (0.0154 mmol, 1 equiv.) was dissolved in [D$_2$]dichloromethane in an NMR tube and the solution was cooled to −78 °C. Dicyclohexylcarbodiimide (7.0 mg, 0.0339 mmol, 2.2 equiv.) was added and the NMR tube was transferred to a precooled NMR spectrometer. After full conversion (*ca.* 3 h at room temperature), the mixture was analyzed by NMR spectroscopy in order to identify the boron-containing product. The spectra showed the presence of complex **17** (resonances not listed) and one other species, which was tentatively assigned as compound **21**.

^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 293 K): δ = 6.85 (s, 4 H, *m*-Mes), 3.45 (m, Cy(III)-1), 3.04 (m, Cy(I)-1), 2.96 (m, Cy(II)-1), 2.24 (s, 6 H, *p*-CH$_3$), 2.13 (s, 12 H, *o*-CH$_3$), 1.75, 1.53, 1.42, 1.07, 0.80 (each m, 10 H, Cy(I)-2, Cy(I)-3, Cy(I)-4), 1.65, 1.49, 1.41, 1.08, 0.77 (each m, 10 H, Cy(II)-2, Cy(II)-3, Cy(II)-4), 1.70, 1.58, 1.27, 1.18 (Cy(III)-2, Cy(III)-3 Cy(III)-4); ^{13}C NMR (126 MHz, [D$_2$]dichloromethane, 293 K): δ = 172.1 (BN=C), 155.9 (N=C(NR$_2$)), 139.7 (i-Mes), 139.1 (*p*-Mes), 136.6 (*o*-Mes), 130.2 (*m*-Mes), 54.7 (Cy(III)-1), 54.6 (Cy(I)-1), 50.8 (Cy(II)-1), 21.6 (*o*-CH$_3$), 21.0 (*p*-CH$_3$); ^{11}B NMR (96 MHz, [D$_2$]dichloromethane, 293 K): δ = 30 ($\nu_{1/2}$ = 350 Hz).

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