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**PAPER**

# Synthesis and solvent dependent reactivity of chelating bis-*N*-heterocyclic carbene complexes of $Fe^{(II)}$ hydrides†

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The synthesis and isolation of low coordinate methylenebis-(*N*-DIPP-imidazole-2-ylidene)iron$^{(II)}$hydrides, $((^{DIPP}C)_2CH_2)FeH_{2-y}I_y$ ((DIPP = 2,6-di-isopropylphenyl, y = 1 or 0), was complicated by competitive reactions with solvent, rapid reductive elimination of $H_2$ and/or dissociation of the bis-*N*-heterocyclic carbene ligand. Addition of KH to $((^{DIPP}C)_2CH_2)FeI_2$ in THF/haloalkane mixtures enabled a short lived mono-hydride to be trapped by reaction with $CH_2Cl_2$ or *cyclo*-heptylbromide to form $((^{DIPP}C)_2CH_2)FeI(X)$ (X = Cl or Br, respectively). Toluene coordination stabilises iron-mono hydride complexes as $((^{DIPP}C)_2CH_2)Fe^{II}H\{\eta^6\text{-(toluene)}\}$ species, which can be isolated in low yield from combination of borohydride salts and $((^{DIPP}C)_2CH_2)FeI_2$ in toluene, including an imidazole C4 deprotonated carbene-borane, methylene(*N*-DIPP-imidazole-2-ylidene)(*N*-DIPP-4-triethyl-borane-imidazole-2-ylidene)](hydrido)($\eta^6$-toluene)iron. In the absence of toluene, or at short reaction times compounds with empirical formula $((^{DIPP}C)_2CH_2)Fe(H)(HB(R)_3)\cdot LiI$ (R = Et or *sec*-Bu) that function as a masked $Fe^{(II)}$-dihydride are isolated. Whilst $((^{DIPP}C)_2CH_2)Fe(H)(HB(R)_3)\cdot LiI$ was stable for days in $Et_2O$, more polar solvents (MeCN, THF) led to formation of the carbene borane adducts $((^{DIPP}C)_2CH_2)(BR_3)_2$. The addition of CO or *cyclo*-heptylbromide to $((^{DIPP}C)_2CH_2)Fe(H)(HB(R)_3)\cdot LiI$ formed $((^{DIPP}C)_2CH_2)Fe(CO)_3$ and $((^{DIPP}C)_2CH_2)FeBr_2$, respectively with $BR_3$ evolved from both reactions as a by-product.

## Introduction

While iron hydrides are well established in homogenous catalysis and in hydrogenases,[1–5] their intermediacy during substrate reduction at the FeMo co-factor of the Mo-dependent nitrogenase has only recently been demonstrated.[6–10] A number of FeMo co-factor states have been calculated to contain unconventional iron hydrides where iron centres are low coordinate (coordination numbers ≤ 5) and paramagnetic.[11–13] Diamagnetic iron hydrides with coordination numbers of 5 or 6 are well studied,[14,15] however by contrast the chemistry of paramagnetic Fe-hydrido complexes with coordination numbers ≤ 5 is underdeveloped. Recent seminal work has made significant progress by synthesising unprecedented low coordinate and paramagnetic iron hydride complexes,[16–22] with a three coordinate Fe(I) hydride a notable achievement.[23] Subsequent reactivity studies have demonstrated that these 'non-conventional' iron hydrides are effective for the reduction of a range of unsaturated moieties[16,19,21,24] and for hydrodefluorination of fluorocarbons.[25] Of particular note is the reductive cleavage of the N–N double bond of azobenzene by high spin (β-diketiminate)FeH,[24] reactivity reminiscent of nitrogenases. The wider development of low coordinate and/or paramagnetic iron hydrides is imperative due to their potential importance in bioinorganic reduction processes combined with the unprecedented reactivity recently uncovered.

We have recently synthesised distorted tetrahedral iron(II) complexes ligated by a bulky bidentate *N*-heterocyclic carbene ligand, methylenebis-(*N*-DIPP-imidazole-2-ylidene) termed $(^{DIPP}C)_2CH_2$, (DIPP = 2,6-di-isopropylphenyl).[26] $((^{DIPP}C)_2CH_2)FeY_2$ complexes are high spin and have a coordination number of 4 with a range of anionic ligands, Y. Simplistically the $(^{DIPP}C)_2CH_2$ ligand represents a 'neutral analogue' of the mono-anionic β-diketiminates that have facilitated the development of low coordinate iron hydride chemistry. Hoping to utilise the additional electronic and steric flexibility afforded by an exchangeable anionic ligand, $Y^-$, the synthesis of related iron hydride complexes $((^{DIPP}C)_2CH_2)FeH(Y)$ was targeted. A question of particular interest was the stability of these low coordinate paramagnetic iron mono-hydrides and $Fe^{(II)}$-dihydrides. Previous work concluded that low coordinate iron complexes have an energetic preference for electronegative anionic ligands, with the relatively more electropositive hydride ligand being comparably unstable when bonded to paramagnetic, low coordinate iron centres.[20] Herein we describe our studies regarding the installation of hydrides onto the $\{((^{DIPP}C)_2CH_2)Fe^{(II)}\}$ fragment, including their solvent dependent reactivity.

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## Experimental

### General considerations

All reactions were performed using standard glovebox or Schlenk line techniques, unless otherwise specified. Solvents used were either purified by an Innovative Technology PS-MD-5 solvent purification system or distilled from appropriate drying agents and degassed. Deuterated solvents were distilled from appropriate drying agents and degassed. $((^{DIPP}C)_2CH_2)FeI_2$ (compound **1**) and $((^{DIPP}C)_2CH_2)FeBr_2$ were synthesised as previously reported.[26] All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz $^1H$; 100 MHz $^{13}C$; 162 MHz, $^{11}B$ 128 MHz). $^1H$ NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and $^{13}C$ NMR using the centre line of $CD_2Cl_2$ (or other solvent as appropriate) as internal standard. Unless otherwise stated all NMR spectra are recorded at 293 K. Protio-solvent suppression experiments were performed on Varian Unity Inova instruments (flame sealed $d_6$-dmso capillaries used to lock field) using pulse sequences written in-house by Prof. Gareth Morris. Elemental analysis of air sensitive compounds was performed by London Metropolitan University service. Solution magnetic moments were recorded at 293 K using the Evans method.[27,28]

### [Methylenebis(*N*-Dipp-imidazole-2-ylidene)]chloroiodoiron, 2

Lithium triethylborohydride (128 μl of 1 M solution in THF, 0.128 mmol) was added to the stirred solution of **1** (100 mg, 0.128 mmol) at ambient temperature in the mixture of THF (5 ml) and DCM (1 ml). An initial reddish colouration disappeared within seconds to form a pale yellow-brownish solution. After overnight stirring the off-white precipitate was isolated by filtration from the pale green-brown supernatant and dried *in vacuo* to give off-white powder (30 mg, 34%). X-ray quality crystals were isolated from the reaction mixture after standing overnight without stirring at ambient temperature. Characterisation by NMR spectroscopy was hindered by the extremely low solubility of this compound in organic solvents.

For $C_{31}H_{40}ClFeIN_4$ calculated: C, 54.21, H, 5.87, N, 8.16; found: C, 54.18, H, 5.77, N, 8.07.

### [Methylenebis(*N*-Dipp-imidazole-2-ylidene)]bromoiodoiron

**Method A.** A J. Young's NMR tube was charged with equimolar compound **1** (15.6 mg, 0.02 mmol) and $((^{DIPP}C)_2CH_2)FeBr_2$ (13.7 mg, 0.02 mmol) and 0.6 ml THF. Initially the $^1H$ NMR spectrum revealed no reaction, but on heating for 72 h at reflux one new paramagnetic product appeared in the $^1H$ NMR spectrum, with residual **1** and $((^{DIPP}C)_2CH_2)FeBr_2$ also observable. This new product is assigned as $((^{DIPP}C)_2CH_2)FeIBr$ based on a similar $^1H$ NMR spectrum to **1** and on subsequent reactivity studies.

$^1H$ NMR (400 MHz, THF with flame sealed $d_6$-dmso capillary, 293 K), $\delta$: 62.4, 28.6, 5.7, −0.9, −4.7, −5.4, −17.8.

**Method B.** A J. Young's NMR tube was charged with compound **1** (40 mg, 0.051 mmol), 0.6 ml THF and benzyl bromide (6 μl, 0.051 mmol). The tube was rotated for 16 h and then heated to reflux for 3 h. $^1H$ NMR spectroscopy revealed that $((^{DIPP}C)_2CH_2)FeIBr$ was the major species present along with **1** and $((^{DIPP}C)_2CH_2)FeBr_2$ present as minor components.

**Method C.** Lithium triethylborohydride (128 μl of 1 M solution in THF, 0.128 mmol) was added to the stirred solution of **1** (100 mg, 0.128 mmol) at ambient temperature in the mixture of THF (5 ml) and *cyclo*-heptylbromide (0.1 ml). An initial reddish colouration disappeared within seconds to form a pale yellow-brownish solution. After stirring for 2 h the solution was concentrated to 0.5 ml and the $^1H$ NMR spectrum was recorded. This revealed that $((^{DIPP}C)_2CH_2)FeIBr$ was the major product along with $((^{DIPP}C)_2CH_2)FeI_2$ as a minor product. No $((^{DIPP}C)_2CH_2)FeBr_2$ was observable by $^1H$ NMR spectroscopy.

Attempts to isolate $((^{DIPP}C)_2CH_2)FeIBr$ from each method by fractional recrystallisation failed, frustrating full characterisation.

### Reaction of compound 1 with $NaBH_4$: formation of 4

A J. Young's NMR tube was charged with **1** (39 mg, 0.05 mmol), sodium borohydride (3.8 mg, 0.1 mmol) and THF (0.6 ml). A dark red-brown solution formed upon sonication (30 min). After overnight mixing the contents of the NMR tube were filtered and layered with pentane, producing a small quantity of X-ray quality crystals of the carbene borane adduct **4**. Compound **4** could not be isolated pure due to intractable paramagnetic and diamagnetic by-products.

### Reaction of 1 with $LiBEt_3H$: formation of 5

A J. Young's NMR tube was charged with **1** (20 mg, 0.026 mmol), MeCN (0.6 ml) and lithium triethylborohydride (51 μl of 1 M solution in THF, 0.051 mmol), resulting in the formation of a dark-yellow solution. After standing overnight at ambient temperature $^1H$ NMR spectroscopy revealed a minor paramagnetic component and a major diamagnetic component. The solution was concentrated to 0.3 ml and left overnight to yield yellow X-ray quality crystals of **5**:

$^1H$ NMR (400 MHz, MeCN, 293 K), $\delta$: 7.45–7.37 (m, 2H, C4 aromatic protons of DIPP), 7.26–7.15 (m, 4H, aromatic protons at C3 and C5 of DIPP), 6.98, 6.89, 6.82 (app. s, 2H + 2H + 2H, N-C*H*$_2$-N + N-C*H*=CH-N + N-CH=C*H*-N), 2.50 (app. s, 4H, C*H*$(CH_3)_2$), 1.26–0.90 (overlapping multiplets, 24H, CH(C*H*$_3)_2$), 0.68–0.44 (overlapping multiplets, 30H, 2 × B(C*H*$_2$-C*H*$_3)_3$).

$^{11}B$ NMR (128 MHz, 293 K), $\delta$ −13.4 (s)

### $((^{DIPP}C)_2CH_2)Fe(H)(HBEt_3)\cdot LiI$ 6

**Method A.** Lithium triethylborohydride (0.77 ml of 1 M solution in THF, 0.77 mmol) was added to the stirred $Et_2O$ suspension (25 ml) of **1** (300 mg, 0.38 mmol) at ambient temperature, leading to immediate formation of a dark-red solution. After 30 min stirring this was filtered, concentrated to 5 ml and stored at −22 °C overnight. The resulting dark-red microcrystalline material was filtered cold (−22 °C), washed with pentane (2 × 10 ml) and dried *in vacuo* to afford a dark-red solid (250 mg, 87%).

$^1$H NMR (300 MHz, $C_6D_6$, 293 K), *δ*: 4.0 (v br), 1.3, −2.7, −5.2, −6.8, −9.0, −12 (v br), −25.2.

For $C_{37}H_{57}BFeILiN_4$ calculated: C, 58.60, H, 7.58, N, 7.39; found: C, 58.45, H, 7.49, N, 7.22.

Evans ($C_6D_6$, toluene capillary): averaged value 4.02 $\mu_B$.

**Method B.** Lithium triethylborohydride (0.256 ml of 1 M solution in THF, 0.256 mmol) was added to a stirred toluene suspension (15 ml) of **1** (100 mg, 0.128 mmol) at ambient temperature, leading to the immediate formation of a dark-red mixture. After 40 min stirring the dark-red solution was separated by filtration, the solvent was removed *in-vacuo*, the resulting solid washed with pentane (2 × 30 ml) and dried *in vacuo* to afford bronze-red powder (50 mg, 52%). The $^1$H NMR spectrum was identical to material produced *via* method A.

For $C_{37}H_{57}BFeILiN_4$ calculated: C, 58.60, H, 7.58, N, 7.39; found: C, 58.47, H, 7.65, N, 7.27.

### $((^{DIPP}C)_2CH_2)Fe(H)(HB(sec\text{-}Bu)_3)\cdot LiI$ 7

Lithium tris(*sec*-butyl)borohydride (0.2 ml of 1 M solution in THF, 0.2 mmol) was added to a stirred benzene suspension (15 ml) of **1** (78 mg, 0.1 mmol) at ambient temperature, leading to the formation of a dark-red solution within 10 min. This solution was concentrated and pentane was added (30 ml). The resulting brown precipitate was separated by filtration, washed with pentane (2 × 10 ml) and dried *in vacuo* to afford bronze-coloured solid (50 mg, 59%).

For $C_{43}H_{69}BFeILiN_4$ calculated: C, 61.30, H, 8.25, N, 6.65; found: C, 61.21, H, 8.09, 6.79.

$^1$H NMR (300 MHz, $C_6D_6$, 293 K): Only four extremely broad resonances were observed at: 7.5, 3.64, 1.44 and 0.91 ppm.

Evans ($C_6D_6$, toluene capillary): average 3.22 $\mu_B$.

### Methylenebis(*N*-Dipp-imidazole-2-ylidene)iron-tricarbonyl, 8

A J. Young's NMR tube was charged with compound **6** (25 mg) and $C_6D_6$ (0.6 ml). The red solution was degassed by three freeze-pump-thaw cycles and exposed to 1 bar of CO. The contents of the NMR tube were allowed to mix overnight under a CO atmosphere by rotation of the tube forming a yellow-brown solution, which was degassed and exposed to $N_2$. The NMR spectra indicated complete consumption of the starting material and formation of a diamagnetic compound along with minor paramagnetic impurities. IR spectroscopy confirmed the major Fe(CO) containing product was consistent with **8**:

IR (THF solution) νCO (cm$^{-1}$): 1968, 1891, 1864.

A small quantity of X-ray quality yellow crystals deposited from $C_6D_6$ solution on standing. Numerous attempts to obtain pure solid material failed due to intractable paramagnetic impurities and the instability of compound **8** under vacuum.

### [Methylene(*N*-Dipp-imidazole-2-ylidene)(*N*-Dipp-4-triethylborane-imidazole-2-ylidene)](hydrido)($\eta^6$-toluene)iron, 9

Lithium triethylborohydride (0.51 ml of a 1 M solution in THF, 0.51 mmol) was added to a stirred toluene suspension (20 ml) of **1** (200 mg, 0.26 mmol) at ambient temperature, leading to immediate formation of a dark-red solution which was stirred for 45 min. This was filtered and the solvent removed *in-vacuo*. The resulting dark-red solid was extracted with pentane (50 ml) and filtered. The filtrate was concentrated to 7 ml and kept at −22 °C for 3 days which resulted in the precipitation of a small amount of X-ray quality red plates.

$^1$H NMR (400 MHz, $CD_2Cl_2$, 293 K), *δ*: 7.63–7.59 (overlapping multiplets, 8H, aromatic protons on DIPP substituents + N-C*H*$_2$-N), 6.30 (app. s, 1H, N-C*H*═CH-N), 6.20 (app. s, 1H, N-CH═C*H*-N), 5.67–5.53 (overlapping multiplets, 1H + 2H + 2H, aromatic protons of coordinated toluene), 5.10 (s, 1H, N-C(BEt$_3$)═C*H*-N), 2.81 ($J_{H\text{-}H}$ = 6.81 Hz), 2.56 ($J_{H\text{-}H}$ = 6.94 Hz), 2.37 ($J_{H\text{-}H}$ = 6.47 Hz), 2.30 ($J_{H\text{-}H}$ = 6.64 Hz) (septets, 1H +1H +1H +1H, 4 × inequivalent C*H*(CH$_3$)$_2$), 1.82 (s, 3H, C*H*$_3$ of coordinated toluene), 1.29 (q, 6H, B(C*H*$_2$-CH$_3$)$_3$, $J_{H\text{-}H}$ = 7.82 Hz), 1.21–1.05 (overlapping multiplets, 24 H, 4 × CH(C*H*$_3$)$_2$), 0.88 (t, 9H, B(CH$_2$-C*H*$_3$)$_3$, $J_{H\text{-}H}$ = 7.06 Hz), −10.26 (s, 1H, hydride).

### [Methylenebis(*N*-Dipp-imidazole-2-ylidene)] (hydrido) ($\eta^6$-toluene)iron(II) iodide, 10

**Method A.** Lithium triethylborohydride (51 µl of 1 M solution in THF, 0.051 mmol) was added to the stirred toluene suspension (5 ml) of **1** (20 mg, 0.026 mmol) at ambient temperature, leading to immediate formation of a dark-red solution which was allowed to stir for 15 min. 12-Crown-4 (8.3 µl, 0.051 mmol) was added and the mixture stirred for 2 h, the dark red solution was then filtered and layered with pentane (15 ml), the mixture was left to crystallise for 7 days. A small quantity of large dark yellow X-ray quality crystals precipitated out of the red solution.

$^1$H NMR (400 MHz, $CD_2Cl_2$, 293 K), *δ*: 7.85 (app. s, 2H, N-C*H*═CH-N) 7.56–7.49, 7.41–7.36, 7.35–7.30 (multiplets, 2H + 2H + 2H, aromatic protons on DIPP substituents), 7.27–7.20, 7.19–7.12, 7.10–7.03 (multiplets), 6.93 (app. s, 2H, N-CH═C*H*-N), 6.12 (s, 2H, N-C*H*$_2$-N), 6.08 (app. s, 2H, aromatic protons of coordinated toluene), 5.80 (app. s, 2H, aromatic protons of coordinated toluene), 4.77 (app. s, 1H, aromatic proton of coordinated toluene), 3.44 and 2.77 (app. singlets, 2H + 2H, 2 × inequivalent C*H*(CH$_3$)$_2$), 1.78 (s, 3H, C*H*$_3$ of coordinated toluene), 1.45–1.35, 1.32–1.21, 1.20–1.09, 0.90–0.84 (overlapped multiplets, 6H + 6H +6H +6H, 4 × inequivalent C(C*H*$_3$)$_2$), −10.22 (s, 1H, hydride).

**Method B.** Lithium triethylborohydride (256 µl of 1 M. solution in THF, 0.256 mmol) was added to a stirred toluene suspension (8 ml) of **1** (100 mg, 0.128 mmol) at ambient temperature, leading to immediate formation of a dark-red solution. This was stirred for 15 min and then 12-crown-4 (41 µl, 0.256 mmol) was added and the mixture stirred for a further 1.5 h. Trimethylphosphine (0.64 ml of 1 M. toluene solution, 0.64 mmol) was then added. Within approx. 5 min the initial dark-red suspension changed colour to dark yellow, stirring was continued for 2 h, then the dark yellow solution was filtered off and layered with pentane (40 ml). A dark yellow precipitate (containing X-ray quality crystals) was filtered off after 7 days and dried *in vacuo* to afford dark-yellow microcrystalline solid of **10** (by NMR spectroscopy and X-ray crystallography).

**Method C.** Lithium triethylborohydride (51 µl of 1 M solution in THF, 0.051 mmol) was added to a stirred toluene suspension (5 ml) of **1** (20 mg, 0.026 mmol) at ambient temperature. After stirring for 15 min 12-crown-4 (8.3 µl, 0.051 mmol) was added and the mixture stirred for a further 1.5 h, followed by addition of cyclooctene (10 µl, 0.77 mmol). Stirring was then continued for 2 h and the dark red solution was filtered and layered with pentane (15 ml). After 7 days a small number of large dark yellow X-ray quality crystals precipitated out of the red solution and were confirmed to be **10** by unit cell measurements and $^1$H NMR.

Reaction of **1** with one eq. of *p*-tolyl magnesium bromide

A J. Young's NMR tube was charged with **1** (20 mg, 0.026 mmol) and THF (0.6 ml). To this solution *p*-tolyl magnesium bromide (26 µl of 1 M solution in THF, 0.026 mmol) was added resulting in a rapid colour change to brown and precipitation of a small amount of light-brown solid. The precipitate was allowed to settle and a $^1$H NMR spectrum recorded. Attempts to isolate analytically pure solid failed.

$^1$H-NMR (400 MHz, THF+(CD$_3$)$_2$SO capillary, 293 K), $\delta$: 59.0 30.1; 7.1; 6.4; −1.6; −4.9l −8.9; −14.2; −19.6; −27.1; −42.8.

## Results and discussion

Addition of one equivalent of LiBEt$_3$H to (($^{\text{DIPP}}$C)$_2$CH$_2$)FeI$_2$, **1**, in THF led to complete consumption of **1** and the formation of a single (($^{\text{DIPP}}$C)$_2$CH$_2$)Fe containing product (by $^1$H NMR) which was diamagnetic and displayed an hydride resonance (at −7.6 ppm). The expected by-product THF-BEt$_3$ was the only observable boron containing species (by $^{11}$B NMR). Attempts to isolate this hydride containing species (with and without removal of the THF-BEt$_3$ by-product) were frustrated by the reformation of **1** (by $^1$H NMR and unit cell comparison on crystallised material). The exact identity of this hydride species has eluded us but its diamagnetic nature precludes a simple (($^{\text{DIPP}}$C)$_2$CH$_2$)FeH(I) formalism as all previously reported structurally characterised four coordinate Fe$^{\text{II}}$-hydrides[23] and all (($^{\text{DIPP}}$C)$_2$CH$_2$)FeY$_2$ complexes synthesised to date are paramagnetic. Support for a mono-hydride formulation for the product from addition of one equivalent of LiBEt$_3$H to **1** in THF was provided by the repeating the reaction in the presence of excess dichloromethane which rapidly led to the precipitation of poorly soluble (($^{\text{DIPP}}$C)$_2$CH$_2$)FeCl(I), **2**. This is consistent with the well precedented trapping of an Fe$^{\text{II}}$-hydride by exchange for halide.[29] The structure of **2** (Fig. 1) is comparable to that previously reported for **1** and (($^{\text{DIPP}}$C)$_2$CH$_2$)FeBr$_2$, with iodide occupying the less sterically congested pseudo-axial site in the distorted tetrahedral geometry.[26] Analogous reactivity was observed when one equivalent of LiBEt$_3$H was added to **1** in THF containing excess *cyclo*-heptylbromide, rapidly (< 1 h) forming (($^{\text{DIPP}}$C)$_2$CH$_2$)FeI(Br). In contrast there is no reaction between **1** and *cyclo*-heptylbromide (over 24 h) whilst CH$_2$Cl$_2$ only reacts slowly with **1** requiring three days for complete consumption of **1**. This disparate reactivity confirms that the haloalkanes are intercepting an iron-hydride, tentatively assigned as [(($^{\text{DIPP}}$C)$_2$CH$_2$)FeI$_2$(H)]$^-$, **3**, to produce (($^{\text{DIPP}}$C)$_2$CH$_2$)FeI(X).

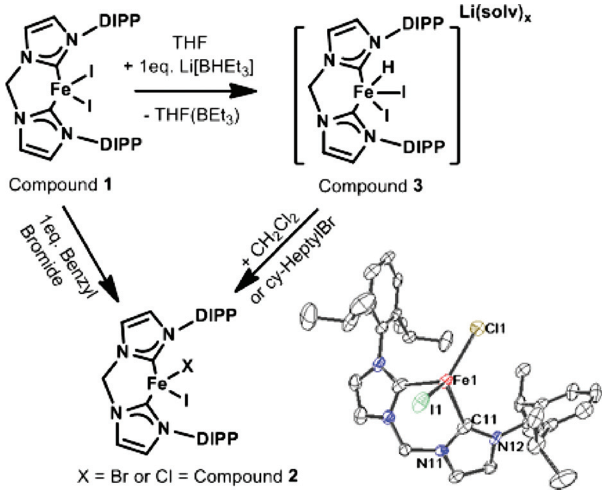

**Fig. 1** Formation of (($^{\text{DIPP}}$C)$_2$CH$_2$)FeI(X). Right, ORTEP structure of **2** (50% probability ellipsoids and hydrogens omitted for clarity) Selected bond lengths (Å) and angles (°): Fe–C = 2.095(14) and 2.105(11), C–Fe–C = 88.7(5).

The observed reformation of **1** on standing from the initially formed diamagnetic mono-hydride, **3**, may proceed by a ligand scrambling mechanism, with mass balance dictating that equimolar **1**, (($^{\text{DIPP}}$C)$_2$CH$_2$)FeH$_2$ and LiI be produced, although **1** is the only (($^{\text{DIPP}}$C)$_2$CH$_2$)Fe containing soluble product observed. Confirmation that ligand scrambling can occur in related (($^{\text{DIPP}}$C)$_2$CH$_2$)FeXY systems was provided by mixing **1** and (($^{\text{DIPP}}$C)$_2$CH$_2$)FeBr$_2$, in THF solution. This results in the formation of a new paramagnetic product consistent with (($^{\text{DIPP}}$C)$_2$CH$_2$)FeBr(I) (by $^1$H NMR), which could also be independently prepared by addition of one equivalent of benzyl bromide to **1**.

The extension of a ligand scrambling mechanism to a mixed hydride/iodide system would require the proposed dihydride by-product '(($^{\text{DIPP}}$C)$_2$CH$_2$)FeH$_2$', to be unstable, or not observable by $^1$H NMR. Low coordinate, paramagnetic Fe$^{(\text{II})}$ hydrides ($\leq$ 5) are extremely rare,[16,20,23,30] with no dihydrido species, L$_2$Fe$^{(\text{II})}$H$_2$, reported to date to the best of our knowledge, suggesting a fundamental instability of these complexes. Indeed Girolami *et al.*, have previously concluded that (dippe)FeH$_2$ (dippe = 1,2-bis-(diisopropyl-phosphinoethane) is unstable with respect to H$_2$ loss.[31] This was indicated by (i) the high spin complex (dippe)FeEt$_2$ undergoing β-hydride elimination followed by rapid H$_2$ loss, and (ii) hydrogenolysis of (dippe) Fe(CH$_2$C$_6$H$_4$-*para*-Me)$_2$ generating ($\eta^6$-arene)Fe(dippe) complexes and no Fe–H species. Exchange of dippe for the bis-NHC chelating ligand ($^{\text{DIPP}}$C)$_2$CH$_2$ will generate a more electron rich iron centre due to the superior σ donor properties of NHCs, classically this would be expected to slow reductive elimination and potentially enhance the stability of a low coordinate Fe-dihydride. Combination of **1** with two equivalents of KH resulted in no reaction in arenes or Et$_2$O due to poor solubility

(**1** is recovered unchanged after 24 h). Use of the more polar solvent THF led to rapid gas evolution and the formation of intractable products. Holland *et al.*, have previously reported that strong field ligands (*e.g.*, CO) result in rapid reductive elimination from a low-coordinate $Fe^{(II)}H$,[16] and it is feasible that strong field NHC ligands also induce rapid $H_2$ reductive elimination from low coordinate $((^{DIPP}C)_2CH_2)FeH_2$. In contrast to the isolable Fe-($N_2$) complexes observed on $H_2$ loss from β-diketiminate ligated iron-hydride complexes, intractable products are formed from addition of KH to **1** under one atmosphere of $N_2$ or Argon, with no evidence for $N_2$ coordinated complexes (by IR spectroscopy) from this and all subsequent reactions.

To facilitate the observation of any intermediate hydrido-iron species addition of two equivalents of soluble sources of hydride to **1** was investigated. The combination of $NaBH_4$, $LiBHEt_3$ or LiBH(*sec*-Bu)$_3$ with **1** in THF or MeCN initially produced short lived paramagnetic complexes which frustrated all isolation attempts. The carbene borane adducts were ultimately the major boron and carbene containing products observed in solution, with **4** and **5** (Fig. 2) isolated from the addition of two equivalents of $NaBH_4$ or $LiBHEt_3$, respectively, to **1**. The structures of **4** and **5** are unremarkable, with **5** having a significantly longer B–C bond relative to **4**, as expected due to steric destabilisation (Fig. 2).[32] The carbene-borane adducts are presumably formed from cleavage of the Fe–C bond followed by subsequent carbene coordination to a borane species present in solution after metathetical transfer of hydride to iron complex **1**. This is consistent with '$((^{DIPP}C)_2CH_2)FeH_2$' complexes being unstable in THF, with dissociation of the bis-carbene taking place, either directly from a $((^{DIPP}C)_2CH_2)FeH_2$ species or after loss of $H_2$.

In contrast the reaction of **1** with two equivalents of $LiBHEt_3$ in $Et_2O$ led to a rapid colour change to red and the formation of one major paramagnetic complex that persisted for days in solution. The $^1H$ NMR spectrum revealed at least six new broad paramagnetically shifted resonances. The formation of the expected by-product THF-$BEt_3$ was confirmed by $^{11}B$ NMR. Filtration, followed by subsequent recrystallisation led to a microcrystalline solid in good yield (87%), on which elemental analysis was consistent with an iron complex with the empirical formula of $((^{DIPP}C)_2CH_2)Fe(H)(HBEt_3)\cdot LiI$, **6**. Replacing $LiBEt_3H$ with LiBH(*sec*-Bu)$_3$ resulted in a similar outcome, generating a paramagnetic species (by $^1H$ NMR) that afforded a microcrystalline solid with an elemental composition consistent with $((^{DIPP}C)_2CH_2)Fe(H)(HB(\textit{sec}\text{-Bu})_3)\cdot LiI$, **7**. Whilst the unambiguous characterisation of **6** or **7** by X-ray diffraction has been frustrated in our hands due to their microcrystalline nature paramagnetic Fe(II) borohydrides are precedented with both bidentate and tridentate supporting ligands.[33,34] Attempts to confirm the presence of B–H and Fe–H moieties in **6** and **7** by infrared spectroscopy (and for B–H by $^{11}B$ NMR spectroscopy) in solution were unsuccessful. Compound **6** was found to be EPR silent disfavouring a reduced $Fe^{(I)}$ $S = ½$ complex and more consistent with a high or intermediate spin $Fe^{(II)}$ complex (supported by the Evans method solution magnetic moments of 4.0 and 3.3 $\mu_B$ for **6** and **7**, respectively).[22] The observed solubility of **6** and **7** in arene solvents disfavours solvent separated ion pairs, instead it is feasible that iodide remains coordinated to Fe and the lithium cations in **6** and **7** are coordinated to two aryl rings of the DIPP *N*-substituents intra- or intermolecularly (Fig. 3). Related arene entrapment of $Na^+$ by an iridium-bis carbene compound and of $Li^+$ by $(aryl)_2MnI$ have been reported.[35,36] A Li—arene coordinated species is also consistent with elemental analyses being free of etherate solvents. Based on the empirical formula, observed paramagnetism and reactivity studies we tentatively

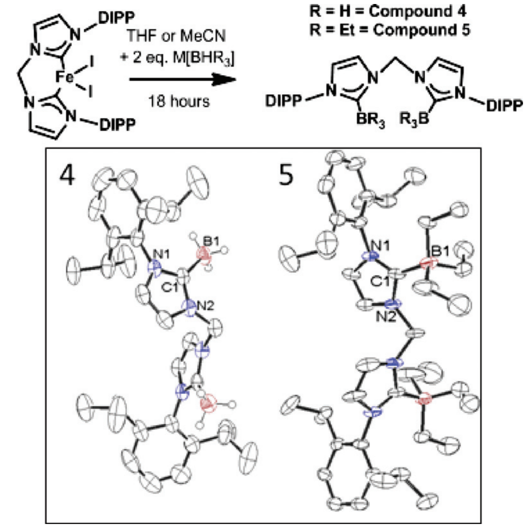

**Fig. 2** Formation of carbene borane adducts from addition of M $[BHR_3]$ to **1** in THF or MeCN. Inset bottom, ORTEP representations of **4** and **5** (50% probability ellipsoids and hydrogens omitted for clarity), selected bond lengths (Å) for **4**: B1–C1 = 1.584 (5), for **5**: B1–C1 1.651(6).

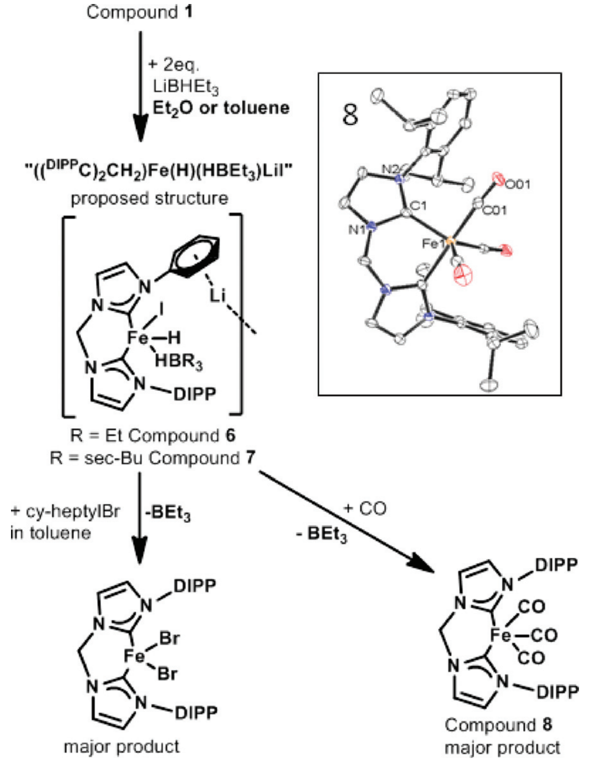

**Fig. 3** Schematic for the production of $((^{DIPP}C)_2CH_2)FeBr_2$ and **8** *via* addition of excess *cyclo*-heptylbromide and CO, respectively to **6** (proposed structure of **6** also shown). Inset right, ORTEP representations of **8** (50% probability ellipsoids and hydrogens omitted for clarity).

assign **6** and **7** as the five coordinate complex, $((^{\text{DIPP}}C)_2CH_2)Fe(H)(HBEt_3)\cdot LiI$ (Fig. 3 centre left).

Compound **7** proved to be extremely sensitive to carbene dissociation, forming complex mixtures on standing in $Et_2O$ that contained carbene borane adducts (by $^{11}B$ NMR). In contrast the $LiBEt_3H$ derived product **6** was stable in $Et_2O$ for days. This disparity we attribute to the greater steric pressure in the iron coordination sphere of **7** generated by the bulkier *sec*-Bu groups, with steric pressure well documented to assist carbene dissociation from electron rich Fe centres.[37–40] All subsequent studies concentrated on **6** in $Et_2O$ or arene solvents, as **6** decomposes readily in neat THF. As the synthesis of **6** utilises $LiBEt_3H$ as a 1 M THF solution the sensitivity to higher concentrations of THF is attributed to enhanced solvation of ionic species (*e.g.*, LiI) in neat THF enabling formation of a different Fe species by loss of $Li(solv)_xI$.

The presence of $BEt_3$ in compound **6** was supported by the addition of excess *cyclo*-heptylbromide to a $C_6D_6$ solution of **6**. This formed $BEt_3$ and $((^{\text{DIPP}}C)_2CH_2)FeBr_2$ as the only $((^{\text{DIPP}}C)_2CH_2)Fe$ containing species. Importantly *cyclo*-heptane was also observed (by $^{13}C\{^1H\}$ NMR spectroscopy) consistent with hydride/halide exchange from an Fe species that reacts as an $Fe^{(II)}$-dihydride equivalent (Fig. 3, bottom left). The functional 'dihydride' formulation of **6** is consistent with the disparate reactivity observed on addition of *cyclo*-heptylbromide to **3** which was tentatively formulated as a mono-hydride Fe species. In contrast to **6**, the latter only forms $((^{\text{DIPP}}C)_2CH_2)FeBrI$ as expected due to the presence of only one hydride ligand to exchange for bromide. Further confirmation of the presence of $BEt_3$ in **6** was forthcoming from the exposure of a $C_6D_6$ solution of **6** (from dissolution of analytically pure red microcrystalline **6**) to one atmosphere of CO. This formed the tricarbonyl complex $((^{\text{DIPP}}C)_2CH_2)Fe(CO)_3$, **8**, as the major Fe(CO) species in solution (by IR spectroscopy), along with $BEt_3$ as the only boron containing by-product (by $^{11}B$ NMR). The repeated evolution of $BEt_3$ from **6** despite the absence of any observable $^{11}B$ resonances in recrystallised **6** clearly indicates that the borane is coordinated to the paramagnetic Fe centre in this complex. As decomposition of **6** in arene solvents is slow at 25 °C (7 days for full consumption of **6**) the formation of **8** must proceed *via* initial ligation of CO to Fe, which starts a multistep reaction that includes borane dissociation, reduction of Fe(II) to Fe(0) (presumably by elimination of $H_2$) and trapping of the Fe(0) species by additional CO. The reductive elimination of $H_2$ from $Fe^{(II)}$ species initiated by Lewis base coordination (*e.g.*, CO, $N_2$, CNR) is documented, including from low coordinate iron hydrides,[16,41] whilst CO coordination to Fe inducing B–H cleavage and subsequent reductive elimination to a $Fe^0(CO)_x$ species is also precedented.[42]

The structure of **8** (Fig. 3) is trigonal-bipyramidal (angles in the equatorial plane sum to 359.9°), with one axial site and two equatorial sites occupied by CO. The Fe–CO bond distances do not show any significant difference between the CO *trans* to carbene and the two carbonyls in the equatorial plane. The metallacycle is not significantly strained, with a bite angle and average yaw angle of 86.31 and 5.7°, respectively (yaw angle is the in-plane distortion of the NHC imposed by metallacycle steric constraints, and is defined as the difference between the two M–C–N angles divided by two).[43] The ν(CO) stretching frequencies of **8** at 1968, 1891 and 1864 $cm^{-1}$ (in THF solution) are lower than the analogous *cis*-phosphine ligated species (*e.g.*, $dppeFe(CO)_3$ = 1978, 1910 and 1891 $cm^{-1}$)[44] consistent with the stronger σ donor power of the NHC. Whilst compound **8** is formed as the major product (by IR spectroscopy) it was stable in solution only under a CO atmosphere, under an $N_2$ atmosphere or dynamic vacuum **8** decomposes to an intractable mixture.

As the persistence of LiI in solution was complicating the formation of low coordinate '$((^{\text{DIPP}}C)_2CH_2)$Fe-hydrides' the reactivity of **1** with $LiBHR_3$ in toluene was investigated to favour rapid precipitation of inorganic salt by-products and enable access to LiI free '$((^{\text{DIPP}}C)_2CH_2)Fe(H)Y$' species. Combination of **1** and one equivalent of $LiBEt_3H$ (1 M in THF) with toluene as solvent led to an $^1H$ NMR spectrum containing two major species consistent with the paramagnetic compounds **1** and **6**. $BEt_3$ was again observed as the only boron containing by-product, along with the precipitation of microcrystalline $Li(THF)_3(I)$ (by unit cell comparison).[45] The observation of **1** suggests a non-stoichiometric reaction in toluene in contrast to reactivity in neat THF, which produced the diamagnetic mono-hydride **3**. The addition of two equivalents of $LiBEt_3H$ to **1** in toluene results in complete consumption of **1** and the formation of **6** as the only observable Fe containing product (by $^1H$ NMR spectroscopy). The solvent disparity between arene/$Et_2O$ compared to THF we attribute to the removal of the first equivalent of LiI from the reaction mixture by precipitation in toluene/$Et_2O$ solvents, converting **3** to a lower coordinate '$((^{\text{DIPP}}C)_2CH_2)FeH(I)$' species, which then rapidly reacts with a second equivalent of $LiBEt_3H$ to produce **6**. In contrast to $Et_2O$ solution (where **6** is stable for > 7 days) in arene solvents **6** reacts slowly to give a mixture of complexes including $^1H$ NMR resonances indicating $\eta^6$-aryl coordination to a diamagnetic iron centre. We therefore subsequently sought to isolate and optimize the synthesis of the $\eta^6$-arylFe species as a potential $((^{\text{DIPP}}C)_2CH_2)FeH$ synthon for subsequent transformations by aryl displacement.[46]

## Synthesis of $[((^{\text{DIPP}}C)_2CH_2)FeH(\eta^6\text{-toluene})]$ complexes

After combination of **1** and two equivalents of $LiBEt_3H$ in toluene the resultant red solution was filtered, dried and washed with pentane (to remove $BEt_3$). This led to the extraction of free $BEt_3$ and surprisingly a diamagnetic pentane soluble $((^{\text{DIPP}}C)_2CH_2)Fe$ containing product that displayed a hydride resonance at −10.26 ppm. Recrystallisation from pentane (10 days −20 °C) produced complex **9** in low yield (Fig. 4 top inset), which contained an $\eta^6$ toluene ligand and a deprotonated anionic abnormal carbene-borane, with the $((^{\text{DIPP}}C)_2CH_2)$ ligand remaining coordinated to Fe in a bidentate fashion. The $\eta^6$-toluene moiety is symmetrically capping the $((^{\text{DIPP}}C)_2CH_2)FeH$ fragment, with the C1–Fe–C5 and arene planes nearly orthogonal (80.35°), with an arene-centroid-Fe distance of 1.577 Å. Both values are closely comparable to the related complex $[(\eta^6\text{-}C_7H_8)(\mu\text{-OH})(H)Fe\{Sn[CH(SiMe_3)_2]_2\}_2]$.[47] The yaw angles for $((^{\text{DIPP}}C)_2CH_2)$ in **9** (average 7.0°) confirm the absence of significant strain in the metallacycle.[43,48,49] The Fe–C(carbene) bonds (1.966(5) and 1.970(5) Å) are unremarkable for octahedral $Fe^{II}$,[50] whilst the B–C bond length (1.647(10) Å) is elongated

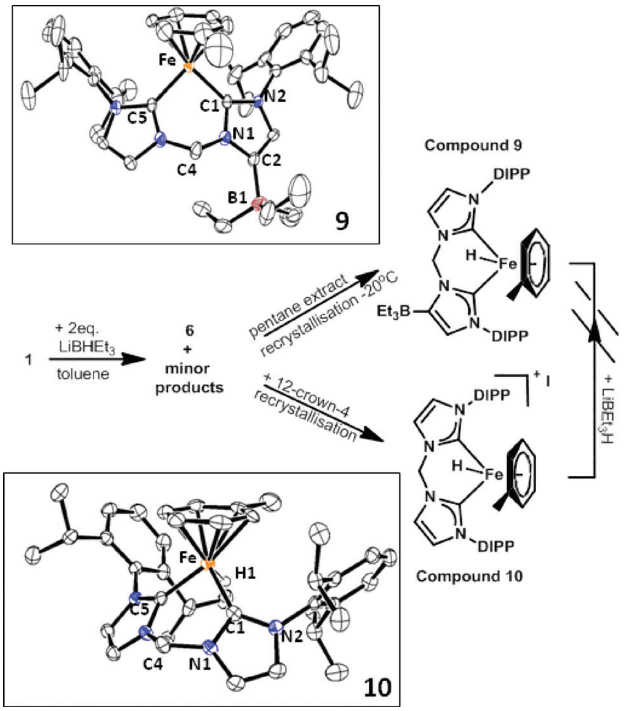

**Fig. 4** Schematic for the formation of compounds **9** and **10**. ORTEP representations of **9** (inset top) and **10** (inset bottom) at 50% probability ellipsoids and hydrogens omitted for clarity apart from the Fe–H of **10** Selected bond lengths (Å) and angles (°) for **9**: B1–C2 = 1.647(10) Fe–C1 = 1.966(5) and Fe–C5 = 1.970(5); for **10** Fe–C1 1.952(3) and Fe–C5 = 1.951(3).

again indicating steric weakening of the B–C bond.[32] The hydride could not be located in the penultimate Fourier difference map, but the formulation of **9** as an $Fe^{(II)}$ hydride is based on the diamagnetism and the integral of one hydride resonance observed spectroscopically on dissolution of these crystals in $CD_2Cl_2$. The existence of **9** as an arene capped species is in contrast to the related (β-diketiminate)-FeH complex, 1,3-$^tBu_2$-1,3-bis-(2,6-diisopropyl-phenylimido)FeH, which is a three coordinate iron-hydride that displays no propensity to bind toluene.[23] This disparity can be attributed to a more open iron centre in **9** (the *N*-DIPP substituent steric bulk is located further from the iron centre relative to the bulky β-diketiminate analogue).[51]

Mechanistically the formation of **6** and **9** can be viewed as addition of a second equivalent of $LiBEt_3H$ to a transient mono hydride species, '$((^{DIPP}C)_2CH_2)$FeH(I)' (Fig. 5). $LiBEt_3H$ can either coordinate to Fe to form **6** or deprotonate the carbene to ultimately form **9** on capping with toluene. Deprotonation of a metal coordinated carbene at the alkenyl position to generate an abnormal carbene has precedent,[52,53] as does deprotonation of carbene precursors by $LiBEt_3H$ to generate carbene borane adducts.[32] The low yield of **9** suggests that the deprotonation pathway is kinetically disfavoured, with coordination of $[HBEt_3]^-$ to iron dominating. Whilst **9** is only produced in poor yield it is noteworthy, as numerous (NHC)M catalysed conversions (including examples using (NHC)Fe based catalysis) involve strong bases (*e.g.* RLi, RMgBr).[54,55] Thus carbene backbone (alkenyl) deprotonation may be a more common decomposition route in catalysis than previously realised, particularly when the NHC is coordinated to a Lewis acidic metal centre which will lower the p$K_a$ of the C4 and C5 protons.[53]

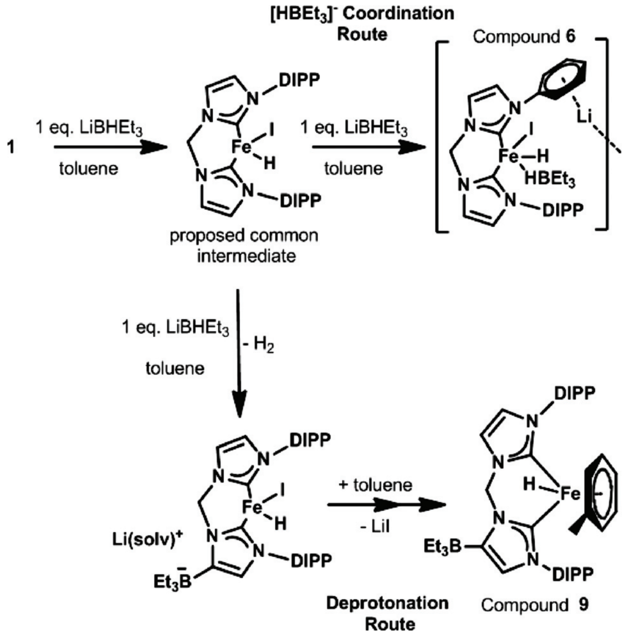

**Fig. 5** Proposed mechanism for the competitive formation of **6** and **9**.

The majority of the $((^{DIPP}C)_2CH_2)$Fe containing material post addition of two equivalents of $LiBEt_3H$ to **1** in toluene is **6** which is insoluble in pentane. In an attempt to remove LiI from **6** two equivalents of 12-crown-4 were introduced shortly (~ 10 min) after formation of **6** in toluene. Post filtration, the only species observed (by $^1H$ NMR) was still consistent with **6**, indicating the continued presence of LiI. On standing there was a gradual colour change from red to yellow and a reduction in the intensity of resonances corresponding to **6** (over seven days) with the concomitant slow growth of new paramagnetic and diamagnetic species in the $^1H$ NMR spectra. Throughout $BEt_3$ is the only observed diamagnetic boron containing product, precluding B–C cleavage as reported by Holland *et al.*, on addition of $KBEt_3H$ to (β-diketiminate)FeCl.[33] Recrystallisation over 7 days of the mixture derived from **6** and 12-crown-4 from toluene/pentane produced $[((^{DIPP}C)_2CH_2)Fe(\eta^6\text{-toluene})H]I$, **10**, in low yield (Fig. 4 bottom inset). The hydride was located in the penultimate Fourier difference map and freely refined, it was also confirmed by dissolution of crystals of **10** in $CD_2Cl_2$ which showed a diamagnetic integral of one hydride resonance (−10.4 ppm). It is noteworthy that addition of $LiBHEt_3$ to **10** resulted in no reaction, confirming that **10** is not an intermediate in the production of **9** (Fig. 4).

The structure of **10** is grossly similar to that of **9**, with the carbene ligand in **10** also having minimal strain in the metallacycle (yaw angles of 5.9°) and similar Fe–C bonds distances and bite angle. The two most significant differences in the structures of **9** and **10** are associated with the disposition of the $\eta^6$-toluene ligand. In **9** the tolyl-methyl is orientated towards the ligand backbone and there is a larger inter-plane angle of 80.3° between the C–Fe–C and toluene aryl planes. Compound **10** in contrast has the *para*-H of the toluene ligand directed towards the ligand backbone $CH_2$ and a smaller angle between the C1–Fe–C5 plane

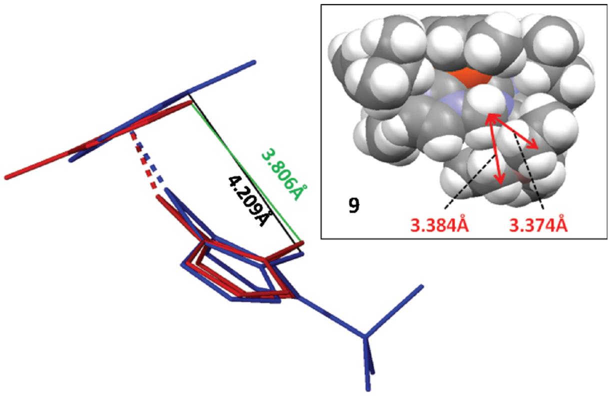

**Fig. 6** Overlay of the wireframe core structures of **9** (blue) and **10** (red), ’including the nearest ligand backbone $CH_2$—arene C distance, annotated in black for **9** and in green for **10** (DIPP groups and hydrogens are omitted for clarity). Inset space filling diagram (100% van der Waals radii) of **9**, showing the close contacts between B-$CH_2$ groups and the backbone $CH_2$ position.

and the tolyl arene plane of 65.3° (Fig. 6). This results in a greater distance between the ligand backbone $CH_2$ and the aryl ring for **9** relative to **10** (4.209 *versus* 3.806 Å). This is attributed to the presence of the $BEt_3$ moiety in compound **9** which results in more steric congestion. This is manifested in; (i) a reduction in the angle between the imidazole $C_3N_2$ plane and the aryl plane of the DIPP substituent to 78.7° in **9** (in comparison the average analogous angle in **10** is closer to orthogonal at 84.1°). (ii) A greater N–$CH_2$–N angle, which is noticeably larger in **9** (112.2(5) compared to 108.6(2)° in **10**) to minimise unfavourable steric interactions with the proximate B–$CH_2$ groups (Fig. 6 inset). Combined these result in more DIPP steric bulk in proximity of the Fe–H site in **9**, preventing the orientation observed in **10** where the sterically larger tolyl-methyl is located away from the ligand $CH_2$ backbone towards the Fe–H site.

With **10** only isolable in low yields a number of alternative routes for its synthesis were explored; (i) The immediate addition of toluene to diamagnetic **3** (proposed to be $[((^{DIPP}C)_2CH_2)FeH(I)_2]^-$) in THF resulted in no change in the $^1H$ NMR spectrum. (ii) Following the synthesis of ($\eta^6$-arene)Fe complexes by hydrogenolysis of (dippe)Fe(benzyl)$_2$ precursors,[31] compound **1** was treated with one equivalent of *p*-tolylMgBr in THF. This produced a new paramagnetic product of low symmetry that was tentatively assigned as $((^{DIPP}C)_2CH_2)$Fe($\eta^1$-*para*-tolyl)(I). The addition of $H_2$ (4 bar) to this reaction mixture resulted in the formation of an intractable mixture which did not contain any compound **10** (by $^1H$ NMR). (iii) To take advantage of the propensity for iron-butyl moieties to undergo β-hydride elimination two equivalents of $^nBuLi$ were added to **1**,[31,56] however no diamagnetic hydride resonances were observed with currently unidentified paramagnetic products formed. (iv) Komiya *et al.*, developed a two step approach to $[(dcype)FeH(arene)]^+$ (dcype = 1,2-bis(dicyclo-hexylphosphinoethane)) by initial reduction of (dcype)$FeCl_2$ to form (dcype)Fe($\eta^6$-arene) followed by subsequent protonation.[46] However, reduction of **1** using a range of reductants, and reducing equivalents (1, 2 or excess) repeatedly failed to produce any isolable $((^{DIPP}C)_2CH_2)Fe^0$ products, even in the presence of a range of Fe(0) trapping agents (*e.g.*, $N_2$, toluene, benzene, naphthalene, cyclooctene). Throughout $^1H$ NMR spectroscopy was uninformative, producing NMR silent soluble products on addition of the reducing equivalents. In contrast the reduction of (dcype)$FeCl_2$ and α-di-imineFe$X_2$ compounds, both produce diamagnetic $L_2$Fe($\eta^6$-arene) coordinated species on reduction.[57] The formation of $((^{DIPP}C)_2CH_2)$Fe($\eta^6$-arene) complexes is clearly sterically accessible (as exemplified by **9** and **10**), and the absence of diamagnetic Fe(0) products is therefore attributed to insufficient stabilisation of the electron rich Fe(0) centre by carbene ligation. This is consistent with the weak, reversible binding of NHCs to Fe(0) observed by Grubbs *et al.*[39] Thus redox flexible neutral bidentate ligands, of which the α-diimines are a paradigm, are more suited to stabilisation of reduced Fe centres being superior π acceptors relative to $((^{DIPP}C)_2CH_2)$.

In an attempt to intercept any $((^{DIPP}C)_2CH_2)Fe^{(II)}$-hydride complexes 12-crown-4 and then cyclooctene or $PMe_3$ (3 equivalents of each) were added to **6** in $d_8$-toluene. Addition of cyclooctene was envisaged to form an Fe-alkyl complex analogous to the work of Holland *et al.*, where insertion products are formed from combination of [β-diketiminateFeH] and alkenes.[58] However, this led to a mixture of paramagnetic and diamagnetic products (by $^1H$ NMR) from which only **10** could be isolated by recrystallisation (from toluene/pentane). Use of $PMe_3$ in place of cyclo-octene (to trap any transient low coordinate hydrides as higher coordinate and more stable species) resulted in a rapid colour change from red to yellow and a $^1H$ NMR spectrum revealing complete consumption of **6** and the growth of new paramagnetic and diamagnetic products. The $^{11}B$ spectrum revealed the major boron containing product was $Me_3P$-$BEt_3$, with carbene-borane adducts also observed as minor products. On recrystallisation from toluene/pentane over 7 days **10** was reproducibly isolated, albeit in low yield (a maximum isolated yield was 16%). The complex reactivity observed herein is consistent with previous attempts to form paramagnetic iron-hydrides ligated with different multidentate ligands using borohydride reagents. These have been equally complicated by competitive reaction pathways which can lead to intractable mixtures.[33,59] Furthermore Deng *et al.*, have recently reported that the hydrogenation of the related complex $(IPr)_2FeMe_2$ (IPr = 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene) led to complex mixtures that eluded isolation and characterisation.[37]

In conclusion, the installation of hydrides onto the $((^{DIPP}C)_2CH_2)$Fe fragment to generate low coordinate $Fe^{(II)}$-hydrido species has been found to be non-trivial, particularly frustrated by competitive reaction with solvents which is summarized in Fig. 7: (i) polar solvents lead to carbene dissociation from the iron centre (ii) haloalkanes result in the expected rapid hydride/halide exchange (iii) arene solvents produce complex mixtures from which ($\eta^6$-arene) capped iron species can be isolated on recrystallisation. Further complexity is introduced by: (i) the coordinated carbene being susceptible to deprotonation and (ii) continued coordination of iodide to iron during attempted metathesis for hydride. The latter combined with continued borane coordination to Fe (presumably as Fe-H-$BEt_3$) has enabled the isolation of a functional ‘masked’ form of a four coordinated Fe-dihydride. Our reactivity studies also indicate a fundamental instability of low coordinate iron(II)-dihydrides towards reductive elimination of $H_2$ analogous to previous unsuccessful attempts to synthesise low coordinate (four and

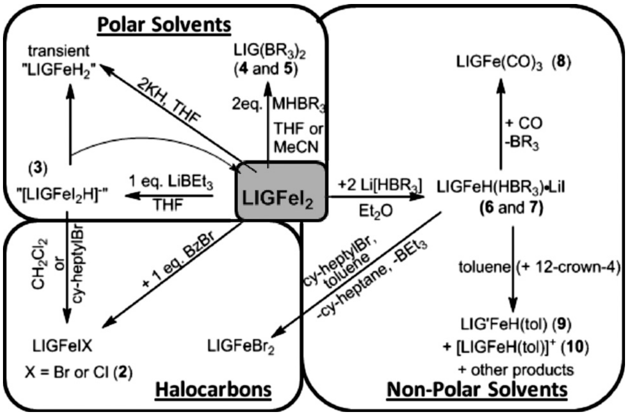

**Fig. 7** Solvent dependent summary for reactions of **1** (termed LIGFeI$_2$ for simplicity, LIG = ((${}^{\mathrm{DIPP}}$C)$_2$CH$_2$)).

five, respectively) Fe$^{(II)}$H$_2$ complexes chelated by diphosphine and 2,6-di-imino-pyridine ligands.

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