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

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Dedicated to the memory of Professor Ken Wade FRS

The synthetic and reaction chemistries of cationic iminoborylene complexes [LmM=B=N=CR3]+, which feature a unique heterocumulene structure, have been systematically investigated. Precursors of the type CpFe(CO)2B(Ph)NCAR2 (Ar = p-Tol/Mes, 5c/d) have been generated by B-centred substitution chemistry using CpFe(CO)2BCl2 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 PCy3 or PPh3), followed by halide abstraction allows for the generation of the cationic iminoborylenes [CpFe(PR3)(CO)(BCNAR2)]+[BArF4]− (R = Cy, Ar = p-Tol/Mes, 12e/d; R = Ph, Ar = Mes, 13d; ArX = 3,5-X2C6H3 where X = Cl, F) 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(PCy3)(CO)(CNR)]+[BArF4]− (R = ‘Pr/Cy, 16/17).

Introduction

The investigation of boron-transition metal complexes has attracted widespread attention in recent years. A number of novel classes of compound 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, LmM(BX), featuring a disubstituted 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, (LmM)(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 (LmMBF) and aminoborylene (LmMBNR) species have been been synthesized, representing isonuclear analogues of classical carbonyl (LmMCO)6 and vinylidene (LmMCCO) 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 activation9 or cycloaddition reactions.9a,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 CR2, Scheme 1).11 Taking this idea further, we have recently communicated12 the first examples of cationic iminoborylene complexes [LmM=B=N=CR3]+ 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

![Scheme 1](image_url)

Scheme 1: Highly unsaturated metal-boron complexes featuring iminoboryl, oxoboryl, alkylidenoboryl (top) and iminoborylene ligands (bottom, also showing the isonodal relationship with allenylidenes).
Herein, we now report in full on synthetic approaches towards iminoborylene systems, and their reaction chemistry 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 borylenes complexes has been achieved using a variety of different approaches, including double salt elimination,\textsuperscript{4,5}C metal-to-metal borylene transfer,\textsuperscript{15} and dehydrogenation of σ-borane complexes.\textsuperscript{16} Moreover, halide abstraction from haloboryl complexes has been shown to give access to cationic borylenes in a reliable fashion.\textsuperscript{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).

\[ \text{Scheme 2: Target synthesis of iminoborylene complexes by halide abstraction from halo(imino)boryl complexes} \]

Synthesis of iminoborylene 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)\textsubscript{2}] unit as the metal fragment, given its successful use for the generation of related cationic aminoborylenes.\textsuperscript{7,8} 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 functionalization (Scheme 3).

Mirroring existing synthetic routes to [CpFe(CO)\textsubscript{2}] boryl complexes,\textsuperscript{18} we initially attempted the generation of complexes of type \textbf{5} by reaction of the anionic [CpFe(CO)\textsubscript{2}] reagent \textbf{1} (as the sodium salt) with the corresponding dichloro-(imino)boryl \textbf{2}, thus establishing the B-N connectivity prior to the formation of the Fe-B bond (Scheme 3, upper). While Cl\textsubscript{2}B(N=CPh\textsubscript{2}), \textbf{2a}, was readily synthesized according to Wade’s original procedure,\textsuperscript{18} it showed no reactivity towards ferrate \textbf{1}. Assuming that the dimeric nature of \textbf{2a} (indicated by its \textsuperscript{11}B NMR shift of \( \delta_B = -7 \) ppm) is responsible for its low reactivity, we attempted to generate monomeric dichloro-(imino)boryl complexes 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\textsubscript{3})], and which prevents isolation of the pure dichloro(ketimino)boryl complexes.\textsuperscript{19} This problem could be circumvented by \textit{in situ} generation (see SI), which generates the corresponding monomeric compounds Cl\textsubscript{2}B(N=CR\textsubscript{3}) (R = Mes/Trip (\textbf{2d/e}), \( \delta_B = 26/27 \) ppm). However, these systems do not show clean reactivity towards \textbf{1}, with the starting borane being the predominant species in the reaction mixtures even under forcing conditions.

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

\[ \text{Scheme 3: Synthesis of iminoboryl complexes \textbf{5} via dichloro-iminoboranes (top) or dichloroboryl iron precursors (bottom)} \]

Complexes \textbf{5c/d} have been characterized spectroscopically, showing the expected NMR resonances for the [CpFe(CO)\textsubscript{2}] fragment (Cp: \( \delta_H = 4.26/4.30 \) ppm, \( \delta_C = 84.4/84.6 \) ppm, CO: \( \delta_C = 215.3/215.3 \) ppm) and [B-N=C] fragments (\( \delta_C = 150.7/153.1 \) ppm, \( \delta_B = 50/47 \) ppm). Additionally, in the case of \textbf{5c} structural authentication could be achieved by X-ray crystallography (Figure 2). In the solid state, \textbf{5c} exhibits a near-linear arrangement of the B-C-N unit [\( \angle B(11)-N(13)-(C(14)) = 175.6(3) \) °], 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 \textbf{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 \textbf{6} (\( \delta_B = 91 \) ppm) alongside its bromo analogue \textbf{7} (\( \delta_B = 84 \) ppm) by reaction of the tungstane Na[CpW(CO)\textsubscript{2}] with the respective trihaloboranes.\textsuperscript{23}

Although \textbf{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 \textbf{6} (Figure 1) features a W-B bond [2.22(2) Å] which is considerably longer than in the corresponding CpFe(CO)\textsubscript{2}Cl\textsubscript{2} complex \textbf{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),\textsuperscript{20a,24} while the B-Cl bonds are in the expected range [e.g. 1.78(1) and 1.79(1) Å for \textbf{6}, cf. 1.781(6) and 1.783(4) Å for \textbf{3}].\textsuperscript{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 BCl₂ unit with respect to the Cp(centroid)-Fe-B plane [∠Cp(centroid)-W(1)-B(13)-Cl(14) = 9.5(9)°, cf. ∠Cp(centroid)-Fe-B(1)-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 complexes 6 or 7. As judged by ¹¹B NMR spectroscopy, breakage of the W-B bond and extrusion of the [CpW(CO)₃] unit generates instead the corresponding dihalo(ketimino)boryl complexes 2a/d (∆δ = 21/26 ppm).

**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 iminoborylène complexes.**

With the iminoboryl complexes 5c/d in hand, we next attempted the synthesis of the corresponding borylène complexes by halide abstraction. Reaction of 5d with Na[BAr₄] \[Ar² = 3,5-(CF₃)₂C₆H₃\] leads to the formation of the corresponding cationic borylène [CpFe(OC₂)(BNCMe₃)]⁺, as indicated by a downfield shift in the ¹¹B NMR signal (∆δ = 75 ppm, cf. 47 ppm for 5d). While this borylène 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 borylène 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 bisphosphines (dppe/dmpe for example), failed to yield the desired products,²⁵ reaction of 5c/d with monodentate donors cleanly gave the corresponding mixed phosphine/borylène complexes (Scheme 5).

Assuming that bulky trialkylphosphines would lead to an additional kinetic stabilization of the corresponding borylène complexes, we first used PCy₃ in this substitution chemistry, leading to the formation of the desired complexes 10c/d in moderate yields (48-60%). In order to further investigate the influence of the steric/electronic properties of the phosphine ligands, we also employed PPh₃ in the reaction with 5d, giving the triphenylphosphine-substituted borylène complex 11d (43%).

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

Spectroscopic characterization of 10c/d and 11d clearly signals the successful introduction of the phosphine co-ligands via ³¹P NMR spectroscopy (∆δ = 77.1/75.0/78.8 ppm for 10c/10d/11d), while little change is observed in the respective ¹¹B spectra (∆δ = 47/50/51 ppm). In addition, diastereotopic splitting is observed for the aryl substituents of the axially prochiral ketiminophenylvinyl fragments, brought about by the formation of a chiral metal centre (e.g. p-CH₃ groups in 10c/10d/11c).
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 [v(CO) = 1902/1905/1909 cm\(^{-1}\) for 10c/10d/11d, cf. \(v\)(CO) = 2002, 1922 / 2005, 1937 cm\(^{-1}\) for 5c/5d].

Crystallographically, complexes 10c/d (Figure 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 \(\pi\)-backbonding compared to 5e [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 dicarboxyl-ligated 5c), complex 10c features a non-linear arrangement of the B-N-C unit \([\angle \text{B-N-C} = 144.8(2)^\circ]\), 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 \(\text{dimesityl} \) system 10d features a linear B-N-C arrangement \([\angle \text{B-N-C} = 174.7(2)^\circ]\) and bond lengths consistent with dominant N→B donation \([\text{B-N 1.386(3) Å, Fe-B 2.015(2) Å}].\)

Utilising the monophosphine boryl complexes 10c/d and 11d as precursors, halide abstraction with Na[BAr\(^{3+}\)] (Ar\(^{3+}\) = 3.5-Cl\(_2\)C\(_6\)H\(_4\)) 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 dicarboxyl-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 \((\delta\(_{\text{B}}\) = 82/85/85 ppm for 12c/12d/13d), while the shifts of the \(^{31}\)P resonances are less informative \((\delta\(_{\text{P}}\) = 84.9/75.0/69.3 ppm). In the \(^1\)H 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 BNAr\(_2\) unit (e.g. \(\delta\(_{\text{H}}\) = 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 \([v\text{(BNC) } = 1763/1753/1779 \text{ cm}^{-1}\), but also blue-shifted carboxyl stretching frequencies in comparison with their chloroboryl precursors \([v\text{(CO)}] = 1962/1969/1844 \text{ cm}^{-1}\) for 12c/12d/13c, consistent with weaker Fe→CO \(\pi\)-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)]\(^+\)[BAr\(^{3+}\)] (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 \([\text{CpFe(PCy}_3\text{(CO)](BNCMes}_3\text{)}]^{+}\) cation (SI). Moreover, the solid state structure (Figure 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 \([\angle \text{Fe(1)-B(28)-N(29)} = 170.9(5)^\circ, \angle \text{B(28)-N(36)-C(37)} = 175.3(2)^\circ]\). In the solid state at least, the ketimino-group is orientated near-parallel to the Cp(centroid)-Fe-B plane \([\angle \text{Cp(centroid)-Fe(1)-C(30)-C(40)} = 7.1^\circ]\), 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\(_3\))]).

However, the observed B-N distance is rather short and the N-C distance is long \([\text{B-N 1.314(6) Å, N-C 1.292(6) Å, cf. 1.368(3) Å and 1.263(3) Å for 10d}].\)

Reactivity of the borylene-complexes 12c/d towards anionic nucleophiles

With the crystallographic and spectroscopic analysis of aminoborylene 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\(_3\)]Cl) could be used to generate products of the type \([\text{CpFe(CO)(PCy}_3\text{(Cl)](BNC(Cl)Mes}_3\text{)}]^{+}\), thus allowing a formal α,γ-isomerization of the precursors 10c/d via aminoborylene intermediates (i.e. a formal reversal of the conversion of \([\text{L}_2\text{M=C=C-CR}_2\text{(OH)]}^{+}\) to \([\text{L}_2\text{M=C(OH)C=CR}_2\text{(CH)]}^{+}\) via the corresponding allenylidene\(^{-}\)). However, exclusive α-attack led to the re-formation of the precursors 10c/d. In similar fashion, the reaction of 12c/d with sodium thioepheneolate leads to the products of boron-centred nucleophilic attack, exclusively giving the B(SPh) complexes 14, independent of the sterlic 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[BArF$_4$], 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$^{-1}$).$^{25}$ The reaction of the pure complex 12d with KCN does, however, lead to addition of cyanide to the borylene. Once again, $\alpha$-selectivity is observed, yielding the corresponding cyanosubstituted boryl-complex 15d. Unfortunately, reaction of KCN with the less sterically encumbered borylene 12c gives only decomposition products, so that the influence of the allyl substituents on the regioselectivity could not be fully investigated in this case.

Complexes 14e/d and 15d were fully characterized by spectroscopic, mass spectrometric and, in case of 14d, by crystallographic methods.$^{15}$ The $^{11}$B and $^{31}$P resonances ($\delta_B = 56/52/41$ ppm, $\delta_P = 76.3/74.1/73.3$ ppm for 14e/14d/15d) are similar to those of the corresponding chloroboryl complexes ($\delta_B = 47/50$ ppm, $\delta_P = 77.1/75.0$ ppm for 10c/10d), which together with the C=N ketimino-resonances ($\delta_C = 147.7/149.9/150.5$ ppm) verify the postulated structures resulting from $\alpha$-attack at boron. The observed high $\alpha$-selectivity is presumably brought about by the high electrophility of the boron centre in each case, bearing in mind the fact that $\gamma$-selectivity has been observed in the addition of a variety of nucleophiles (including thiolate and cyanide) to cationic allenylidene complexes.$^{4,29}$

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,$^{11}$ insertion reactions with carbodiimides,$^{32}$ and metathesis-type reactivity with isocyanates and phosphine sulfides.$^{70}$

In order to investigate the reactivity of our iminoborylene complexes towards unsaturated substrates, we used the mesitylsubstituted complex 12d which shows the highest resistance towards undesired hydrolysis and decomposition reactions. Mixing of 12d with non-polar substrates such as 2,3-dimethylbutadiene and trimethylsilylacetylene 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 isopropylisocyanate also did not lead to any conversion (as judged from in situ $^1$H and $^{13}$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 disopropyl- or dicyclohexylcarbodiimide (RN=C=NR, R = 'Pr/Cy) gives clean conversion within hours at room temperature, to a single $^{31}$P containing species ($\delta_P = 76.4/76.5$ ppm, respectively) and a compound giving rise to a $^{11}$B signal at $\delta_B = 29/30$ 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. [CpFe(CO)$_2$(C(NC)$_2$BNCy)$_2$]$^+$, $\delta_C = 251.5$ ppm or [CpFe(CO)$_2$(C(NC)$_2$B(NCy)$_2$C(NC)$_2$]$^+$, $\delta_C = 224.0$ ppm)$^{12b}$, we observe the corresponding quaternary carbon resonance at $\delta_C = 153.6/153.8$ ppm (for R = 'Pr/Cy). This observation suggests the formation of the isonitrile complexes [CpFe(CO)(PCy$_3$)(NCR)]$^+${BArF$_4$} (16/17, R = 'Pr/Cy, Scheme 7), which could also be detected by positive-ion ESI MS (SI).

![Scheme 7: Reaction of iminoborylene complex 12d with carbodiimides to give isonitrile complexes 16/17](image)

Figure 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).

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 (Figure 3). In the solid state, complex 16 shows a piano-stool geometry, with the isonitrile unit featuring a linear geometry ([16c(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 ($\delta_H = 4.92/4.92$ ppm, $\delta_C = 84.2/84.3$ ppm for 16/17 and C=N-CHR$_2$ units (CH: $\delta_H = 4.08/3.85$ ppm, $\delta_C = 51.3/57.3$ 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 [B=N=CMes$_2$] heterocumulene fragment.
Upon mixing of the 12d with the respective carbodiimide RN=NC=NR at \(-60^\circ C\) in CD_{2}Cl_{2}, we observe the immediate formation of an intermediate (18/19 for \(R = Pr/Cy\)), which is stable at temperatures below \(0^\circ C\). 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 ketimine aryl substituents (e.g. mesityl p-CH_{3}) in 18/19: \(\delta_H = 2.30, 2.25 / 2.31, 2.25 \text{ ppm}\), as is also seen for the boryl precursor 10d. In addition, we also observe two sets of resonances for the carbodiimide Pr/Cy substituents (e.g. for the N-CHR groups in 18/19: \(\delta_H = 3.73, 3.01 / 3.24, 2.54 \text{ ppm}\), consistent with desymmetrization of the RCCN 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, or with the formation of a [2+2]-cycloaddition product, 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 (\(\delta_B = 91/91 \text{ ppm, } \delta_P = 80/80.4 \text{ ppm for 18/19, cf. } \delta_B = 85 \text{ ppm, } \delta_P = 75.0 \text{ ppm for 12d}\)). 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 [CpFe(CO)]_{2}(BNR_{3})\(^{+}\) (\(\delta_B = 94 \text{ ppm}\)) with carbodiimides or imines (adducts: \(\delta_B = 71/54 \text{ ppm}\)) and the [2+2] cycloaddition product of CpMn(CO)\(_{2}\)(B'Pr) \(\delta_B = 144 \text{ ppm}\) with carbodiimide (\(\delta_B = 62 \text{ ppm}\)) show upfield shifts in the \(^{11}B\) signal, consistent with an increased coordination number at boron.

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 aminoborylene complexes (e.g. \(\delta_B = 25 \text{ ppm for } [\text{CpFe(CO)}_{2}(\text{C(NC})_{2}\text{BNCy}_{2})]^{+}\))

In the \(^{13}C\) spectra the downfield shifts observed for the carbodiimide quaternary carbons (\(\delta_C = 168.8/168.3 \text{ ppm for 18/19, cf. } \delta_C = 140.2/139.9 \text{ ppm for free RN=NC=NR with } R = Pr/Cy\))\(^{32a/b,32c}\) are consistent with the formation of a direct metal-carbon interaction [cf. \(\delta_C = 151.0, 162.0 \text{ for CpMn(CO)}_{2}(\text{C}^\beta-\text{B'(Pr)}\text{N(Cy)}\text{CNCy}) \text{ and with } \text{CpMn(CO)}_{2}(\text{C}^\beta-\text{B'(Pr)}\text{OCPH}_{2})\), respectively], although not with complete insertion into the Fe=B bond (cf. \(\delta_C = 251.0 \text{ ppm for } [\text{CpFe(CO)}_{2}(\text{C(NC})_{2}\text{BNCy}_{2})]^{+}\), which features partial Fe=C carbonyl character). Moreover, the observation of resonances at \(\delta_C \approx 180 \text{ ppm for the } \gamma\text{- carbons of the FeBNC units (along with the downfield }^{11}B \text{ shifts for 18/19), suggests retention of a substantial degree of delocalization along the hetero-cumulene framework. With this in mind, we 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=\rightarrow 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'Pr)\(^{30a}\), 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 \(T = 25^\circ C\)) 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 \(^11B\) resonances (\(\delta_B = 29/30 \text{ ppm for } R = Pr/Cy\)) indicate a three-coordinate boron centre without any metal-boron interaction, while the \(^1H\) NMR spectra show the presence of three inequivalent Pr or Cy-groups [e.g. C/H/R units: \(\delta_H = 3.90/3.39/3.61 \text{ for } Pr=Pr/II/III\), 3.04/2.96/3.45 for Cy=I/II/III, (for numbering see Scheme 8)]. The \(^13C\)-NMR and GHSQC data indicate that all three alkylamino-sustituents are bound to a central quaternary carbon (\(\delta_C = 152.4/155.9 \text{ ppm}\)), 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 extra carbodiimide, \(R^{11}=C=NR^{II}\)\(^{32a}\), coordinate trapping of the initial metathesis product \([R^{11}=BN=NC=CMes]_{2}\) leads to the formation of a trialkyl-guanidine, which is bound to the \(B=NC=Me\) heterocumulene fragment. The resulting triaminoboranes of the type RN=C(NR)\(_{2}\)BNCMe\(_{2}\)\(^{32c}\) resemble the metalla-amidinates \([\text{CpFe(CO)}_{2}(\text{C(NC})_{2}\text{BNCy}_{2})]^{+}\) formed by mono-carbodiimide insertion in the case of aminoborylene systems.

Conclusions

Our investigation of the possible synthetic routes to aminoborylene complexes (12/13) has given insight into the
scope of metal-fragments, ketiminato 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(NO)₂[B(Cl)NCr₂] (Ar = p-Tol/Mes, 5c/d). The use of reagents with increased steric bulk on either the metal [CpW(CO)₅ vs. CpFe(CO)₅] 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 phospine drastically increases complex stability, leading to the isolation of the cationic heteroallenylenes [CpFe(PR₃)(CO)(BNCAr)]⁺ 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 heteroallenenes (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

(a) 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 SI): Na[B(3,5-Cl₂C₆H₄)]₂, Na[B(3,5-(CF₃)C₆H₄)]₂, Na[CpW(CO)₅], Na[CpFe(CO)₅] (1), Ph₂CNBCl₂ (2h), CpFe(NO)₂BCl₃ (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 SI.

The following instruments were used for physical characterization of novel compounds: IR: Nicolet Magna-IR 560; NMR: Bruker AHC500 (1H: 500 MHz; 13C: 125 MHz); Bruker DRX500 (1H: 500 MHz; 13C: 125 MHz; 11B: 160 MHz), Varian Unity500 (1H: 500 MHz; 13C: 125 MHz; 11B: 160 MHz), Varian Mercury VX-300 (1H: 122 MHz, 13C: 282 MHz, 11B: 96 MHz). Mass spectra of compounds 12d, 16 and 17 were recorded on a Bruker Microtuf 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 SI.

(b) Syntheses

CpW(CO)₅BCl₃ (6):²³ Na[CpW(CO)₅] (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. ¹H NMR (300 MHz, D₆-toluene, 248 K): δ = 4.38 (s, 5 H, Cp); ¹³C NMR (75 MHz, D₆-toluene, 248 K): δ = 218.1 (CO), 215.7 (CO), 94.1 (P); !B NMR (96 MHz, D₆-toluene, 248 K): δ = 91 (ν/υ/τ = 940 Hz); Crystallographic data: C₆H₆BCl₃O₂W, M, 414.69, monoclinic, P2₁/n, a = 7.8664(4), b = 11.0772(5), c = 12.3944(6) Å, β = 97.450(2)°, V = 1073.65(9) Å³, Z = 4, ρc = 2.565 Mg m⁻³, T = 150 K, λ = 0.71073 Å. 11681 reflections collected, 2427 independent [R(int) = 0.0069], which were used in all calculations. R₁ = 0.0578, wR₂ = 0.1389 for observed unique reflections [F² > 2σ(F²)] and R₁ = 0.0834, wR₂ = 0.1558 for all unique reflections. Max. and min. residual electron densities 3.87 and −4.01 e Å⁻³. CSD reference: 1037787.

CpFe(PPh₃)₃(BCl)(BCl₂NCMe₃) (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 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 x 20 mL) and dried in vacuo.

The product 11d was isolated as a beige solid (160 mg, 0.222 mmol, 43.3%). ¹H NMR (500 MHz, D₆-toluene, 298 K): δ = 7.56 (m, 6 H, p-Ph), 6.99 (m, 3 H, p-Ph), 6.90 (m, 6 H, m-Ph), 6.70 (s, 2 H, m-Mes), 6.66 (s, 2 H, m-Mes), 4.42 (d, J/P, 1H) = 1.0 Hz, 5 H, Cp), 2.40 (s, 6 H, o-CH₃), 2.27 (s, 6 H, o-CH₃), 2.12 (s, 3 H, p-CH₃), 2.11 (s, 3 H, p-CH₂), 1.31 (m, 16 H, p-Mes) ¹³C NMR (126 MHz, D₆-toluene, 298 K): δ = 221.8 (d, J/P, 1H) = 29.7 Hz, CO), 150.1 (CN), 138.3 (d, J/P, 1H) = 41.9 Hz, i-Ph), 137.9 (o-Mes), 137.8 (p-Mes), 137.7 (i-Mes), 137.6 (i-Mes), 137.4 (p-Mes), 136.6 (o-Mes), 133.6 (d, J/P, 1H) = 9.9 Hz, o-Ph), 130.2, 130.1 (m-Mes), 129.4 (d, J/P, 1H) = 1.8 Hz, p-Ph), 127.8 (m-Ph), 84.5 (C), 21.9 (α-CH₃), 21.6 (α-CH₂), 20.92, 20.89 (p-CH₃), !B NMR (160 MHz, D₆-toluene, 298 K): δ = 51 (ν/τ = 1150 Hz); !P NMR (122 MHz, D₆-toluene, 298 K): δ = 78.8; IR (KBr): ν = 3059 (ν), 2976 (v), 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, HI-MS (EI): m/z: 414.2262, calcd for [C₆H₂BClFeN]⁺ = 692.2217 (M⁺); elemental microanalysis: (calcd for C₂₆H₂₆BClFeN) C 71.53, H 5.86, N 1.94; (meas’d) C 71.16, H 5.66, N 2.10.

[CpFe(PPh₃)(CO)(BNCMe₃)][B(3,5-Cl₂C₆H₄)] (13d): 1d (30.0 mg, 0.0416 mmol, 1 equiv.) and Na[B(3,5-(CF₃)C₆H₄)] (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%).  

1H NMR (500 MHz, [D]_2dichloromethane, 298 K; δ = 7.74 (bs, 8 H, α-OAr); 7.56 (s, 4 H, p-Ar); 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, CH(CH_3)); 2.03 (s, 12 H, O-CH_3); 13C NMR (126 MHz, [D]_2dichloromethane, 298 K; δ = 213.4 (d, 1/J(P,C) = 25.8 Hz, CO), 188.3 (CN), 162.1 (q, 1/J(B,C) = 50.0 Hz, i-Ar), 144.1 (p-Mes), 139.5 (i-Mes), 138.8 (o-Mes), 135.2 (b, α-OAr), 134.4 (d, 1/J(P,C) = 50.6 Hz, i-Ph), 132.8 (d, 1/J(P,C) = 10.3 Hz, o-Ph), 131.7 (d, 1/J(P,C) = 2.4 Hz, p-Ph), 131.4 (m-Mes), 129.3 (d, 1/J(P,C) = 10.7 Hz, m-Ph), 129.2 (q, 1/J(F,C) = 31.5 Hz, 129.3 (d, 1/J(P,C) = 2.9 Hz, m-Ar); 124.9 (q, 1/J(F,C) = 272.6 Hz, CF_2), 117.8 (sept, 1/J(F,C) = 3.8 Hz, p-Ar), 86.0 (Cp), 21.6 (o-CH_3), 21.5 (p-CH_3); 11B NMR (96 MHz, [D]_2dichloromethane, 298 K; δ = 85 (ν_{1/2} = 820 Hz), −6 (ν_{1/2} = 6 Hz); [D]_2F NMR (282 MHz, [D]_2dichloromethane, 298 K; δ = −62.8; 13P NMR (122 MHz, [D]_2dichloromethane, 298 K; δ = 69.3 (b, ν_{1/2} = 10 Hz); IR (KBr): ν bar = 2963 (w), 1984 (s, CO), 1779 (m, 1608 (s), 1482 (w), 1435 (m), 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.

[![Chemical structure of (16)](https://example.com/chemicalstructure.png)](https://example.com/chemicalstructure.png)
A boron-containing product was identified by NMR spectroscopy. The spectra showed the presence of complex 17 (resonances not listed) and one other species, which was tentatively assigned as compound 21.

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in the 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 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.

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Notes and references

1 H NMR (500 MHz, [D$_2$]dichloromethane, 293 K): $\delta = 6.85$ (s, 4 H, m-Mes), 3.45 (m, Cy(III)-1), 3.04 (m, Cy(III)-1), 2.96 (m, Cy(III)-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(II)-2, Cy(III)-1, Cy(III)-4), 1.65, 1.49, 1.41, 1.08, 0.77 (each m, 10 H, Cy(II)-2, Cy(III)-2, Cy(III)-4), 1.70, 1.58, 1.27. 1.18 (Cy(III)-2, Cy(III)-3, Cy(III)-4); 13C NMR (126 MHz, [D$_2$]dichloromethane, 293 K): $\delta = 172.1$ (BN=C), 155.9 ($\equiv$(N=NR$_2$)), 139.7 (t-Mes), 136.6 (o-Mes), 130.2 (m-Mes), 54.7 (Cy(III)-1), 54.6 (Cy(III)-1), 50.8 (Cy(II)-1), 21.6 (o-CH$_3$), 21.0 (p-CH$_3$); 11B NMR (96 MHz, [D$_2$]dichloromethane, 293 K): $\delta = 30$ (v$_{1/2} = 350$ Hz).

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/


The iminoborylene complex \([\text{CpFe(PCy}_3\text{)(CO)(BNCMes}_2\text{)}]^+\) undergoes M=B metathesis reactivity with carbodiimides, resulting in Fe=B cleavage and the formation of isonitrile complexes.