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

J. Niemeyer,*[a] M. J. Kelly,[b] I. M. Riddlestone,[b] D. Vidovic,[c] and S. Aldridge*[b]

[a] Institute of Organic Chemistry, Department of Chemistry, University of Duisburg-Essen, Universitätsstrasse 7, 45141 Essen, Germany. Email: jochen.niemeyer@uni-due.de.
[b] Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK. E-mail: SimonAldridge@chem.ox.ac.uk.
[c] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological, University, 21 Nanyang Link, 637371 Singapore.

Supporting information (13 pages)

General remarks:

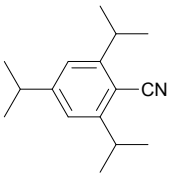
Materials: All reactions involving air- or moisture-sensitive compounds were carried out under an inert atmosphere by using Schlenk-type glassware or in a glovebox. UV photolysis experiments were carried out using a Spectral Energy mercury arc lamp (1 kW) with samples contained within quartz Schlenk 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 prepared according to literature procedures: $NaB(3,5\text{-}Cl_2\text{-}Ph)_4$[s1], $NaB(3,5\text{-}(CF_3)_2Ph)_4$[s2], Mes_2CNH[s3], $[CpW(CO)_3]Na$[s4], $[CpFe(CO)_2]Na$ (**1**)[s4], $(Ph_2CN\text{-}BCl_2)_2$ (**2b**)[s5], $CpFe(CO)_2\text{-}BCl_2$ (**3**)[s6], $^tBu_2CNLi$ (**4a**)[s7], Ph_2CNLi (**4b**)[s8], $(p\text{-}Tol)_2CNLi$ (**4c**)[s8], Mes_2CNLi (**4d**)[s9], $CpFe(CO)_2\text{-}B(Cl)NC(p\text{-}Tol)_2$ (**5c**)[s9], $CpFe(CO)_2\text{-}B(Cl)NCMes_2$ (**5d**)[s9], $CpFe(PCy_3)(CO)\text{-}B(Cl)NC(p\text{-}Tol)_2$ (**10c**)[s9], $CpFe(PCy_3)(CO)\text{-}B(Cl)NCMes_2$ (**10d**)[s9], $[CpFe(PCy_3)(CO)(BNC(p\text{-}Tol)_2)]^+[B(3,5\text{-}Cl_2\text{-}Ph)_4]^-$ (**12c**)[s9], $[CpFe(PCy_3)(CO)(BNCMes_2)]^+[B(3,5\text{-}Cl_2\text{-}Ph)_4]^-$ (**12d**)[s9], $CpFe(PCy_3)(CO)\text{-}B(SPh)NC(p\text{-}Tol)_2$ (**14c**)[s9], $CpFe(PCy_3)(CO)\text{-}B(SPh)NCMes_2$ (**14d**)[s9], $CpFe(PCy_3)(CO)\text{-}B(CN)NCMes_2$ (**15d**)[s9].

Analytical techniques: The following instruments were used for physical characterization of the compounds: IR: Nicolet Magna-IR 560; NMR: Bruker AVC500 (^1H: 500 MHz; ^{13}C: 125 MHz); Bruker DRX500 (^{11}B: 160 MHz), Varian Unity500 (^1H: 500 MHz; ^{13}C: 125 MHz, 11B: 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[s10] or an Oxford Diffraction/Agilent Technologies SuperNova instrument; structures were solved with SIR92[s11] or SuperFlip[s12] and refined using the CRYSTALS software suite,[s13] as per the information contained in the CIF. Where necessary PLATON/SQUEEZE was used to deal with disordered solvent.[s14]

Syntheses:

Precursors:

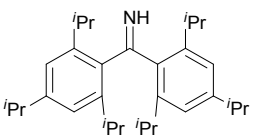
2,4,6-Triisopropylbenzonitrile[s15]



2,4,6-Triisopropylbromobenzene (11.6 g, 41.0 mmol, 1 eq) was dissolved in tetrahydrofurane (150 ml). A solution of *n*-butyllithium (2.0 M solution in hexanes, 22.5 ml, 45.0 mmol, 1.1 eq) was added at −78 °C and the mixture was stirred at −78 °C for 60 minutes. Dimethylformamide (4.75 ml, 4.49 g, 61.4 mmol, 1.5 eq) was added, the solution was stirred at −78 °C for 30 minutes and at room temperature overnight. Hydrochloric acid (2 N, 50 ml) was added, the phases were separated and the organic phase was washed with water (50 ml) and brine (50 ml). The combined aqueous phases were extracted with dichloromethane (100 ml) and the combined organic phases were dried over magnesium sulfate. Filtration and evaporation of the solvent gave a colourless liquid (9.78 g), which contained both 2,4,6-triisopropylbenzaldehyde and 1,3,5-triisopropylbenzene in a ratio of 1 : 0.24 according to ^{1}H-NMR.
The crude mixture (containing ca. 34.8 mmol 2,4,6-triisopropylbenzaldehyde) and hydroxylamine hydrochloride (5.35 g, 77.0 mmol, 2.21 eq) were dissolved in ethanol (50 ml). The mixture was refluxed for four hours and water (50 ml) was added. The aqueous phase was extracted with ether (3 x 100 ml) and the combined organic extracts were dried over magnesium sulfate. Filtration and evaporation of the solvent gave a colourless residue, which was purified by column chromatography (pentane : diethyl ether = 40 : 1, after elution of 1,3,5-triisopropylbenzene: pentane : diethyl ether = 10 : 1). This gave the product as a slightly yellow oil (7.94 g, 34.6 mmol, 84.4 % over two steps).

^{1}H NMR (300 MHz, [D$_1$]chloroform, 298 K): δ = 7.03 (s, 2 H, Ph), 3.37 (sept, ^3J(H,H) = 6.9 Hz, 2 H, *o*-C<u>H</u>(CH$_3$)$_2$), 2.90 (sept, ^3J(H,H) = 6.9 Hz, 1 H, *p*-C<u>H</u>(CH$_3$)$_2$), 1.28 (d, ^3J(H,H) = 6.9 Hz, 12 H, *o*-CH(C<u>H</u>$_3$)$_2$), 1.23 (d, ^3J(H,H) = 6.9 Hz, 6 H, *p*-CH(C<u>H</u>$_3$)$_2$).

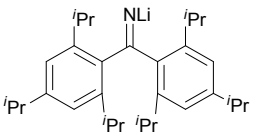
2,2´,4,4´,6,6´-Hexaisopropylbenzophenone imine



Magnesium turnings (834 mg, 34.3 mmol, 2.4 eq) were suspended in tetrahydrofurane (10 ml). A solution of 2,4,6-triisopropylbromobenzene (8.10 g, 28.6 mmol, 2 eq) in tetrahydrofurane (30 ml) was slowly added, maintaining a gentle reflux over the addition period. The mixture was refluxed for three hours and the solvent was removed *in vacuo*. The residue was suspended in toluene (30 ml) and a solution of 2,4,6-triisopropylbenzonitrile (3.28 g, 14.3 mmol, 1 eq) in toluene (30 ml) was added. The mixture was refluxed for 36 hours and methanol (5.79 ml, 4.58 g, 143 mmol, 10 eq) was added. The mixture was filtered and the residue was washed with toluene (2 x 20 ml). The combined toluene fractions were evaporated and the residue was purified by column chromotography (pentane : diethyl ether = 30 : 1, after elution of 2,4,6-triisopropylbenzonitrile: pentane : diethyl ether 10 : 1). This gave the product as a white solid (1.81 g, 4.17 mmol, 29.2%).

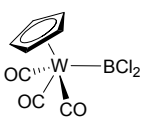
^{1}H NMR (300 MHz, [D$_1$]chloroform, 298 K): δ = 9.92 (bs, 1 H, NH), 7.00 (bs, 4 H, Ph), 3.01 (bs, 4 H, *o*-C<u>H</u>(CH$_3$)$_2$), 2.87 (sept, ^3J(H,H) = 7.0 Hz, 2 H, *p*-C<u>H</u>(CH$_3$)$_2$), 1.23 (d, ^3J(H,H) = 7.0 Hz, 12 H, *p*-CH(C<u>H</u>$_3$)$_2$), 1.04 (bs, 24 H, *o*-CH(C<u>H</u>$_3$)$_2$).

2,2´,4,4´,6,6´-Hexaisopropylbenzophenone imine lithium salt (4e)



2,2´,4,4´,6,6´-Hexaisopropylbenzophenone imine (923 mg, 2.13 mmol, 1 eq) was dissolved in diethyl ether (10 ml) and *n*-butyllithium (2.0 M solution in hexanes, 1.11 ml, 2.23 mmol, 1.05 eq) was added at −78 °C. The solution was warmed to room temperature and stirred overnight. The solvent was removed to give the product as a yellow powder (930 mg, 2.12 mmol, 99.3%).

CpW(CO)$_3$BCl$_2$ (6)[s16]



Sodium (η^5-Cyclopentadienyl)tricarbonyltungstate(II) (250 mg, 0.702 mmol, 1 eq) was suspended in hexanes (20 ml) and boron trichloride (0.70 ml of a 1 M solution in hexanes, 0.702 mmol, 1 eq) was added at −78 °C. The mixture was stirred at −78 °C for 30 minutes, warmed to room temperature and stirred for another four hours. The mixture was filtered and the filtrate was stored at −30 °C for one day. After one day, the supernatant was removed to give to product as a white powder (35 mg, 0,0844 mmol, 12%). Storage of the mother liquor at −30 °C for another day gave X-ray quality crystals (yield not determined).

^{1}H NMR (300 MHz, [D_8]toluene, 248 K): δ = 4.38 (s, 5 H, Cp).
^{13}C NMR (75 MHz, [D_8]toluene, 248 K): δ = 218.1 (CO), 215.7 (CO), 94.1 (Cp).
^{11}B NMR (96 MHz, [D_8]toluene, 248 K): δ = 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, β = 97.450(2)°, V = 1073.65(9) Å^3, Z = 4 ρ_c = 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. R_1 = 0.0578, wR_2 = 0.1389 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0834, wR_2 = 0.1558 for all unique reflections. Max. and min. residual electron densities 3.87 and –4.01 e Å^{-3}. CSD reference: 1037787.

Boryl-complexes:

General procedure: Reactions of iminodihaloboranes (2) with Na[CpFe(CO)$_2$] (1).

For 2b: Diphenylketiminodichloroborane-dimer (**2b**) (60.0 mg, 0.115 mmol, 0.45 eq) and sodium (η^5-cyclopentadienyl)-dicarbonylferrate(II) (**1**) (50.4 mg, 0.252 mmol, 1 eq) were suspendend in toluene (4 ml) and the mixture was stirred at room temperature. Analysis of the reaction *via* ^{11}B-NMR showed no conversion.
For 2c/d: The respective ketimine (2,2´,4,4´,6,6´-hexamethylbenzophenone imine or 2,2´,4,4´,6,6´-hexaisopropylbenzophenone imine) (3.77 mmol, 1 eq) was dissolved in dichloromethane (10 ml), boron trichloride (1.0 M solution in heptane, 4.15 ml, 4.15 mmol, 1.1 eq) was added at −78 °C and the mixture was stirred for 30 minutes. The solution was warmed to room temperature and stirred for one hour. The solvent was removed and the residue was re-dissolved in benzene (10 ml). Triethylamine (525 ul, 383 mg, 3.77 mmol, 1 eq) was added, the mixture was stirred for 3 hours and then filtered onto a suspension of sodium (η^5-cyclopentadienyl)dicarbonylferrate(II) (**1**) (830 mg, 4.15 mmol, 1.1 eq) in toluene (10 ml). Analysis of the reaction *via* ^{11}B-NMR showed no conversion.

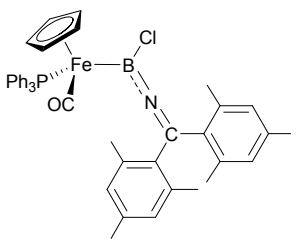
General procedure: Reactions of ketiminolithium salts (4) with CpW(CO)$_3$BCl$_2$ (6) and CpW(CO)$_3$BBr$_2$ (7).

Sodium (η^5-cyclopentadienyl)tricarbonyltungstate (223 mg, 0.627 mmol, 1 eq) was suspended in toluene (5 ml) and the respective boron trihalide (0.627 ml of a 1 M solution in heptane, 0.627 mmol, 1 eq) was added at −78 °C. The solution was warmed to room temperature and stirred for three hours. The resulting solution of CpW(CO)$_3$BX$_2$ (X=Cl for **6** and X=Br for **7**) was then slowly filtered onto a suspension of the respective ketiminolithium salt (hexamethylacetone imine lithium salt (**4a**) or 2,2´,4,4´,6,6´-hexamethylbenzophenone imine lithium (**4d**)) in toluene (5 ml). Analysis of the reaction *via* ^{11}B-NMR showed mostly products of W-B bond breakage, resulting in the formation of the ketiminodihaloboranes.

General procedure: Reactions of ketiminolithium salts (4) with CpFe(CO)$_2$BCl$_2$ (1).

Sodium (η^5-cyclopentadienyl)dicarbonylferrate (**1**) (1.86 g, 9.29 mmol, 1 eq) was suspended in toluene (40 ml) and boron trichloride (1.0 M solution in heptane, 9.29 ml, 9.29 mmol, 1 eq) was added at −78 °C. The solution was warmed to room temperature and stirred for four hours. The resulting solution of Cp(CO)$_2$FeBCl$_2$ was then slowly filtered onto a suspension of the respective ketimino lithium salt (hexamethylacetone imine lithium salt (**4a**), benzophenone imine lithium salt (**4b**), 4,4´-dimethylbenzophenone imine lithium salt (**4c**), 2,2´,4,4´,6,6´-hexamethylbenzophenone imine lithium salt (**4d**) or 2,2´,4,4´,6,6´-hexaisopropylbenzophenone imine lithium salt (**4e**)) (9.29 mmol, 1 eq) in toluene (40 ml) at −78 °C. The resulting mixture was slowly warmed to room temperature and stirred overnight.
In cases of **4a-d**, analysis of the reaction *via* ^{11}B-NMR showed the formation of the desired complexes **5a-d**. While complexes **5a** and **5b** could not be purified, compounds **5c** and **5d** were isolated as previously reported.[s9] In case of **4e**, analysis of the reaction *via* ^{11}B-NMR showed mostly the product of Fe-B bond breakage, resulting in the formation of the ketiminodihaloborane.

CpFe(PPh$_3$)(CO){B(Cl)NCMes$_2$} (11d)



Complex **5d** (250 mg, 0.512 mmol, 1 eq) and triphenylphosphine (148 mg, 0.564 mmol, 1.1 eq) were dissolved in toluene (20 ml, quartz schlenk). The mixture was irradiated (UV-lamp) and the reaction was monitored by ^{1}H-NMR. After complete consumption of the starting material (ca. 4 hours), 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 minutes, the resulting solid was isolated by filtration, washed with pentane (2 x 20 ml) and dried *in vacuo*. This gave the product as a beige solid (160 mg, 0.222 mmol, 43.3%).

^{1}H NMR (500 MHz, [D_6]benzene, 298 K):[1] δ = 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).

[1] All resonances resulting from the triphenylphosphine-ligand will be described as „Ph“, all resonances resulting from the Mesityl-units will be described as

^{13}C NMR (126 MHz, [D$_6$]benzene, 298 K): δ = 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[2] (*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): δ = 51 ($\nu_{1/2}$ = 1150 Hz).
^{31}P NMR (122 MHz, [D$_6$]benzene, 298 K): δ = 78.8.
GCOSY (500 MHz / 500 MHz, [D$_6$]benzene, 298 K): δ (^{1}H) / δ (^{1}H) = 7.56 / 6.90 (*o*-Ph / *m*-Ph), 6.99 / 6.90 (*p*-Ph / *m*-Ph), 6.90 / 7.56, 6.99 (*m*-Ph / *o*-Ph, *p*-Ph), 6.70 / 2.40, 2.11 (*m*-Mes^A / *o*-CH_3^A, *p*-CH_3^A), 6.66 / 2.27, 2.12 (*m*-Mes^B / *o*-CH_3^B, *p*-CH_3^B), 2.40 / 6.70, 2.11 (*o*-CH_3^A / *m*-Mes^A, *p*-CH_3^A), 2.27 / 6.66, 2.12 (*o*-CH_3^B / *m*-Mes^B, *p*-CH_3^B), 2.12 / 6.66, 2.27 (*p*-CH_3^B / *m*-Mes^B, *o*-CH_3^B), 2.11 / 6.70, 2.40 (*p*-CH_3^A / *m*-Mes^A, *o*-CH_3^A).
GHSQC (500 MHz / 126 MHz, [D$_6$]benzene, 298 K): δ (^{1}H) / δ (^{13}C) = 7.56 / 133.6 (*o*-Ph), 6.99 / 129.4 (*p*-Ph), 6.90 / 127.8 (*m*-Ph), 6.70, 6.66 / 130.2, 130.1 (*m*-Mes$^{A/B}$), 4.42 / 84.5 (Cp), 2.40 / 21.6 (*o*-CH_3^A), 2.27 / 21.9 (*o*-CH_3^B), 2.12, 2.11 / 20.92, 20.89 (*p*-$CH_3^{A/B}$).
GHMBC (500 MHz / 126 MHz, [D$_6$]benzene, 298 K): δ (^{1}H) / δ (^{13}C) = 7.56 / 133.6, 129.4 (*o*-Ph / *o*-Ph, *p*-Ph), 6.99 / 133.6 (*p*-Ph / *o*-Ph), 6.90 / 138.3, 133.6, 127.8 (*m*-Ph / *i*-Ph, *o*-Ph, *m*-Ph), 6.70 / 150.1, 137.6, 130.2, 130.1, 20.92, 20.89 (*m*-Mes^A / CN, *i*-Mes^A, *m*-Mes$^{A/B}$, *p*-$CH_3^{A/B}$), 6.66 / 150.1, 137.7, 130.2, 130.1, 20.92, 20.89 (*m*-Mes^B / CN, *i*-Mes^B, *m*-Mes$^{A/B}$, *p*-$CH_3^{A/B}$), 2.40 / 150.1, 136.6, 130.2, 130.1 (*o*-CH_3^A / CN, *o*-Mes^A, *m*-Mes$^{A/B}$), 2.27 / 150.1, 137.9, 130.2, 130.1 (*o*-CH_3^B / CN, *o*-Mes^B, *m*-Mes$^{A/B}$), 2.12 / 137.4, 130.2, 130.1 (*p*-CH_3^B / *p*-Mes^B, *m*-Mes$^{A/B}$), 2.11 / 137.8, 130.2, 130.1 (*p*-CH_3^A / *p*-Mes^A, *m*-Mes$^{A/B}$).

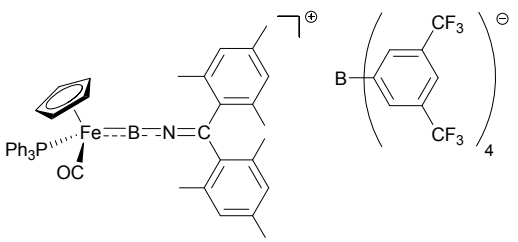
IR (KBr): ν bar = 3059 (w), 2976 (w), 2923 (w), 2857 (w), 1909 (s, CO), 1769 (m), 1747 (m), 1609 (w), 1479 (w), 1438 (m), 1261 (w), 1161 (w), 1092 (w), 1073 (w), 1029 (w), 877 (w), 851 (m), 824 (w) cm^{-1}.

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.

Borylene-complexes:

[CpFe(PPh$_3$)(CO)(BNCMes$_2$)]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$ (13d)[I]



Complex **1d** (30.0 mg, 0.0416 mmol, 1 eq) and tetrakis(3,5-di(trifluoromethyl)phenyl)borate (36.9 mg, 0.0416 mmol, 1 eq) were dissolved in fluorobenzene (2 ml) and the mixture was stirred for five minutes. 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):[3] 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$_6$]benzene, 298 K): δ = 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): δ = 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): δ = 69.3 (b, ($\nu_{1/2}$ =10 Hz).
GCOSY (500 MHz / 500 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H) / δ (^{1}H) = 7.74 / 7.56 (*o*-Ar^F / *p*-Ar^F), 7.56 / 7.74 (*p*-Ar^F / *o*-Ar^F), 7.43 / 7.29 (*p*-Ph / *m*-Ph), 7.29 / 7.43, 7.26 (*m*-Ph / *p*-Ph, *o*-Ph), 7.26 / 7.29 (*o*-Ph / *m*-Ph), 6.96 / 2.34, 2.03 (*m*-Mes / *p*-CH_3, *o*-CH_3), 2.34 / 6.96, 2.03 (*p*-CH_3 / *m*-Mes, *o*-CH_3), 2.03 / 6.96, 2.34 (*o*-CH_3 / *m*-Mes, *p*-CH_3).
GHSQC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 7.74 / 135.2 (*o*-Ar^F), 7.56 / 117.8 (*p*-Ar^F), 7.43 / 131.7 (*p*-Ph), 7.29 / 129.3 (*m*-Ph), 7.26 / 132.8 (*o*-Ph), 6.96 / 131.4 (*m*-Mes), 4.95 / 86.0 (Cp), 2.34 / 21.5 (*p*-CH_3), 2.03 / 21.6 (*o*-CH_3).
GHMBC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 7.74 / 162.1, 135.2, 124.9, 117.8 (*o*-Ar^F / *i*-Ar^F, *o*-Ar^F, CF_3, *p*-Ar^F), 7.56 / 135.2, 124.9 (*p*-Ar^F / *o*-Ar^F, CF_3), 7.43 / 132.8, (*p*-Ph / *o*-Ph), 7.29 / 134.4, 129.3 (*m*-Ph / *i*-Ph, *m*-Ph), 7.26 / 132.8, 131.7 (*o*-Ph / *o*-Ph, *p*-Ph), 6.96 / 188.3, 139.5, 131.4, 21.6, 21.5 (*m*-Mes / CN, *i*-Mes, *m*-Mes, *o*-CH_3, *p*-CH_3), 2.34 / 144.1, 131.4 (*p*-CH_3 / *p*-Mes, *m*-Mes), 2.03 / 139.5, 138.8, 131.4 (*o*-CH_3 / *i*-Mes, *o*-Mes, *m*-Mes).

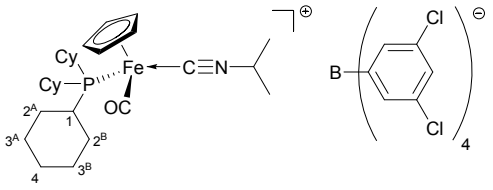
„Mes". Two independent signals set were observed for the mesityl groups, which were labelled A and B for this reason.
[2] Signal overlaps with solvent signal. ^{13}C-chemical shift was deduced from the GHSQC.
[3] All resonances resulting from the triphenylphospine-ligand will be described as „Ph". All resonances resulting from the Mesityl-units will be described as „Mes".

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}.

HR-MS (ESI): not possible, only hydrolysis product observed (*m/z* = 439.06 $[CpFe(CO)_2(PPh_3)^+]$).

Reactions products from borylene-complexes:

$[CpFe(PCy_3)(CO)(CN^iPr)]^+[B(3,5\text{-}Cl_2\text{-}C_6H_3)_4]^-$ (16)



Complex **10d** (126 mg, 0.170 mmol, 1 eq) and and tetrakis(3,5-dichlorophenyl)borate sodium (105 mg, 0.170 mmol, 1 eq) were dissolved in fluorobenzene (5 ml). The mixture was stirred for five minutes and *N,N´*-diisopropylcarbodiimide (26.5 µl, 21.5 mg, 0.170 mmol, 1 eq) was added. The mixture was stirred overnight, filtered into a layering schlenk and layered with hexanes. After one week, the supernatant was removed and the product was isolated as yellow crystals suitable for X-ray analysis (55.0 mg, 0.0503 mmol, 29.6%).

^{1}H NMR (500 MHz, [D_2]dichloromethane, 298 K):[4] 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-$3^{A´/B´}$), 1.29 (m, 9 H, H-$2^{A´/B´}$, 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.
GCOSY (500 MHz / 500 MHz, [D_6]benzene, 298 K): δ (^{1}H) / δ (^{1}H) = 4.08 / 1.39 (CH / CH_3), 1.89 / 1.34, 1.29 (H-$2^{A/B}$, H-$3^{A/B}$ / H-$3^{A´/B´}$, H-$2^{A´/B´}$, H-4´), 1.79 / 1.29 (H-4 / H-$2^{A´/B´}$, H-4´), 1.39 / 4.08 (CH_3 / CH), 1.34 / 1.89 (H-$3^{A´/B´}$ / H-$2^{A/B}$, H-$3^{A/B}$), 1.29 / 1.89, 1.79 (H-$2^{A´/B´}$, H-4´ / H-$2^{A/B}$, H-$3^{A/B}$, H-4).
GHSQC (500 MHz / 126 MHz, [D_2]dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 133.2 (*o*-Ar^{Cl}), 7.00 / 123.4 (*p*-Ar^{Cl}), 4.92 / 84.2 (Cp), 4.08 / 51.3 (CH), 1.95 / 38.7 (1), 1.89, 1.34 / 30.8, 30.7 ($3^{A/B}$), 1.89, 1.29 / 27.9, 27.8 ($2^{A/B}$), 1.79, 1.29 / 26.4 (4), 1.39 / 23.29, 23.27 (CH_3, CH_3´).
GHMBC (500 MHz / 126 MHz, [D_2]dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 165.0, 133.4, 133.2, 123.4 (*o*-Ar^{Cl} / *i*-Ar^{Cl}, *m*-Ar^{Cl}, *o*-Ar^{Cl}, *p*-Ar^{Cl}), 7.00 / 133.4, 133.2 (*p*-Ar^{Cl} / *m*-Ar^{Cl}, *o*-Ar^{Cl}), 4.92 / 215.7, 153.6 (Cp / CO, CN), 4.08 / 153.6, 23.29, 23.27 (CH / CN, CH_3, CH_3´), 1.95 / 30.8, 30.7 (H-1 / C-$3^{A/B}$), 1.89 / 38.7, 30.8, 30.7, 27.9, 27.8, 26.4 (H-$2^{A/B}$, H-$3^{A/B}$ / C-1, C-$3^{A/B}$, C-$2^{A/B}$, C-4), 1.79 / 30.8, 30.7, 27.9, 27.8 (H-4 / C-$3^{A/B}$, C-$2^{A/B}$), 1.39 / 51.3, 23.29, 23.27 (CH_3 / CH, CH_3, CH_3´), 1.34 / 27.9, 27.8, 26.4 (H-$3^{A´/B´}$ / C-$2^{A/B}$, C-4), 1.29 / 30.8, 30.7, 27.9, 27.8, 26.4 (H-$2^{A´/B´}$, H-4´ / C-$3^{A/B}$, C-$2^{A/B}$, C-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}.

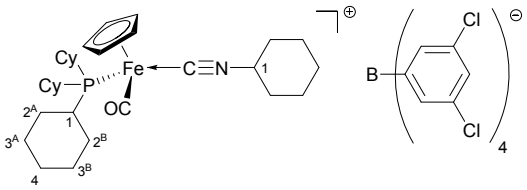
HR-MS (EI): *m/z*: 498.2545, calcd for $(C_{24}H_{45}FeNOP)^+$ = 498.2583 $[(M\text{-}B(C_6H_3Cl_2)_4)^+]$.

Elemental microanalysis: (calcd for $C_{52}H_{57}BCl_8FeNOP$) C 57.12, H 5.25, N 1.28; (measd) C 56.88, H 4.99, N 1.30.

Crystallographic data: $C_{52}H_{57}BCl_8FeNOP$, 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. 23500 reflections collected, 11969 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.

[4] All resonances resulting from the isopropylisonitrile-unit will be described as CH and CH_3.The diastereotopic geminal CH_3-groups of the isopropyl-unit were labelled as CH_3 and CH_3´, respectively. The resonances resulting from the tricyclohexylphosphine-unit will be described as 1 to 4.
The diastereotopic (CH_2)-2 and (CH_2)-3 groups of the cyclohexyl units were also labelled A and B. The diastereotopic geminal protons of each methylene-unit were labelled as H and H´, respectively.
The ^{1}H chemical shifts of the cyclohexyl units were partially deduced from the GHSQC-spectrum.

[CpFe(PCy$_3$)(CO)(CNCy)]$^+$[B(3,5-Cl$_2$-C$_6$H$_3$)$_4$]$^-$ (17)

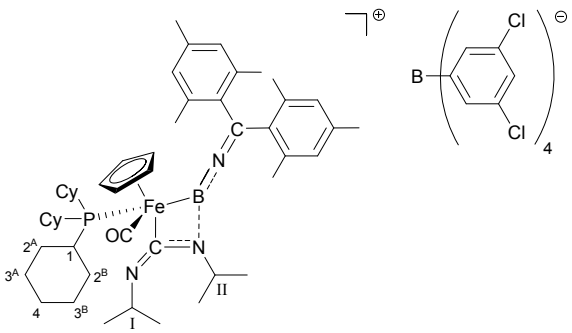


Complex **12d** (20.0 mg, 0.0154mmol, 1 eq) and dicyclohexylcarbodiimide (7.0 mg, 0.0339 mmol, 2.2 eq) were dissolved in [D$_2$]dichloromethane in an NMR tube at −78 °C. The NMR-tube was warmed to room temperature and allowed to stand for 4 h. The mixture, containing of complex **17** and adduct **21** (resonances not listed), was analyzed by NMR-spectroscopy and mass-spectrometry.

^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 293 K):[5] 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$^{A'/B'}$), 1.27 (m, 9 H, H-2$^{A'/B'}$, 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.
GCOSY (500 MHz / 500 MHz, [D$_2$]dichloromethane, 293 K): δ (^{1}H) / δ (^{1}H) = 3.85 / 1.96, 1.57 (Cy-1 / Cy), 1.96 / 3.85, 1.57, 1.36 (Cy / Cy-1, Cy), 1.88 / 1.32, 1.27 (H-2$^{A/B}$, H-3$^{A/B}$ / H-3$^{A'/B'}$, H-2$^{A'/B'}$, H-4′), 1.74 / 1.27 (H-4 / H-2$^{A'/B'}$, H-4′), 1.57 / 3.85, 1.96 (Cy / Cy-1, Cy), 1.36 / 1.96 (Cy / Cy), 1.32 / 1.88 (H-3$^{A'/B'}$ / H-2$^{A/B}$, H-3$^{A/B}$), 1.27 / 1.88, 1.74 (H-2$^{A'/B'}$, H-4′ / H-2$^{A/B}$, H-3$^{A/B}$, H-4).
GHSQC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 293 K): δ (^{1}H) / δ (^{13}C) = 7.04 / 133.3 (*o*-Ar^{Cl}), 7.01 / 123.4 (*p*-Ar^{Cl}), 4.92 / 84.3 (Cp), 3.85 / 57.3 (Cy-1), 1.94 / 38.8 (1), 1.88, 1.32 / 30.9, 30.7 (3$^{A/B}$), 1.88, 1.27 / 28.0, 27.9 (2$^{A/B}$), 1.74, 1.27 / 26.4 (4).
GHMBC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 293 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 165.0, 133.5, 123.4 (*o*-Ar^{Cl} / *i*-Ar^{Cl}, *m*-Ar^{Cl}, *p*-Ar^{Cl}), 7.00 / 133.5 (*p*-Ar^{Cl} / *m*-Ar^{Cl}), 4.92 / 215.8, 153.8 (Cp / CO, CN), 1.94 / 30.9, 30.7 (H-1 / C-3$^{A/B}$), 1.88 / 38.8, 30.9, 30.7, 28.0, 27.9, 26.4 (H-2$^{A/B}$, H-3$^{A/B}$ / C-1, C-3$^{A/B}$, C-2$^{A/B}$, C-4), 1.74 / 30.9, 30.7, 28.0, 27.9 (H-4 / C-3$^{A/B}$, C-2$^{A/B}$), 1.32 / 28.0, 27.9 (H-3$^{A'/B'}$ / C-2$^{A/B}$), 1.27 / 30.9, 30.7, 28.0, 27.9, 26.4 (H-2$^{A'/B'}$, H-4′ / C-3$^{A/B}$, C-2$^{A/B}$, C-4).
2D-TOCSY (500 MHz / 500 MHz, [D$_2$]dichloromethane, 293 K, selected resonances): δ (^{1}H) / δ (^{1}H) = 3.85 / 1.96, 1.69, 1.57, 1.36 (Cy-1 / 2-Cy, 3-Cy, 4-Cy),

HR-MS (EI): *m/z*: 538.2876, calcd for $(C_{31}H_{49}FeNOP)^+$ = 538.2896 $[(M\text{-}B(C_6H_3Cl_2)_4)^+]$.

Intermediate from reaction of 12d with diisopropylcarbodiimide (18)



Complex **12d** (41.7 mg, 0.0321 mmol, 1 eq), 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 eq) was added and the NMR-tube was transferred to a precooled NMR spectrometer. The NMR-spectra for intermediate **18** were recorded at 263 K.

^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 263 K):[6] 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$^{A'/B'}$), 1.31 (d, ^3J(H,H) = 6.6 Hz, 3 H, CH$_3$(I′), 1.18 (m, 6 H, H-2$^{A'/B'}$), 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)′).

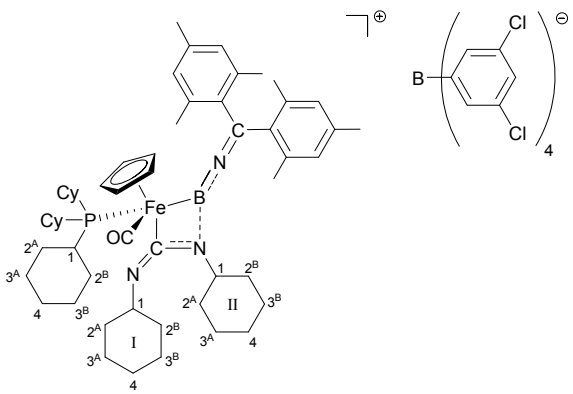
---

[5] All resonances resulting from the cyclohexylisonitrile-unit will be described as Cy. Due to the presence of many cyclohexyl-groups, the ^{1}H- and ^{13}C-chemical shifts of the Cy-2, Cy-3- and Cy-4-units of the cyclohexylisonitrile could not be fully determined.
The resonances resulting from the tricyclohexylphosphine-unit will be described as 1 to 4. The diastereotopic (CH$_2$)-2 and (CH$_2$)-3 groups of the cyclohexyl units were labelled A and B. The diastereotopic geminal protons of each methylene-unit were labelled as H and H′, respectively.
The ^{1}H chemical shifts of the cyclohexyl units were partially deduced from the TOCSY and GHSQC-spectra. The ^{13}C-chemical shift of the isonitrile quaternary carbon was deduced from the GHMBC-spectrum.

[6] The resonances resulting from the diisopropylcarbodiimide-unit will be described as CH and CH$_3$. Two independent signals set were observed for the two isopropyl groups, which were labelled I and II for this reason. The diastereotopic geminal CH$_3$-groups of each isopropyl-unit were labelled as CH$_3$ and CH$_3$′, respectively. The resonances resulting from the mesityl-methyl groups will be described as *o*-CH$_3$ and *p*-CH$_3$. Two independent signals set were observed for the two mesityl groups, which were each labelled A and B for this reason. The resonances resulting from the tricyclohexylphosphine-unit will be described as 1 to 4.
The diastereotopic (CH$_2$)-2 and (CH$_2$)-3 groups of the cyclohexyl units were also labelled A and B. The diastereotopic geminal protons of each methylene-unit were labelled as H and H′, respectively.
The ^{1}H chemical shifts of the cyclohexyl units were partially deduced from the GHSQC-spectrum.

^{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 x 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).
GCOSY (500 MHz / 500 MHz, [D$_2$]dichloromethane, 263 K): δ (^{1}H) / δ (^{1}H) = 7.03 / 7.00 (*o*-Ar^{Cl} / *p*-Ar^{Cl}), 7.00 / 7.03 (*p*-Ar^{Cl} / *o*-Ar^{Cl}), 6.99 / 2.30 (*m*-Mes^A / *p*-CH$_3^A$), 6.93 / 2.25 (*m*-Mes^B / *p*-CH$_3^B$), 3.73 / 1.35, 1.31 (CH(I) / CH$_3$(I), CH$_3$(I)´), 3.01 / 1.13, 0.52 (CH(II) / CH$_3$(II), CH$_3$(II)´), 2.30 / 6.99 (*p*-CH$_3^A$ / *m*-Mes^A), 2.25 / 6.93 (*p*-CH$_3^B$ / *m*-Mes^B), 1.82 / 1.32 (H-1, H-3$^{A/B}$ / H-3$^{A´/B´}$), 1.79 / 1.18 (H-2$^{A/B}$ / H-2$^{A´/B´}$), 1.71 / 1.17 (H-4 / H-4´), 1.35 / 3.73 (CH$_3$(I) / CH(I)), 1.32 / 1.82 (H-3$^{A´/B´}$ / H-3$^{A/B}$), 1.31 / 3.73 (CH$_3$(I)´ / CH(I)), 1.18 / 1.79 (H-2$^{A´/B´}$ / H-2$^{A/B}$), 1.17 / 1.71 (H-4´ / H-4), 1.13 / 3.01 (CH$_3$(II) / CH(II)), 0.52 / 3.01 (CH$_3$(II)´ / CH(II)).
GHSQC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 263 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 133.0 (*o*-Ar^{Cl}), 7.00 / 123.1 (*p*-Ar^{Cl}), 6.99 / 131.4 (*m*-Mes^A), 6.93 / 130.9 (*m*-Mes^B), 4.70 / 81.2 (Cp), 3.73 / 46.7 (CH(I)), 2.30 / 21.2 (*p*-CH$_3^A$), 2.25 / 21.1 (*p*-CH$_3^B$), 1.82 / 39.5 (1), 1.82, 1.32 / 29.9 (3$^{A/B}$), 1.79, 1.18 / 27.9, 27.6 (2$^{A/B}$), 1.71, 1.17 / 26.2 (4), 1.35 / 21.8 (CH$_3$(I)), 1.31 / 23.8 (CH$_3$(I)´), 1.13 / 22.5 (CH$_3$(II)), 0.52 / 21.3 (CH$_3$(II)´).
GHMBC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 263 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 164.7, 133.1, 133.0, 123.1 (*o*-Ar^{Cl} / *i*-Ar^{Cl}, *m*-Ar^{Cl}, *o*-Ar^{Cl}, *p*-Ar^{Cl}), 7.00 / 133.0 (*p*-Ar^{Cl} / *o*-Ar^{Cl}), 6.99 / 180.9, 138.8, 135.0, 131.4 (*m*-Mes^A / CN, *o*-Mes^A, *i*-Mes^A, *m*-Mes^A), 6.93 / 180.9, 136.0, 130.9 (*m*-Mes^B / CN, *i*-Mes^B, *m*-Mes^B), 4.70 / 220.9 (Cp / CO), 3.73 / 23.8, 21.8 (CH(I) / CH$_3$(I)´, CH$_3$(I)), 3.01 / 168.8, 22.5, 21.3 (CH(II) / NCN, CH$_3$(II), CH$_3$(II)´), 2.30 / 143.6, 131.4 (*p*-CH$_3^A$ / *p*-Mes^A, *m*-Mes^A), 2.25 / 143.2, 130.9 (*p*-CH$_3^B$ / *p*-Mes^B, *m*-Mes^B), 2.11 / 138.8, 135.0, 131.4 (*o*-CH$_3^A$ / *o*-Mes^A, *i*-Mes^A, *m*-Mes^A), 2.05 / 137.0, 136.0, 130.9 (*o*-CH$_3^B$ / *o*-Mes^B, *i*-Mes^B, *m*-Mes^B), 1.82 / 39.5, 29.9, 27.9, 27.6, 26.2 (H-1, H-3$^{A/B}$ / C-1, C-3$^{A/B}$, C-2$^{A/B}$, C-4), 1.79 / 39.5, 29.9, (H-2$^{A/B}$ / C-1, C-3$^{A/B}$), 1.71 / 29.9 (H-4 / C-3$^{A/B}$), 1.35 / 46.7, 23.8 (CH$_3$(I) / CH(I), CH$_3$(I)´), 1.31 / 46.7, 21.9 (CH$_3$(I)´ / CH(I), CH$_3$(I)), 1.17 / 29.9 (H-4´ / C-3$^{A/B}$), 1.13 / 46.0, 21.3 (CH$_3$(II) / CH(II), CH$_3$(II)´), 0.52 / 46.0, 22.5 (CH$_3$(II)´ / CH(II), CH$_3$(II)).

Intermediate from reaction of 12d with dicycohexylcarbodiimide (19)



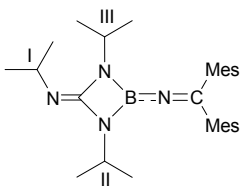
Complex **12d** (20.0 mg, 0.0154 mmol, 1 eq), was dissolved in [D$_2$]dichloromethane in an NMR tube and the solution was cooled to −78 °C. Dicyclohexylcarbodiimide (3.5 mg, 0.0170 mmol, 1.1 eq) was added and the NMR-tube was transferred to a precooled NMR spectrometer. The NMR-spectra for intermediate **19** were recorded at 263 K.

^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 263 K):[7] 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 x Cy-3^A), 1.72 (m, 3 H, H-4), 1.71 (m, 1 H, Cy(I)-2$^{B´}$), 1.60 (m, 1 H, Cy(I)-2$^{A´}$), 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$^{A´/B´}$), 1.31 (m, 1 H, Cy(II)-2$^{A´}$), 1.23 (m, 8 H, 2 x Cy-3$^{A´}$, H-2$^{A´/B´}$), 1.22 (m, 3 H, H-4´), 1.04 (m, 1 H, Cy-4´), 0.95 (m, 1 H, Cy-3$^{B´}$), 0.94 (m, 1 H, Cy-3$^{B´}$), 0.70 (m, 1 H, Cy-4´), 0.12 (m, 1 H, Cy(II)-2$^{B´}$).
^{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 x 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$_3^B$).

[7] The resonances resulting from the dicyclohexylcarbodiimide-unit will be described as Cy-1 to Cy-4. Two independent signals set were observed for the two dicyclohexylcarbodiimide-cyclohexyl units groups, which were labelled Cy(I) and Cy(II) for this reason. Due to the strong overlap of signals, the Cy-3 and Cy-4 units could not be assigned to I or II. The resonances resulting from the tricyclohexylphosphine-unit will be described as 1 to 4.
The diastereotopic (CH$_2$)-2 and (CH$_2$)-3 groups of all cyclohexyl units were labelled A and B. The diastereotopic geminal protons of each methylene-unit were labelled as H and H´, respectively.
Two independent signals set were observed for the two mesityl groups, which were each labelled A and B for this reason.
The ^{1}H chemical shifts of the cyclohexyl units were partially deduced from the GHSQC-spectrum.

^{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).
GCOSY (500 MHz / 500 MHz, [D$_2$]dichloromethane, 263 K): δ (^{1}H) / δ (^{1}H) = 7.03 / 7.00 (*o*-Ar^{Cl} / *p*-Ar^{Cl}), 7.00 / 7.03 (*p*-Ar^{Cl} / *o*-Ar^{Cl}), 6.99 / 2.31, 2.10 (*m*-Mes^A / *p*-CH$_3^A$, *o*-CH$_3^A$), 6.93 / 2.25, 2.06 (*m*-Mes^B / *p*-CH$_3^B$, *o*-CH$_3^B$), 3.24 / 1.90, 1.60 (Cy(I)-1 / Cy(I)-2^B, Cy(I)-2$^{A\prime}$), 2.54 / 1.85, 1.55 (Cy(II)-1 / Cy(II)-2^A, Cy(II)-2^B), 2.31 / 6.99 (*p*-CH$_3^A$ / *m*-Mes^A), 2.25 / 6.93 (*p*-CH$_3^B$ / *m*-Mes^B), 2.10 / 6.99 (*o*-CH$_3^A$ / *m*-Mes^A), 2.06 / 6.93 (*o*-CH$_3^B$ / *m*-Mes^B), 1.90 / 3.24, 1.71 (Cy(I)-2^B / Cy(I)-1, Cy(I)-2$^{B\prime}$), 1.86 / 1.34 (H-3$^{A/B}$ / H- 3$^{A\prime/B\prime}$), 1.85 / 2.54, 1.31 (Cy(II)-2^A / Cy(II)-1, Cy(II)-2$^{A\prime}$), 1.84 / 1.60 (Cy(I)-2^A / Cy(I)-2$^{A\prime}$), 1.83, 1.82 / 1.23 (H-2$^{A/B}$, Cy-3^A / H- 2$^{A\prime/B\prime}$, Cy-3$^{A\prime}$), 1.72 / 1.22 (H-4 / H-4′), 1.71 / 1.90 (Cy(I)-2$^{B\prime}$ / Cy(I)-2^B), 1.60 / 3.24, 1.84 (Cy(I)-2$^{A\prime}$ / Cy(I)-1, Cy(I)-2^A), 1.58 / 1.04 (Cy-4 / Cy-4′), 1.55 / 2.54, 0.12 (Cy(II)-2^B / Cy(II)-1, Cy(II)-2$^{B\prime}$), 1.49 / 0.70 (Cy-4 / Cy-4′), 1.46 / 0.95 (Cy-3^B / Cy-3$^{B\prime}$), 1.43 / 0.94 (Cy-3^B / Cy-3$^{B\prime}$), 1.34 / 1.86 (H-3 $^{A\prime/B\prime}$ / H-3$^{A/B}$), 1.31 / 1.85 (Cy(II)-2$^{A\prime}$ / Cy(II)-2^A), 1.23 / 1. 83, 1.82 (Cy-3$^{A\prime}$, H-2$^{A\prime/B\prime}$ / H-2$^{A/B}$, Cy-3^A), 1.22 / 1.72 (H-4′ / H-4), 1.04 / 1.58 (Cy-4′ / Cy-4), 0.95 / 1.46 (Cy-3$^{B\prime}$ / Cy-3^B), 0.94 / 1.43 (Cy-3$^{B\prime}$ / Cy-3^B), 0.70 / 1.49 (Cy-4′ / Cy-4), 0.12 / 1.55 (Cy(II)-2$^{B\prime}$ / Cy(II)-2^B).
GHSQC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 263 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 133.0 (*o*-Ar^{Cl}), 7.00 / 123.1 (*p*-Ar^{Cl}), 6.99 / 131.5 (*m*-Mes^A), 6.93 / 131.1 (*m*-Mes^B), 4.68 / 81.2 (Cp), 3.24 / 55.5 (Cy(I)-1), 2.54 / 53.5 (Cy(II)-1), 2.31 / 21.3 (*p*-CH$_3^A$), 2.25 / 21.0 (*p*-CH$_3^B$), 2.10 / 22.0 (*o*-CH$_3^A$), 2.06 / 22.2 (*o*-CH$_3^B$), 1.90, 1.71 / 32.5 (Cy(I)-2^B), 1.86, 1.34 / 30.0 (3$^{A/B}$), 1.85, 1.31 / 32.7 (Cy(II)-2^A), 1.84, 1.60 / 34.5 (Cy(I)-2^A), 1.84 / 39.7 (1), 1.83, 1.23 / 28.0, 27.7 (2$^{A/B}$), 1.82, 1.23 / 26.62, 26.57 (2 x Cy-3^A), 1.72, 1.22 / 26.2 (4), 1.58, 1.04 / 25.0 (Cy-4), 1.55, 0.12 / 31.6 (Cy(II)-2^B), 1.49, 0.70 / 26.0 (Cy-4), 1.46, 0.95 / 26.3 (Cy-3^B), 1.43, 0.94 / 24.4 (Cy-3^B).
GHMBC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 263 K): δ (^{1}H) / δ (^{13}C) = 7.03 / 164.7, 133.2, 123.1 (*o*-Ar^{Cl} / *i*-Ar^{Cl}, *m*-Ar^{Cl}, *p*-Ar^{Cl}), 7.00 / 133.2 (*p*-Ar^{Cl} / *m*-Ar^{Cl}), 6.99 / 180.8, 143.6, 138.8, 135.0, 131.5 (*m*-Mes^A / CN, *p*-Mes^A, *o*-Mes^A, *i*-Mes^A, *m*-Mes^A), 6.93 / 180.8, 143.1, 136.0, 131.1 (*m*-Mes^B / CN, *p*-Mes^B, *i*-Mes^B, *m*-Mes^B), 2.31 / 143.6, 138.8, 131.5 (*p*-CH$_3^A$ / *p*-Mes^A, *o*-Mes^A, *m*-Mes^A), 2.25 / 143.1, 136.8, 131.1 (*p*-CH$_3^B$ / *p*-Mes^B, *o*-Mes^B, *m*-Mes^B), 2.06 / 136.8, 131.1 (*o*-CH$_3^B$ / *o*-Mes^B, *m*-Mes^B), 1.83 / 30.0 (H-2$^{A/B}$ / C-3$^{A/B}$), 1.72 / 30.0 (H-4 / C-3$^{A/B}$).

Boron-containing product from reaction of 12d with diisopropylcarbodiimide (20)

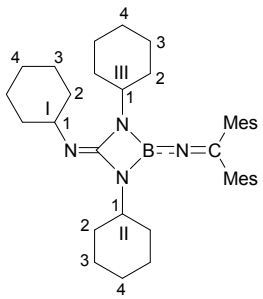


Complex **12d** (10 mg, 0.00770 mmol, 1 eq) was dissolved in [D$_2$]dichloromethane in an NMR tube and the solution was cooled to –78 °C. Diisopropylcarbodiimide (5.0 µl, 4.05 mg, 0.0321 mmol, 4.2 eq) was added and the NMR-tube was transferred to a precooled NMR spectrometer. After full conversion (ca. three hours at room temperature), the mixture was analyzed by NMR in order to identify the B-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):[8] 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).
GCOSY (500 MHz / 500 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H) / δ (^{1}H) = 6.84 / 2.27, 2.15 (*m*-Mes / *p*-CH$_3$, *o*-CH$_3$), 3.90 / 1.10 (CH(I) / CH$_3$(I)), 3.61 / 0.93 (CH(III) / CH$_3$(III)), 3.39 / 0.82 (CH(II) / CH$_3$(II)), 2.27 / 6.84 (*p*-CH$_3$ / *m*-Mes), 2.15 / 6.84 (*o*-CH$_3$ / *m*-Mes), 1.10 / 3.90 (CH$_3$(I) / CH(I)), 0.93 / 3.61 (CH$_3$(III) / CH(III)), 0.82 / 3.39 (CH$_3$(II) / CH(II)).
GHSQC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 6.84 / 130.1 (*m*-Mes), 3.90 / 46.2 (CH(I)), 3.61 / 46.3 (CH(III)), 3.39 / 42.9 (CH(II)), 2.27 / 21.0 (*p*-CH$_3$), 2.15 / 21.5 (*o*-CH$_3$), 1.10 / 25.5 (CH$_3$(I)), 0.93 / 23.2 (CH$_3$(III)), 0.82 / 22.3 (CH$_3$(II)).
GHMBC (500 MHz / 126 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H) / δ (^{13}C) = 6.84 / 171.8, 139.4, 130.1, 21.5, 21.0 (*m*-Mes / CN, *p-Mes*, *m*-Mes, *o*-CH$_3$, *p*-CH$_3$), 3.90 / 152.4, 25.5 (CH(I) / N=C(NR$_2$), CH$_3$(I)), 3.61 / 152.4, 23.2 (CH(III) / N=C(NR$_2$), CH$_3$(III)), 3.39 / 152.4, 22.3 (CH(II) / N=C(NR$_2$), CH$_3$(II)), 2.27 / 139.1, 130.1 (*p*-CH$_3$ / *i-Mes*, *m*-Mes), 2.15 / 171.8, 139.4, 136.4, 130.1 (*o*-CH$_3$ / CN, *p-Mes*, *o*-Mes, *m*-Mes), 1.10 / 46.2, 25.5 (CH$_3$(I) / CH(I), CH$_3$(I)), 0.93 / 46.3, 23.2 (CH$_3$(III) / CH(III), CH$_3$(III)), 0.82 / 42.9, 22.3 (CH$_3$(II) / CH(II), CH$_3$(II)).
NOE (500 MHz, [D$_2$]dichloromethane, 298 K): δ (^{1}H)$_{irr}$ / δ (^{1}H)$_{res}$ = 6.84 / 2.27, 2.15 (*m*-Mes / *p*-CH$_3$, *o*-CH$_3$), 3.90 / 3.61 (CH(I) / CH(III)), 3.61 / 3.90 (CH(III) / CH(I)), 2.27 / 6.84 (*p*-CH$_3$ / *m*-Mes), 2.15 / 6.84 (*o*-CH$_3$ / *m*-Mes).

[8] The resonances resulting from different isopropyl-units will be described as I, II and III, respectively.

Boron-containing product from reaction of 12d with dicycohexylcarbodiimide (21)



Complex **12d** (20.0 mg (0.0154mmol, 1 eq) 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 eq) was added and the NMR-tube was transferred to a precooled NMR spectrometer. After full conversion (ca. three hours at room temperature), the mixture was analyzed by NMR in order to identify the B-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_6]benzene, 293 K):[9] 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).

GCOSY (500 MHz / 500 MHz, [D_2]dichloromethane, 293 K): δ (^{1}H) / δ (^{1}H) = 6.85 / 2.24, 2.13 (*m*-Mes / *p*-CH_3, *o*-CH_3), 3.45 / 1.70, 1.27 (Cy(III)-1 / Cy(III)), 3.04 / 1.75, 0.80 (Cy(I)-1 / Cy(I)), 2.96 / 1.65, 0.77 (Cy(II)-1 / Cy(II)), 2.24 / 6.85 (*p*-CH_3 / *m*-Mes), 2.13 / 6.85 (*o*-CH_3 / *m*-Mes), 1.75 / 3.04, 0.80 (Cy(I) / Cy(I)-1, Cy(I)), 1.70 / 3.45, 1.27 (Cy(III) / Cy(III)-1, Cy(III)), 1.65 / 2.96, 0.77 (Cy(II) / Cy(II)-1, Cy(II)), 0.80 / 3.04, 1.75 (Cy(I) / Cy(I)-1, Cy(I)), 1.27 / 3.45, 1.70 (Cy(III) / Cy(III)-1, Cy(III)), 0.77 / 2.96, 1.65 (Cy(II) / Cy(II)-1, Cy(II)).

GHSQC (500 MHz / 126 MHz, [D_2]dichloromethane, 293 K): δ (^{1}H) / δ (^{13}C) = 6.85 / 130.2 (*m*-Mes), 3.45 / 54.7 (Cy(III)-1), 2.24 / 21.0 (*p*-CH_3), 2.13 / 21.6 (*o*-CH_3).

GHMBC (500 MHz / 126 MHz, [D_2]dichloromethane, 293 K): δ (^{1}H) / δ (^{13}C) = 6.85 / 172.1, 139.7, 130.2, 21.6, 21.0 (*m*-Mes / CN, *i*-Mes, *m*-Mes, *o*-CH_3, *p*-CH_3), 3.04 / 155.9 (Cy(I)-1 / N=C(NR_2)), 2.24 / 139.1, 130.2 (*p*-CH_3 / *p*-Mes, *m*-Mes), 2.13 / 172.1, 139.7, 136.6, 130.2 (*o*-CH_3 / CN, *i*-Mes, *o*-Mes, *m*-Mes).

2D-TOCSY (500 MHz / 500 MHz, [D_2]dichloromethane, 293 K, selected resonances): δ (^{1}H) / δ (^{1}H) = 3.45 / 1.70, 1.58, 1.27, 1.18 (Cy(III)-1 / Cy(III)), 3.04 / 1.75, 1.53, 1.42, 1.07, 0.80 (Cy(I)-1 / Cy(I)), 2.96 / 1.65, 1.49, 1.41, 1.08, 0.77 (Cy(II)-1 / Cy(II)).

Kinetic analysis of the reaction of 12d with diisopropylcarbodiimide

The kinetics of the reaction of **12d** with diisopropylcarbodiimide were followed by ^{1}H-NMR (20 °C, ^{1}H-NMR taken every minute). The Cp-signal of the intermediate **18** (δ = 4.70) and the product **16** (δ = 4.92) were integrated to calculate the respective concentrations.

Series 1: Complex **12d**: 10 mg (0.00770 mmol, 1 eq), diisopropylcarbodiimide: 5.0 µl (4.05 mg, 0.0321 mmol, 4.2 eq).
Series 2: Complex **12d**: 41.7 mg (0.0321 mmol, 1 eq), diisopropylcarbodiimide: 5.00 µl (4.05 mg, 0.0321 mmol, 1 eq).

Calculation of the activation barrier

Consumption of the intermediate:
$[I] = [I]_0 \exp(-k_{obs}\, t)$
$\ln [I] = -k_{obs}\, t + \ln [I]_0$
$[I]_0 = [I] + [P]$

Calcution of k_{obs}:
Linear fit in an ln[I] / t plot

Basis equations:
$\Delta G^{\ddagger} = -R\, T \ln((k_{obs}\, h)/(k_b\, T))$
R = 8.31451 $(m^2 \cdot kg)/(s^2 \cdot K \cdot mol)$
k_b = 1.380658 10^{-23} J/K
h = 6.6260755 10^{-34} J s

[9] The resonances resulting from different cyclohexyl-units will be described as I, II and III, respectively.
Due to the presence of many cyclohexyl-groups, the ^{1}H- and ^{13}C-chemical shifts of the Cy-2, Cy-3- and Cy-4-units could not be fully determined.
The ^{13}C-chemical shift of the carbodiimide-carbon was deduced from the GHMBC.

	k_{obs}	Pearson R^2 for linear fit	$\Delta G^{\ddagger}$ (kJ / mol)	$\Delta G^{\ddagger}$ (kcal / mol)
Series 1	$2.6667\ 10^{-4}\ s^{-1}$	0,9996	91.7	21.9
Series 2	$3.9581\ 10^{-4}\ s^{-1}$	0,9990	90.8	21.7

Kinetic analysis of the reaction of 12d with dicycohexylcarbodiimide

The kinetics of the reaction of **12d** with dicyclohexylcarbodiimide were followed by ^{1}H-NMR (20 °C, ^{1}H-NMR taken every minute). The Cp-signal of the intermediate **19** (δ = 4.68) and the product **17** (δ = 4.92) were integrated to calculate the respective concentrations.

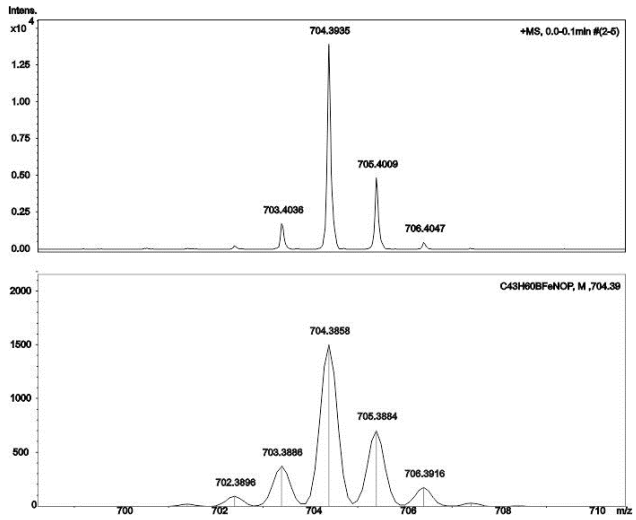
Series 1: Complex **12d**: 20.0 mg (0.0154mmol, 1 eq), dicyclohexylcarbodiimide: 7.0 mg (0.0339 mmol, 2.2 eq).
Series 2: Complex **12d**: 20.0 mg (0.0154mmol, 1 eq), dicyclohexylcarbodiimide: 3.5 mg (0.0170 mmol, 1.1 eq).

Calculation of the activation barrier: see above

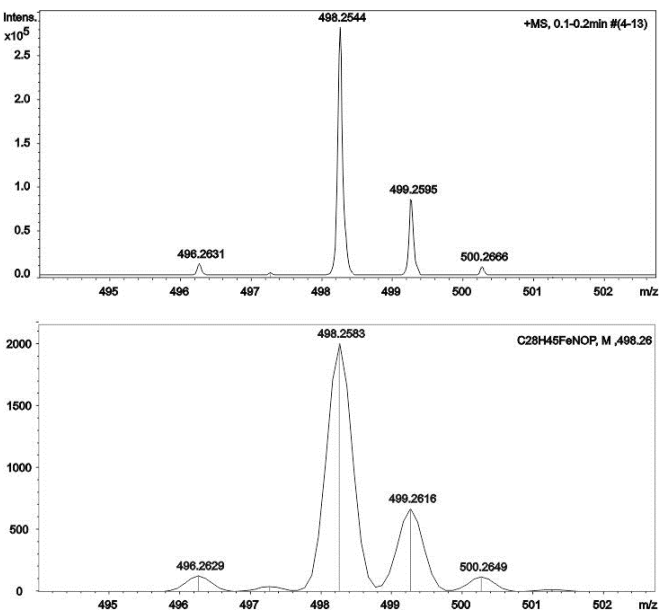
	k_{obs}	Pearson R^2 for linear fit	$\Delta G^{\ddagger}$ (kJ / mol)	$\Delta G^{\ddagger}$ (kcal / mol)
Series 1	$1.5188\ 10^{-4}\ s^{-1}$	0,9997	93.1	22.2
Series 2	$2.0854\ 10^{-4}\ s^{-1}$	0,9985	92.4	22.1

Mass-spectrometric analyses (ESI-MS, positive-ion mode):

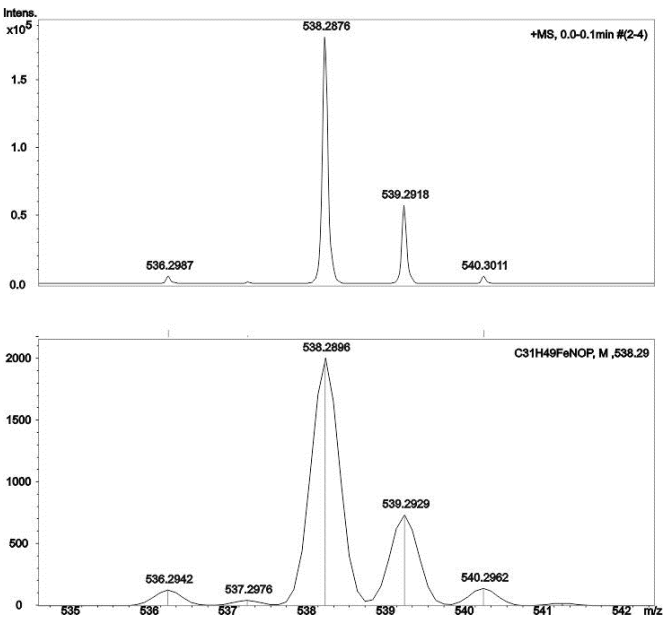
[CpFe(PCy$_3$)(CO)(CNCy)]$^+$[B(3,5-Cl$_2$-Ph)$_4$]$^-$ (12d)



[CpFe(PCy$_3$)(CO)(CN^{i}Pr)]$^+$[B(3,5-Cl$_2$-Ph)$_4$]$^-$ (16)



[CpFe(PCy$_3$)(CO)(CNCy)]$^+$[B(3,5-Cl$_2$-Ph)$_4$]$^-$ (17)



References for supporting information

[s1] R. Anulewicz-Ostrowska, T. Kliś, D. Krajewski, B. Lewandowski, J. Serwatowski, *Tetrahedron Lett.*, 2003, **44**, 7329-7331.

[s2] D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba, M. D. Smith, *Inorg. Chem.*, 2001, **40**, 3810-3814.

[s3] S. Fergus, S. J. Eustace, A. F. Hegarty, *J. Org. Chem.*, 2004, **69**, 4663-4669.

[s4] T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1956**, *3*, 104-124; U. Behrens, F. Edelmann, *J. Organomet. Chem.* **1984**, *263*, 179-182.

[s5] J. R. Jennings, I. Pattison, C. Summerford, K. Wade, B. K. Wyatt, *Chem. Commun.* 1968, 250-251; J. R. Jennings, I. Pattison, K. Wade, *J. Chem. Soc. A*, 1969, 565-568.

[s6] S. Aldridge, R. J. Calder, R. E. Baghurst, M. E. Light, M. B. Hursthouse, *J. Organomet. Chem*., 2002, **649**, 9-14; H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics*, 2004, **23**, 4178-4180.

[s7] W. Clegg, R. Snaith, H. M. M. Shearer, K. Wade, G. Whitehead, *J. Chem. Soc., Dalton Trans.* **1983**, 1309-1317.

[s8] I. Pattison, K. Wade, B. K. Wyatt, *J. Chem. Soc. A*, 1968, 837-842.

[s9] J. Niemeyer, D. A. Addy, I. Riddlestone, M. Kelly, A. L. Thompson, D. Vidovic, S. Aldridge, *Angew. Chem. Int. Ed.* 2011, **50**, 8908-8911.

[s10] Z. Otwinowski, W. Minor, in *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, Methods Enzymol. (Eds: C.W. Carter, R.M. Sweet), Academic Press, 1997, pp 276.

[s11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.

[s12] L. Palatinus, G. Chapuis, *J. Appl. Cryst.*, 1997, **40**, 786-790.

[s13] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487; A. L. Thompson, D. J. Watkin, *J. Appl. Cryst.*, 2010, **43**, 1100-1107.

[s14] A. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13; P. van der Sluis, A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194-201.

[s15] For the synthesis of 2,4,6-triisopropylbenzaldehyde see: D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.*, 2008, **73**, 2811-2818. The synthesis of 2,4,6-triisopropylbenzonitrile was adapted from the correspoding synthesis of 2,4,6-trimethylbenzonitrile. See ref. [s3].

[s16] G. Schmid, H. Nöth, *J. Organomet. Chem.*, 1967, **7**, 129-134