

Three-Coordinate Iron(II) Expanded Ring *N*-Heterocyclic Carbene Complexes

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Supporting Information Placeholder

ABSTRACT: A sterically demanding 7-membered expanded ring *N*-heterocyclic carbene (NHC) ligand allows access to rare examples of 3-coordinate iron(II)-NHC complexes incorporating only halide co-ligands of the general formulae, [Fe(NHC)X₂] (NHC = 7-DiPP, X = Br or Cl), **1** and **2**, respectively. Reducing the steric influence of the ancillary NHC ligand through modulation of the *N*-aryl substituents leads to either 4- or 3-coordinate complexes of the general formula, [Fe(NHC)Br₂(THF)], **3** or [Fe(NHC)Br₂], **4** (NHC = 7-Mes) dependent upon the solvent of recrystallization. The further reduction of NHC steric influence results in 4-coordinate geometries at iron in the form of either the dimeric species, [Fe(NHC)Br(μ-Br)]₂, **5** or [Fe(NHC)Br₂(THF)], **6** (NHC = SDiPP), again dependent upon the solvent of recrystallization. The series of compounds **1-6** have been analyzed by ¹H NMR spectroscopy, X-ray crystallography, elemental microanalysis, Mössbauer spectroscopy (for **1**, **3-5**) and Evans method magnetic susceptibility. In addition to these measurements the 3-coordinate species **1** and **4** have been further analyzed by SQUID magnetometry and CASSCF calculations which show significant magnetic anisotropy that is extremely sensitive to the coordination geometry.

INTRODUCTION

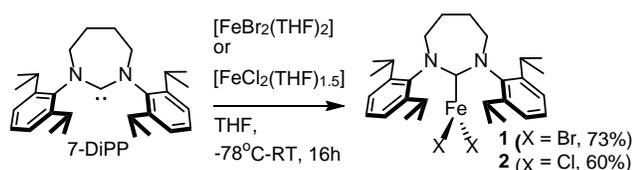
Low-coordinate iron-NHC complexes have been the topic of significant interest within the recent literature in terms of their intrinsic fundamental properties as well as their potential roles in homogeneously catalyzed processes.¹⁻³ In particular, reports concerning the synthesis and reactivity of stable three-coordinate iron-NHC complexes of the general formulae [Fe(NHC)Y₂] have been prevalent, where Y = aryl,⁴ benzyl,^{4b, 5} CH₂SiMe₃,^{4, 5} N(SiMe₃)₂,⁶ OSiPh₃,⁷ NH(DiPP),⁸ SePh,⁹ alkenyl,¹⁰ divinyl¹¹ or imido.^{11, 12, 13} Examples where both Y groups correspond to halides however, are considerably more scarce, generally as a consequence of the propensity of such species to dimerize leading to stable halide bridged dimers of the general formulae, [Fe(NHC)X₂]₂ (X = Cl or Br).^{2c, 5} In select cases employing NHCs with small steric profiles can lead to higher oligomers of the form, [Fe(NHC)Cl₂]₄.¹⁴ To the best of our knowledge there are no reports of monomeric, three-coordinate iron(II)-NHC complexes, i.e. [Fe(NHC)X₂] (X = halide). However, there has been a recent report of a closely related system containing a cyclic bent allene (CBA) ancillary ligand with bulky, yet flexible phenoxide wingtip substituents, [Fe(CBA)Cl₂] by Stephan and co-worker.¹⁵ The flexibility of the phenoxide wingtip substituents permit coordination numbers at iron of 3-5 due to free rotation around the C-O bonds leading to large changes in the effective steric shielding of iron center with percent buried volume (%V_{bur}) values¹⁶ ranging from 51.9 to 24.3 for the 3-coordinate [Fe(CBA)Cl₂] and 5-coordinate [Fe(CBA)(CO)₄], respectively.¹⁷

Given the scarcity of monomeric [Fe(NHC)X₂] complexes within the literature we became interested in the preparation of

such species, particularly examples with less flexibility in the wingtip substituents (and consequently the %V_{bur}). To enable the isolation of stable, well-defined [Fe(NHC)X₂] complexes, clearly the choice of ancillary NHC ligand is an important consideration as dimerization to [Fe(NHC)X₂]₂ species needs to be suppressed.^{2c, 5} The classical choices of bulky NHC ligand such as 5-DiPP (*N,N*-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) and SDiPP (1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) have been previously reported to generate μ-X bridged dimeric iron(II) species of the general formulae [Fe(NHC)X₂]₂ (X = Cl, Br).^{2c, 5} Hence, a NHC ligand generating a steric environment greater than that of 5-DiPP or SDiPP is required in order to perturb dimerization. With this strategy in mind, we chose the easily prepared and extremely sterically imposing 7-membered expanded ring NHC ligand, 7-DiPP^{18, 19} as a starting point for our studies. The increase in the steric profile of the 7-DiPP ligand in relation to common bulky 5-membered NHCs can be exemplified through a comparison of percent buried volume values^{16, 20} of the linear gold(I) complexes [Au(7-DiPP)Cl] and [Au(5-DiPP)Cl] which are found to be 52.6 and 44.5 %, respectively.²¹ This significant modulation of percent buried volume through simple heterocycle ring expansion comes as a consequence of an increase in the N-C_{NHC}-N bond angle and also a decrease in the corresponding C_{NHC}-N-C_{Ar} bond angles which force the *N*-aryl substituents further into the ligand coordination sphere.¹⁸ Herein we report that this approach enables facile access to monomeric 3-coordinate iron [Fe(NHC)X₂] complexes, that display varying propensity to coordinate additional Lewis bases.

RESULTS AND DISCUSSION

Our investigation began with the addition of 1.1 equivalents of 7-DiPP to $[\text{FeBr}_2(\text{THF})_2]$ in anhydrous THF at -78°C before warming to ambient temperature and stirring for 16h. Filtration and subsequent concentration of the reaction mixture followed by storage at -30°C over a period of two days afforded the desired compound $[\text{Fe}(7\text{-DiPP})\text{Br}_2]$, **1** as colorless crystals in an isolated yield of 73% (Scheme 1). Analysis of **1** by single crystal X-ray diffraction confirmed **1** to be both 3-coordinate and monomeric (Figure 1). The three coordinate structure demonstrates the significant steric protection of the iron(II) center by the 7-DiPP ligand which serves to prevent dimerization. The ^1H NMR spectrum of **1** recorded in d_8 -THF at 298 K (see Supporting Information) demonstrated seven non-overlapping, paramagnetically shifted resonances in the range of +37.76 to -14.26 ppm indicating non-equivalent isopropyl CH_3 environments. Solution state magnetic susceptibility measurements employing the Evans method²² confirmed the expected high-spin, $S = 2$ configuration, $\mu_{\text{eff}} = 6.0 \mu\text{B}$ (298 K). This is assigned as the 3-coordinate complex **1** and not a 4-coordinate at iron THF adduct as dissolution of crystalline **1** in C_6D_6 led to extremely similar ^1H NMR spectra before and after the addition of a large excess of d_8 -THF (see Supporting Information).



Scheme 1. The synthesis of monomeric $[\text{Fe}(7\text{-DiPP})\text{Br}_2]$, **1** and $[\text{Fe}(7\text{-DiPP})\text{Cl}_2]$, **2**.

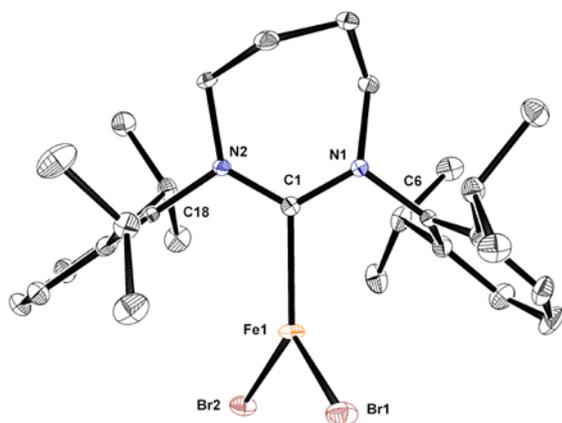


Figure 1. ORTEP²³ representation of $[\text{Fe}(7\text{-DiPP})\text{Br}_2]$, **1**. Thermal ellipsoids are depicted at 50% probability and all hydrogen atoms have been omitted for clarity.

The related complex $[\text{Fe}(7\text{-DiPP})\text{Cl}_2]$, **2** could be generated in a similar manner to **1** through addition of 7-DiPP to $[\text{FeCl}_2(\text{THF})_{1.5}]$ in THF (Scheme 1) followed by recrystallization from either benzene/hexane or toluene/hexane. Single crystal X-ray diffraction confirmed the 3-coordinate formulation of **2** (Figure 2). Interestingly, depending on recrystallization conditions, **2** formed two different solvated solid-state structures, **2.C₆D₆** and **2.C₇H₈** with disparate Cl-Fe-C-N dihedral angles²⁴ of 39.05° and 68.15° , respectively, suggesting there is a low barrier to rotation about the Fe-C bond. For comparison the structure of **1** has a di-

hedral angle²⁴ of 69.22° . Other metrics between the two structures, **2.C₆D₆** and **2.C₇H₈** are extremely similar, thus only, **2.C₆D₆** is discussed in the subsequent structural discussion section.

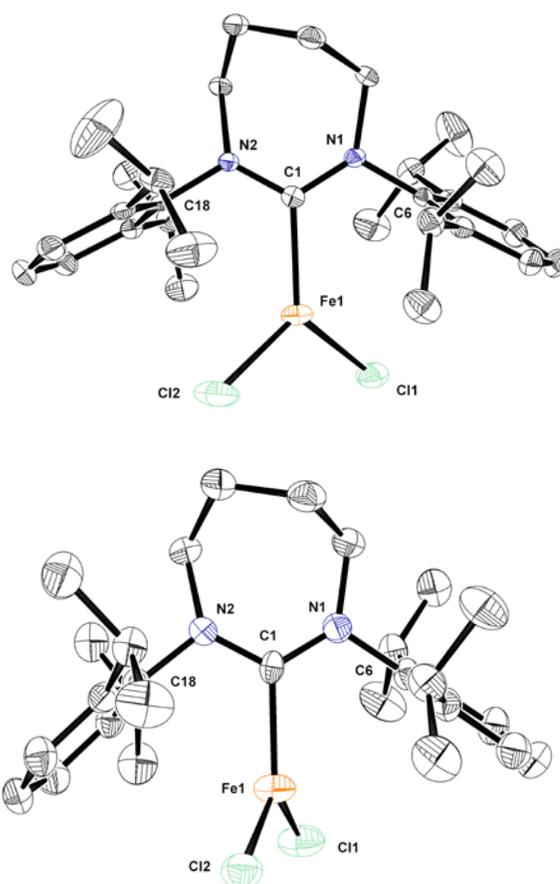
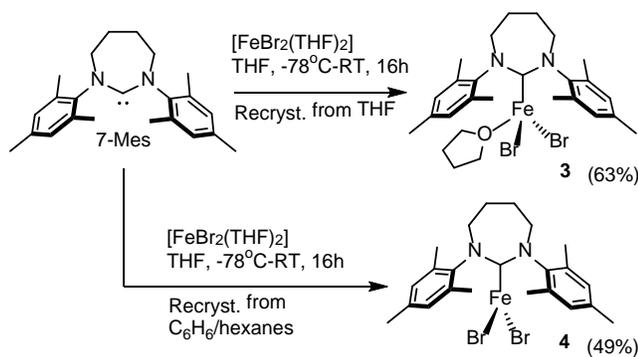


Figure 2. ORTEP²³ representations of $[\text{Fe}(7\text{-DiPP})\text{Cl}_2]\cdot\text{C}_6\text{D}_6$, **2.C₆D₆** (top) and $[\text{Fe}(7\text{-DiPP})\text{Cl}_2]\cdot\text{C}_7\text{H}_8$, **2.C₇H₈** (bottom). Thermal ellipsoids are depicted at 50% probability and all hydrogen atoms and molecules of solvation have been omitted for clarity.

With well-defined examples of a 3-coordinate iron(II) species, containing only halide co-ligands in hand, **1** and **2**, we next became interested in where the steric limit for favoring monomeric, 3-coordinate iron(II)-NHC complexes over 4-coordinate, $\mu\text{-X}$ bridged dimeric species lay. To probe this question, the steric profile of the 7-membered NHC ligand employed was reduced by moving to 7-Mes¹⁸ (containing 2,4,6-trimethylphenyl N -aryl substituents, $\%V_{\text{bur}}[\text{Au}(7\text{-Mes})\text{Cl}] = 43.6$).²¹ The addition of 7-Mes (1.1 equiv.) to $[\text{FeBr}_2(\text{THF})_2]$ in anhydrous THF at -78°C before warming to ambient temperature and for 16 h led to the isolation of the 4-coordinate species $[\text{Fe}(7\text{-Mes})\text{Br}_2(\text{THF})]$ **3** after recrystallization from a concentrated THF solution in 63% yield (Scheme 2, Figure 3). Reducing the steric constraint of the 7-membered NHC ligand through modulation of the N -aryl substituents clearly allows for the coordination of one THF ligand, giving the tetrahedral, 4-coordinate complex **3** (Figure 3, top). This is not the case in the more sterically congested 7-DiPP derivatives, **1** and **2** (Figures 1 and 2). Interestingly, the application of a vacuum and alteration of the crystallization conditions from a concentrated THF solution to a benzene/hexanes layer provided access to the monomeric, 3-coordinate species, $[\text{Fe}(7\text{-Mes})\text{Br}_2]$, **4** (Scheme 2, Figure 3, bottom). Despite facile loss of THF from **3** on the appli-

cation of a vacuum, coordination of THF to $\text{Fe}(7\text{-Mes})\text{Br}_2$ is observed in solution. For example, addition of excess d_8 -THF to a C_6D_6 solution of **4** results in significant changes in the ^1H NMR spectra, indicating coordination of THF, and is in contrast to the addition of THF to **1** in C_6D_6 , where no significant changes are observed. The formation of **4** is noteworthy considering the relative steric profiles of 7-Mes, 5-DiPP and SDiPP in the two coordinate (NHC)AuCl complexes ($\%V_{\text{bur}} = 43.6, 44.5$ and 47.0 , respectively)²¹ and the fact that 5-DiPP and SDiPP are reported to generate $\mu\text{-X}$ bridged dimeric species of the general formulae, $[\text{Fe}(\text{NHC})\text{X}_2]_2$.^{2c, 5}

The ability of the 7-Mes ligand to allow both trigonal planar and tetrahedral coordination geometries dependent upon the solvent of recrystallization is intriguing. Clearly the flexible nature of the 7-membered heterocyclic backbone is able to modulate the relative spatial orientation of the *N*-mesityl substituents, and hence the ligand coordination sphere. This statement can be quantified by an analysis of the respective $\%V_{\text{bur}}$ values of **3** and **4** calculated from their solid state structures (Table 1). Complex **4** has an extremely large $\%V_{\text{bur}}$ value of 48.4, unusually, even surpassing that of its 7-DiPP congener, **1** (47.1) whereas the 4-coordinate analogue **3** has a significantly reduced $\%V_{\text{bur}}$ value of 40.1. This observation is distinct from the more rigid steric environments provided by classical 5-membered NHC systems, which generally show minimal change in $\%V_{\text{bur}}$ on coordination number variation.²⁰ Flexibility in steric influence could play a potential role in catalytic transformations involving these ligands through the reversible modulation of steric environment. This feature is considered to be increasingly important in select catalytic transformations where the employment of bulky yet flexible NHC ligand scaffolds developed by Marko (IPr*);²⁵ Organ (Ipent);²⁶ and Nolan (Itent)²⁷ provide superior outcomes in relation to traditional 5-membered NHC motifs such as IMes, 5-DiPP and SDiPP.



Scheme 2. The synthesis of $[\text{Fe}(7\text{-Mes})\text{Br}_2]$, **3** and $[\text{Fe}(7\text{-Mes})\text{Br}_2(\text{THF})]$, **4** dependent upon the solvent of recrystallization.

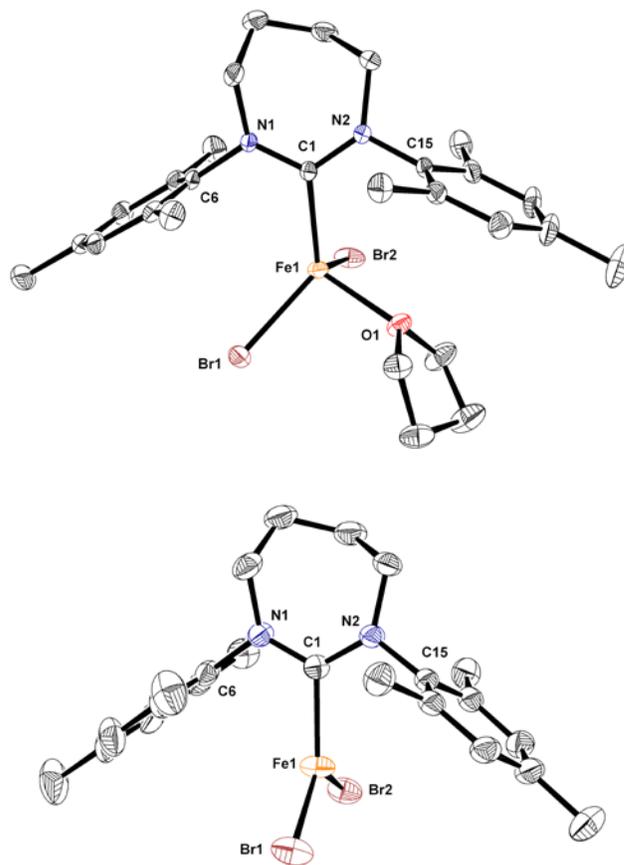
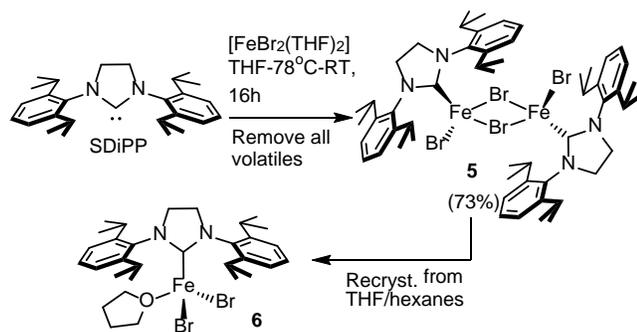


Figure 3. ORTEP²³ representations of $[\text{Fe}(7\text{-Mes})\text{Br}_2(\text{THF})]$, **3** (top) and $[\text{Fe}(7\text{-Mes})\text{Br}_2] \cdot 2\text{C}_6\text{H}_6$, **4** (bottom). Thermal ellipsoids are depicted at 50% probability and all hydrogen atoms and molecules of solvation have been omitted for clarity.

The formation of **3** and **4** is an interesting outcome considering the prevalence of similar systems in terms of $\%V_{\text{bur}}$ values on linear Au(I) complexes²⁰ to provide $\mu\text{-halide}$ bridged dimeric species.^{2c, 12} It is noteworthy that the previously reported $[\text{Fe}(\text{SDiPP})\text{Cl}_2]_2$ structure was obtained from single crystals derived from weakly-coordinating solvent systems,⁵ thus the existence of a monomeric THF adduct of $[\text{Fe}(\text{SDiPP})\text{X}_2]$ has not been definitively probed. The addition of SDiPP (1.1 equiv.) to $[\text{FeBr}_2(\text{THF})_2]$ in anhydrous THF, followed by removal of volatiles *in-vacuo*, afforded $[\text{Fe}(\text{SDiPP})\text{Br}_2]_2$ **5** as a colorless microcrystalline solid in 73% yield (Scheme 3). Single crystals of **5** suitable for X-ray diffraction could be obtained from a concentrated C_6H_6 solution at ambient temperature. The solid state structure of **5** confirmed its expected $\mu\text{-Br}$ bridged dimeric formulation (Figure 4). Alternatively, recrystallization of **5** from THF/hexanes afforded the 4-coordinate THF adduct $[\text{Fe}(\text{SDiPP})\text{Br}_2(\text{THF})]$, **6** in an analogous fashion to **3** (Scheme 3, Figure 5). The full characterization of the crystalline sample of **6** was hampered by the fact that THF loss was facile under both dynamic vacuum and with storage at ambient pressure under an inert atmosphere. However, the ^1H NMR spectrum could be obtained in either d_8 -THF or a C_6D_6 solution spiked with d_8 -THF (see Supporting Information).



Scheme 3. The synthesis of $[\text{Fe}(\text{SDiPP})\text{Br}_2]_2$, **5** and $[\text{Fe}(\text{SDiPP})\text{Br}_2(\text{THF})]$, **6** dependent upon the solvent and recrystallization conditions.

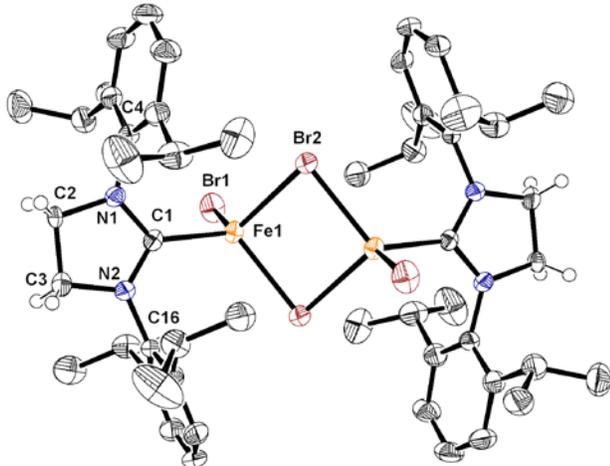


Figure 4. ORTEP²³ representation of $[\text{Fe}(\text{SDiPP})\text{Br}_2]_2$, **5**. Thermal ellipsoids depicted at 50% probability and most hydrogen atoms and molecules of solvation have been omitted for clarity.

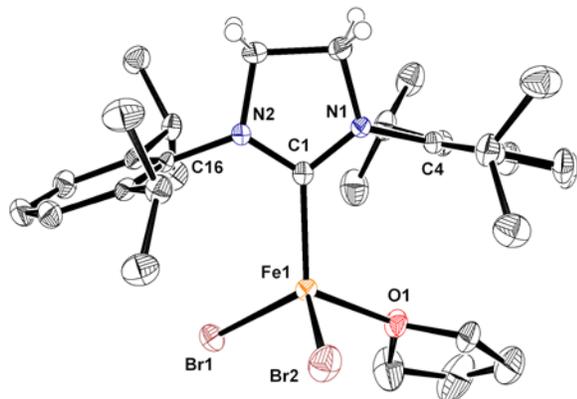


Figure 5. ORTEP²³ representation of $[\text{Fe}(\text{SDiPP})\text{Br}_2(\text{THF})]$, **6**. Thermal ellipsoids are depicted at 50% probability and most hydrogen atoms have been omitted for clarity.

The propensity of the dimer **5** to coordinate THF is in contrast to the unsaturated 5-DiPP analogues $[\text{Fe}(5\text{-DiPP})\text{X}_2]_2$ ($\text{X} = \text{Cl}$ and Br) previously reported by Tonzetich and co-workers to not coordinate THF, although the more nucleophilic Lewis base *N*-Me-imidazole does lead to formation of $\text{Fe}(5\text{-DiPP})\text{X}_2(\text{N-Me-imidazole})$ from $[\text{Fe}(5\text{-DiPP})\text{X}_2]_2$.^{2c} There are therefore at least three different Lewis base dependent regimes for compounds of general formula $[\text{Fe}(\text{NHC})\text{X}_2]$ containing NHCs of similar $\%V_{\text{bur}}$

(derived from $[\text{Au}(\text{NHC})\text{Cl}]$ complexes); (i) exclusively three-coordinate $[\text{Fe}(\text{NHC})\text{X}_2]$ with no Lewis base coordination or dimer formation; (ii) an equilibrium between $[\text{Fe}(\text{NHC})\text{X}_2]$ and $[\text{Fe}(\text{NHC})\text{X}_2(\text{LB})]$ ($\text{LB} = \text{Lewis base}$) with no $[\text{Fe}(\text{NHC})\text{X}_2]_2$ dimer formation; (iii) an equilibrium between $[\text{Fe}(\text{NHC})\text{X}_2(\text{LB})]$ and $[\text{Fe}(\text{NHC})\text{X}_2]_2$. The sensitivity of the $[\text{Fe}(\text{NHC})\text{X}_2]$ complexes to subtle steric and electronic changes in the NHC ligand is presumably a contributing factor leading to the significant differences observed in the catalytic performance of iron(II) complexes incorporating 5-DiPP and SDiPP ancillary ligands.²⁸

Solid-State Structural Analysis. With a series of FeX_2 compounds bearing ancillary NHC ligands of varying steric profiles, which give rise to distinct coordination modes, an analysis of the solid state structures is informative (Table 1). The $\text{Fe}-\text{C}_{\text{NHC}}$ bond distances are found to be broadly similar across the series of compounds, ranging from 2.142(2) to 2.092(3) Å regardless of steric influence or σ -donor ability of the ancillary NHC ligand in question. The *N*-aryl *ipso* carbon-Fe bond distances are sufficiently long to preclude any significant interaction, which confirms **1**, **2** and **4** as genuine 3-coordinate compounds. Further analysis of the unusual trigonal planar 3-coordinate compounds **1**, **2** and **4** reveals broadly similar key bond metrics (Table 1) apart from the dihedral angles²⁴ which for **4** (86.77°) is disparate to those of **1** and both solvated structures of **2**.

It is interesting to compare the bond metrics of **3** and **4** which both bear the 7-Mes ancillary ligand but adopt different coordination geometries based upon the choice of recrystallization solvent. The difference in the key $\text{N}-\text{C}_{\text{NHC}}-\text{N}$ and $\text{C}_{\text{NHC}}-\text{N}-\text{C}_{\text{Aryl}}$ bond angles which dictate the steric demand of this class of NHC ligand are significantly different for **3** and **4** (Table 1). The smaller $\text{N}-\text{C}_{\text{NHC}}-\text{N}$ and larger $\text{C}_{\text{NHC}}-\text{N}-\text{C}_{\text{Aryl}}$ angles of **3** in relation to **4** afford a decrease in $\%V_{\text{bur}}$ value (40.1 and 48.4, respectively) which allows THF coordination. The ability of the 7-Mes ligand to provide varying steric protection of the iron(II) center is an interesting observation that evidences the novel steric parameters enabled by the flexible heterocyclic backbone.

Analysis of the SDiPP compounds **5** and **6**, revealed $\%V_{\text{bur}}$ values of 37.8 and 37.7, comparable to that for the previously reported chloride congener of **5** ($\%V_{\text{bur}} = 37.4$).⁵ It is notable that this is a significant reversal in relative steric influence of 7-Mes *Vs* SDiPP compared to that indicated by the $\%V_{\text{bur}}$ in $[\text{Au}(\text{NHC})\text{Cl}]$ complexes. Structural metrics for **5** are unremarkable and closely comparable to the previously reported complexes $[\text{Fe}(5\text{-DiPP})\text{X}_2]_2$ ($\text{X} = \text{Cl}$ and Br , $\%V_{\text{bur}} = 36.1$ and 38.0, respectively) and $[\text{Fe}(\text{SDiPP})\text{Cl}_2]_2$. Based upon these observations it is reasonable to suggest that the transition to monomeric, 3-coordinate iron(II)-NHC complexes being favored over more conventional 4-coordinate, $\mu\text{-X}$ bridged dimeric species in terms of $\%V_{\text{bur}}$ value occurs between 38 and 40 % (based on four coordinate iron complexes and not $[\text{Au}(\text{NHC})\text{Cl}]$ complexes).

Table 1. Selected bond lengths (Å), angles (°), torsion angles (°) and percent buried volume (% V_{bur}) values for complexes **1-6**.

	1	2.C₆H₆	3	4	5	6
N-C _{NHC} -N	121.42(14)	121.5(5)	118.83(18)	121.7(2)	107.9(3)	107.7(2)
C _{NHC} -N-C _{Aryl}	116.19(13)	115.8(4)	119.55(17)	116.0(2)	126.7(3)	126.1(2)
C _{NHC} -N-C _{Aryl}	114.99(13)	113.9(4)	118.21(17)	114.7(2)	126.3(3)	125.9(2)
X-Fe-X	112.677(12)	117.56(7)	-	121.70(2)	-	-
C _{NHC} -Fe	2.1227(16)	2.099(5)	2.142(2)	2.092(3)	2.107(4)	2.121(2)
Fe-X	2.3602(3)	2.2211(18)	2.4387(4)	2.3410(15)	2.5051(8)	2.4091(5)
Fe-X	2.3664(3)	2.2201(18)	2.4363(4)	2.3558(6)	2.386(2)	2.4153(5)
Fe-O	-	-	2.1171(15)	-	-	2.0926(18)
C _{ipso} -Fe	3.026	2.989	3.198	3.049	3.543	3.444
C _{ipso} -Fe	3.099	3.059	3.226	3.014	3.457	3.556
Dihedral Angle ^a	69.22	39.05	-	86.77	-	-
% V_{bur} ^b	47.1	48.5	40.1	48.4	37.8	37.7

^a Dihedral angle defined as the angle between the N-C_{NHC}-N and X-Fe-X planes. ^b Parameters applied for SambVca calculations: 3.50 Å was selected as the value for sphere radius, 2.10 Å was used as the distance for the metal-ligand bond, hydrogen atoms were omitted and bond radii were scaled by 1.17.

Mössbauer Spectroscopy of **1, **3-5**.** The Mössbauer spectra at 80 K in zero field obtained for **1**, **3-5** (see Supporting Information) are all consistent with high-spin iron(II) species, in line with solution state magnetic susceptibility measurements. In terms of isomer shift (i.s.) there is a clear distinction observed between 3-coordinate species **1** and **4** and 4-coordinate species **3** and **5** (3-coordinate species 0.65-0.66, 4-coordinate species 0.82-0.88). The values for **1** and **4** are comparable to the three coordinate complex [Fe(CBA)Cl₂] (i.s. = 0.65 q.s. = 1.06 mm/s).¹⁵ Comparison of the quadrupolar splitting (q.s.) values of **1** and **4** (both solvent free by combustion analysis), 0.86 and 1.68 mm/s, respectively, indicates different degrees of asymmetry in the electric field gradient, despite similar solid state structures. However, both q.s. values are in the range previously reported for three-coordinate iron-NHC complexes in the +2 oxidation state.^{5, 6b, 11} It was not possible to collect Mössbauer data for **6** due to the facile loss of THF in the solid state.

Table 2. Mössbauer parameters (80 K) for complexes **1**, **3-5**^a

	1	3	4	5 ^b
i.s.	0.66	0.88	0.65	0.82
q.s.	0.86	2.59	1.68	3.42(2)
h.w.h.m.	0.13	0.19	0.14	0.14

^a Errors $\leq \pm 0.01$ mms⁻¹ unless shown otherwise in parenthesis. ^b minor impurity repeatedly observed despite accurate elemental microanalysis and analysis of multiple batches of **5**.

SQUID Magnetometry and CASSCF Calculations. To further probe the electronic configuration of **1** and **4**, solid state magnetic susceptibility and magnetization measurements were performed (Figure 6). The room temperature magnetic moments for **1** and **4** of 4.1 cm³ mol⁻¹ K (~ 5.7 μ_B) and 4.5 cm³ mol⁻¹ K (~ 6.0 μ_B), respectively, are in good agreement with the Evan's method measurements and suggest an $S = 2$ ground state with $g > 2$. For **1** the magnetic moment is constant with decreasing temperature until 50 K, below which a sharp decrease is observed. There appears to be a slight field dependence at 10 K where a small plateau is observed in an 0.1 T field.

The reduced magnetization data (Figure 6, inset) show non-superimposable isotherms, indicating significant magnetic anisotropy, while conversely, the magnetization data show superimposed isotherms – direct evidence of easy-plane anisotropy. Broadly, the magnetic properties of **4** are similar to that of **1**, however, there is a linear decrease in the magnetic susceptibility at high temperatures that is too significant to owe to diamagnetic corrections alone, suggesting influence of an excited state via temperature independent paramagnetism (TIP). Furthermore, there is no low temperature plateau in the 0.1 T data. Similarly to **1**, **4** shows the same hallmarks of significant easy-plane magnetic anisotropy (Figure 6).

The magnetic susceptibility and magnetization data were fitted simultaneously for **1** and **4**, using the Hamiltonian (1) with PHI.²⁹ The best fit is found with $D > 0$ and $g > 2$ in both cases, where for **1** $D_1 = +16.8(2)$ cm⁻¹, $E_1 = -3.3(1)$ cm⁻¹ ($|E_1/D_1| = 0.20$) and $g_1 = 2.40(1)$, and for **4** $D_4 = +14.3(1)$ cm⁻¹, $E_4 = -3.69(3)$ cm⁻¹ ($|E_4/D_4| = 0.26$), $g_4 = 2.32(1)$, $TIP_4 = 0.0016(2)$ cm³ mol⁻¹.

$$\hat{H} = \mu_B g \hat{S} \cdot \vec{B} + D \left(\hat{S}_z^2 - \frac{1}{3} S(S+1) \right) + \frac{E}{2} \left(\hat{S}_+^2 + \hat{S}_-^2 \right) \quad (1)$$

To confirm the easy-plane anisotropy for **1** and **4**, we performed complete active space self-consistent field (CASSCF) ab initio calculations on the solid state X-Ray structures (see Experimental Section for details). The calculations for **1** yielded $D_1 = +25.2$ cm⁻¹, $E_1 = -6.3$ ($|E_1/D_1| = 0.25$) and $g_1 = 2.39$, and for **4** $D_4 = -39.4$ cm⁻¹, $E_4 = -0.2$ cm⁻¹ ($|E_4/D_4| < 0.01$) and $g_4 = 2.34$. The sign of D , the rhombicity ($|E/D|$) and the g -value for **1** are in very good agreement with experiment, given the tendency of CASSCF to overestimate the magnitude of the zero field splitting (ZFS). However, despite the calculated g -value for **4** being in excellent agreement, the sign of D and rhombicity are completely wrong. The only significant difference in the local coordination environment of iron between **1** and **4** is a minor distortion of the bromide ions, which differ in absolute position by ~ 0.9 Å and have dihedral angles between the respective Br-Fe-Br / N-C-N planes of 69° and 93°, respectively.

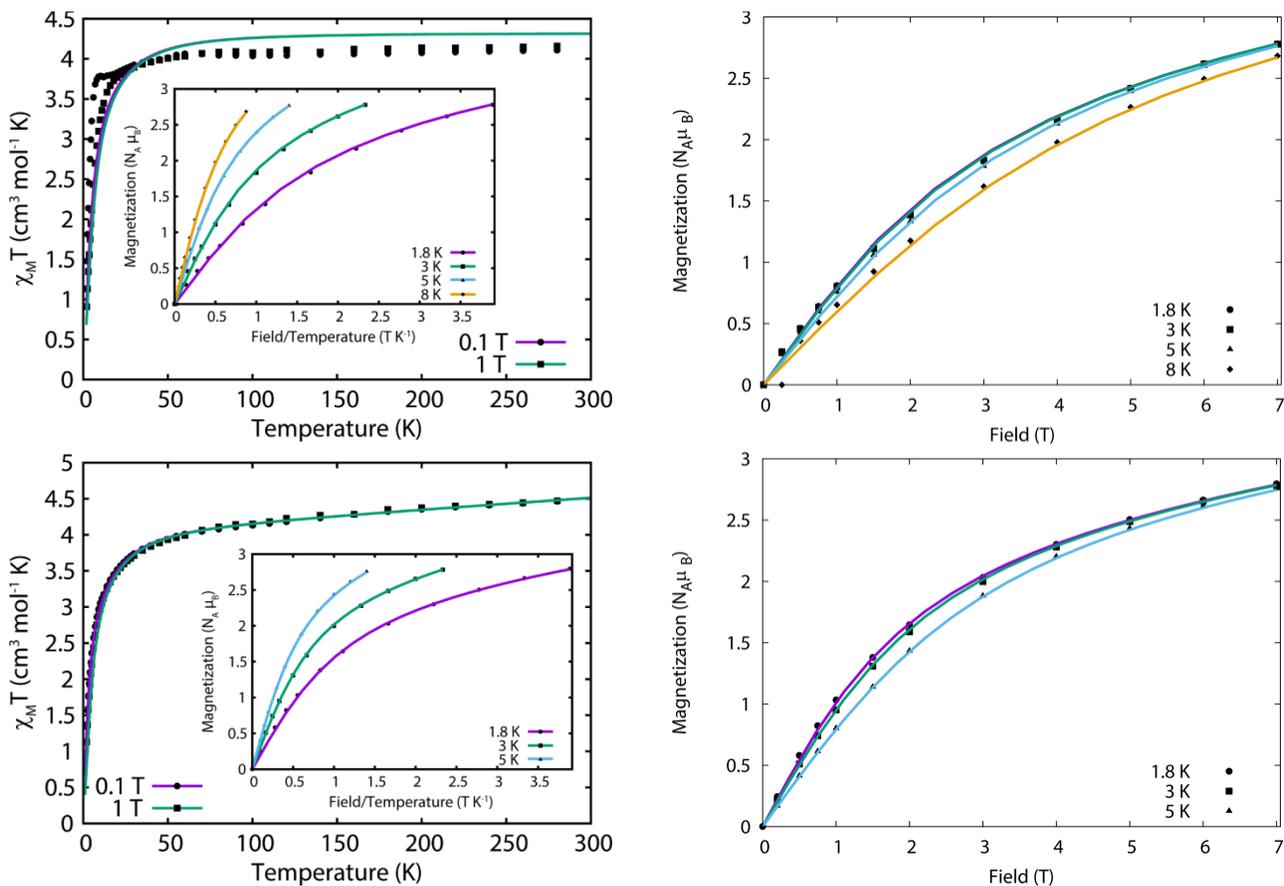


Figure 6. Magnetic susceptibility and reduced magnetization (inset) of **1** (top left) and **4** (bottom left). Magnetization of **1** (top right) and **4** (bottom right). Black points are experimental data, colored lines are fits with models given in the text.

To examine if this small distortion can really cause such a dramatic change in the magnetic properties, we performed further CASSCF calculations where the positions of the bromide ions in **4** were shifted along a deformation pathway ending in the relative geometry of the bromide ions in **1**, where the rest of the structure of **4** remained static. Both complexes exhibit three low-lying 3d orbitals in the $S = 2$ configuration which are nearly degenerate, split by 500 – 800 cm^{-1} , and correspond to the non-bonding d_{xz} , d_{yz} and d_z^2 orbitals.³⁰ As a function of the deformation coordinate δ ($\delta = 0$ is native **4**, $\delta = 1$ is **4** with relative bromide geometry of **1**), the relative energies of these orbitals change significantly (Figure 7, bottom) along with the angular momentum matrix elements between them (Figure S5). At $\delta = 0$, the two lowest orbitals are very close in energy and it is the excitation between them which dominates and leads to a large negative D value (Figure 7, top).³⁰ As δ increases, the lowest two orbitals exhibit an anti-crossing and then separate in energy. Naturally this impacts the $1 \rightarrow 2$ and $1 \rightarrow 3$ orbital excitation energies, but when this is coupled with the change in angular momentum matrix elements, the $1 \rightarrow 3$ excitation becomes important and the $1 \rightarrow 2$ excitation no longer dominates the D tensor. This is plainly observed in the RMS value of the D tensor, separated into contributions from each excitation (2) (Figure 7, middle).

$$C_j = \frac{1}{E_j - E_1} \sqrt{\sum_{\alpha, \beta \in x, y, z} (\langle \varphi_1 | \hat{L}_\alpha | \varphi_j \rangle \langle \varphi_j | \hat{L}_\beta | \varphi_1 \rangle)^2} \quad (2)$$

Therefore, it is the competition between the $1 \rightarrow 2$ and $1 \rightarrow 3$ orbital excitations that account for the dramatic change in the sign

of D , which occurs at $0.75 < \delta < 0.80$ and corresponds to a dihedral angle of 74.5° between the Br-Fe-Br and N-C-N planes. Ultimately, the origin of the sensitive electronic structure in these compounds is the near-degeneracy of the lowest three 3d orbitals.

The solid state structure of **4** contains solvent of recrystallization, and due to the facile loss of these solvent molecules during isolation, the magnetic data was collected on desolvated material (confirmed by combustion analysis). Thus we believe that the positions of the bromide ions in **4'** (desolvated) are slightly perturbed by the loss of solvent and no longer match those found by X-Ray crystallography. This hypothesis is consistent with the significant variation in the angle between the Cl-Fe-Cl / N-C-N planes observed in the closely related complex **2** when the solid state structure contains different solvent of crystallization indicating a low barrier to a degree of rotation around the Fe-C axis in these compounds.

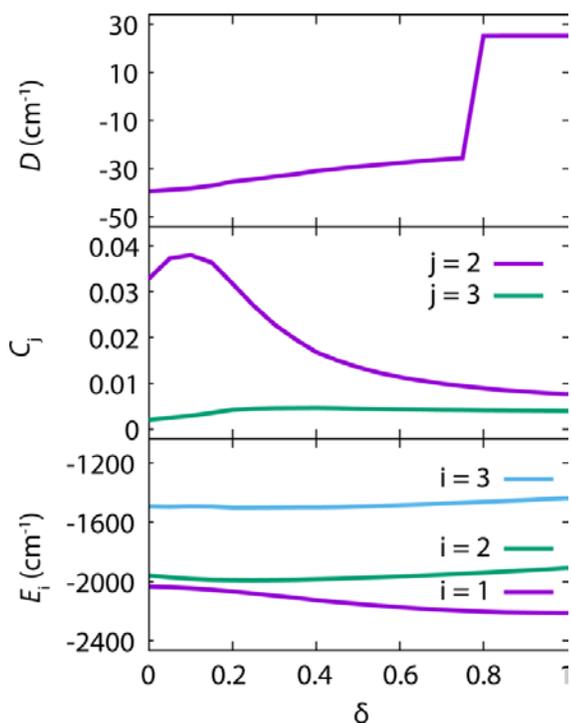


Figure 7. D parameter (top), C_j parameter (middle) and orbital energies (bottom) for **4** as the bromide ions are deformed along the coordinate δ .

CONCLUSIONS

In summary, we have presented the synthesis of rare examples of 3-coordinate iron(II)-NHC complexes incorporating only halide co-ligands of the general formulae, $[\text{Fe}(\text{NHC})\text{X}_2]$. The employment of extremely bulky 7-membered expanded ring NHC ancillary ligands, provides sufficiently hindered iron coordination spheres to prevent dimerization which leads to more prevalent monomeric iron species, $[\text{Fe}(\text{NHC})\text{X}_2]$. Reducing the steric impact of the ancillary ligand leads to either four-coordinate THF adducts, $[\text{Fe}(\text{NHC})\text{Br}_2(\text{THF})]$ or μ -Br bridged dimeric species, $[\text{Fe}(\text{NHC})\text{Br}_2]_2$ dependent upon the bulk of the NHC and / or the solvent of recrystallization. A number of complexes have been analyzed by Mössbauer spectroscopy, which revealed differences in the quadrupolar shift (and thus electric field gradient around the iron center) despite structurally similar three-coordinate solid-state structures. Both 3-coordinate compounds were also analyzed by SQUID magnetometry and CASSCF calculations affording detailed insight into the magnetic anisotropy, which is very sensitive to the local geometry, owing to near-degeneracy of the non-bonding d_{xz} , d_{yz} and d_z^2 orbitals.

EXPERIMENTAL SECTION

General Remarks: All manipulations were carried out using standard Schlenk techniques under argon, or in an MBraun UniLab glovebox, under an argon atmosphere (< 0.1 ppm $\text{O}_2/\text{H}_2\text{O}$). Solvents were distilled from appropriate drying agents: THF, toluene and benzene (potassium), hexanes (NaK). Toluene, benzene and hexanes were stored over potassium mirrors and THF over activated 3 Å molecular sieves. Deuterated solvents for NMR measurements (benzene- d_6 and THF- d_8) were distilled from potassium, degassed by three consecutive freeze-pump-thaw cycles and stored under argon. All iron complexes after their formation were stored at -30°C in the internal freezer of an MBraun Unilab glovebox. 7-DIPP,²⁰ 7-Mes²⁰ and SDiPP³¹ were all prepared according to previously reported literature procedures. NMR spectra were recorded on a Bruker AV-400 spectrometer.

Chemical shifts are reported as dimensionless δ values and are frequency referenced relative to residual *protio*-impurities in the NMR solvents. Solution state magnetic moments were calculated according to the Evans method²² at 298 K on a Bruker AV-400 spectrometer. Microanalysis was performed by Mr. Stephen Boyer at the London Metropolitan University microanalytical service. Magnetic properties were measured using a Quantum Design MPMS-7 SQUID magnetometer at temperatures in the range of 1.8-300 K. Mössbauer spectra were recorded in zero magnetic field at 80 K on an ES-Technology MS-105 Mössbauer spectrometer with a 90 MBq ^{57}Co source in a rhodium matrix at ambient temperature. Spectra were referenced against a 25 μm iron foil at 298 K and spectrum parameters were obtained by fitting with Lorentzian lines. CASSCF calculations were performed with MOLCAS 8.0.³² The active space consisted of six electrons in the five 3d orbitals. The 5 $S = 2$, 45 $S = 1$ and 50 $S = 0$ configurations were considered both in the orbital optimisation (RASSCF) and the spin-orbit mixing (RASSI) procedures, and the ZFS of the $S = 2$ ground state was extracted from the spin-orbit mixed states (SINGLE_ANISO). Given orbital energies are the energies of the five $S = 2$ states calculated in the CASSCF procedure. Basis sets from the ANO-RCC library of VTZP (Fe), VDZP (Br, C) and VDZ (H) quality were employed,³³ along with Cholesky decomposition of the two-electron integrals. All parameters took their default values. Matrix elements of orbital angular momentum between the spin-free states of the $S = 2$ configurations taken from the output of the RASSI routine.

[Fe(7-DIPP)Br₂] (1): In a glovebox, an oven dried Schlenk tube was charged with 7-DiPP (700 mg, 1.67 mmol) and $[\text{FeBr}_2(\text{THF})_2]$ (553 mg, 1.54 mmol). Outside the glovebox, the combined solids were cooled to -78°C and cold THF was added (50 mL). The reaction mixture was allowed to stir at -78°C for 1h prior to slowly warming to ambient temperature and the homogeneous pale yellow reaction mixture was then allowed to stir for 16h. After this time, the reaction mixture was filtered *via* an oven dried PTFE filter cannula into a separate oven dried Schlenk tube and the solution concentrated to approximately 5 mL. Storage at -30°C over a period of two days to afforded **1** as colourless crystals (716 mg, 73%). Analysis calculated for $\text{C}_{29}\text{H}_{42}\text{Br}_2\text{FeN}_2$: C, 54.91; H, 6.67; N, 4.42. Found: C, 54.83; H, 6.64; N, 4.36. ^1H NMR (400 MHz, THF- d_8 , 298 K): δ 37.76 (4H, s); 11.54 (4H, s); 4.85 (4H, s(br)); -0.61 (12H, s); -4.23 (4H, s); -6.75 (12H, s (br)); -14.26 (2H, s). μ_{eff} (Evans method, THF- d_8 solution, *protio*-toluene capillary, concentration 25 mg/mL, 298 K): 6.0 μB . Crystals suitable for X-ray diffraction were grown at ambient temperature from a concentrated THF solution of **1**.

[Fe(7-DIPP)Cl₂] (2): In a glovebox, an oven dried Schlenk tube was charged with 7-DIPP (500 mg, 1.19 mmol) and $[\text{FeCl}_2(\text{THF})_{1.5}]$ (250 mg, 1.07 mmol). Outside the glovebox, the combined solids were cooled to -78°C and cold THF was added (50 mL). The reaction mixture was allowed to stir at -78°C for 1h prior to slowly warming to ambient temperature and the homogeneous pale yellow reaction mixture was then allowed to stir for 16h. After this time, the reaction mixture was filtered *via* an oven dried PTFE filter cannula into a separate oven dried Schlenk tube and all volatiles removed to afford **2** as a free-flowing white solid (416 mg, 60%). Anal Calcd for $\text{C}_{29}\text{H}_{42}\text{Cl}_2\text{FeN}_2$: C, 63.74; H, 7.93; N, 5.13. Found: C, 63.10; H, 7.78; N, 4.91. ^1H NMR (400 MHz, C_6D_6 , 298 K): 29.65 (bs); 11.02 (bs); 9.47 (s); 3.54 (s); 1.40 (s); -2.38 (bs); -13.29 ppm (bs). μ_{eff} (Evans method, d_8 -THF solution, *protio*-toluene capillary, concentration 14.9 mg/mL, 298 K): 5.9(1) μB . Crystals suitable for X-ray diffraction were grown at ambient temperature by layering either a C_6D_6 or toluene solution of **2** with hexanes to afford **2.C₆D₆** or **2.C₇H₈**.

[Fe(7-Mes)Br₂(THF)] (3): In a glovebox, an oven dried Schlenk tube was charged with 7-Mes (200 mg, 0.60 mmol) and

[FeBr₂(THF)₂] (198 mg, 0.55 mmol). Outside the glovebox, the combined solids were cooled to -78°C and cold THF added (20 mL). The reaction mixture was allowed to stir at -78°C for 1h prior to slowly warming to ambient temperature and the homogeneous pale yellow reaction mixture was then allowed to stir for 16h at ambient temperature. After this time, the reaction mixture was filtered *via* an oven dried PTFE filter cannula into a separate oven dried Schlenk tube and the solution concentrated to approximately 5 mL. Storage of the concentrated solution at -30°C over a period three days to afford **3** as colourless crystals (215 mg, 63%). Analysis calculated for C₂₇H₃₈Br₂FeN₂O: C, 52.12; H, 6.16; N, 4.50. Found: C, 51.91; H, 6.33; N, 4.48. ¹H NMR (400 MHz, C₆D₆, 298 K): δ 39.69 (4H, s, (br)); 28.56 (12H, s, (br)); 8.59 (4H, s); 4.91 (4H, s (br)); 2.09 (4H, s); -9.61 (6H, s (br)); -21.06 (4H, s (br)). μ_{eff} (Evans method, THF-*d*₈ solution, *protio*-toluene capillary, concentration 14 mg/mL, 298 K): 6.2 μB. Crystals suitable for X-ray diffraction could be grown at ambient temperature from a concentrated THF solution of **3**.

[Fe(7-Mes)Br₂] (**4**): In a glovebox, a flame dried Schlenk tube was charged with 7-Mes (200 mg, 0.60 mmol) and [FeBr₂(THF)₂] (198 mg, 0.55 mmol). Outside the glovebox, the combined solids were cooled to -78°C and cold THF added (20 mL). The reaction mixture was allowed to stir at -78°C for 1h prior to slowly warming to ambient temperature and the homogeneous pale yellow reaction mixture was then allowed to for 16h at ambient temperature. After this time, the reaction mixture was filtered *via* an oven dried PTFE filter cannula into a separate flame dried Schlenk tube and all volatiles were removed. The remaining residue was washed with hexanes (3x20 mL) to afford **4** as colourless free-flowing solid (148 mg, 49%) Analysis calculated for C₂₃H₃₀Br₂FeN₂: C, 50.21; H, 5.50; N, 5.09. Found: C, 50.82; H, 5.63; N, 4.87. ¹H NMR (400 MHz, C₆D₆, 298K): δ 40.55 (bs); 27.65 (bs); 9.55 (s); 7.03 (s); 2.11 (s); -9.07 (bs); -20.41 (bs) ppm. μ_{eff} Evans method, THF-*d*₈ solution, *protio*-toluene capillary, concentration 14 mg/mL, 298 K): 5.2 μB. Crystals suitable for X-ray diffraction were grown at ambient temperature by layering a benzene solution of **4** with hexanes.

[Fe(SDiPP)Br₂] (**5**): In a glovebox, a flame dried Schlenk tube was charged with SDiPP (300 mg, 0.77 mmol) and [FeBr₂(THF)₂] (252 mg, 0.70 mmol). Outside the glovebox, the combined solids were cooled to -78°C and cold THF was added (30 mL). The reaction mixture was allowed to stir at -78°C for 1h prior to slowly warming to ambient temperature and the homogeneous pale yellow reaction mixture was then allowed to stir for 16h. After this time, the reaction mixture was filtered into a separate flame dried Schlenk tube *via* an oven-dried PTFE filter cannula and all volatiles removed to afford an off-white microcrystalline solid. The solid was washed with anhydrous hexanes (3x20 mL) prior to drying under vacuum to afford **5** as a free-flowing off-white powder (346 mg, 73%) Analysis calculated for C₅₄H₇₈Br₄Fe₂N₄: C, 53.49; H, 6.32; N, 4.62. Found: C, 53.26; H, 6.17; N, 4.42. ¹H NMR (400 MHz, C₆D₆, 298K): δ 5.74 (bs); 2.64 (bs); 1.89 (bs); 1.14 (bs); 0.82 (bs); -0.38 (bs). μ_{eff} (Evans method, *d*₆-benzene solution, *protio*-toluene capillary, concentration 11 mg/mL, 298 K): 6.1 μB. Crystals suitable for X-ray diffraction were grown at ambient temperature from a concentrated benzene solution of **5**.

[Fe(SDiPP)Br₂(THF)] (**6**): [Fe(SDiPP)Br₂] (**5**) was taken up in THF-*d*₈ and analyzed by ¹H NMR spectroscopy. ¹H NMR (400 MHz, THF-*d*₈, 298K): δ 8.13 (4H, bs); 7.61 (2H, bs); 3.00 (4H, bs); 1.72 (bs, overlapping with solvent); 1.15 (24H, bs, CH(CH₃)₂). μ_{eff} (Evans method, THF-*d*₈ solution, *protio*-toluene capillary, concentration 12 mg/mL, 298 K): 6.1 μB. Crystals suitable for X-ray diffraction were grown at ambient temperature by layering a concentrated THF-*d*₈ solution of **5** with hexanes. It was not possible to obtain satisfactory microanalytical data due to the

facile loss of THF under either dynamic vacuum or under ambient pressure.

ASSOCIATED CONTENT

Supporting Information

NMR spectra for all novel compounds, crystallographic information and Mössbauer spectra are provided. A text file containing Cartesian coordinates in .xyz format for all of the structures used in the deformation of **4** is provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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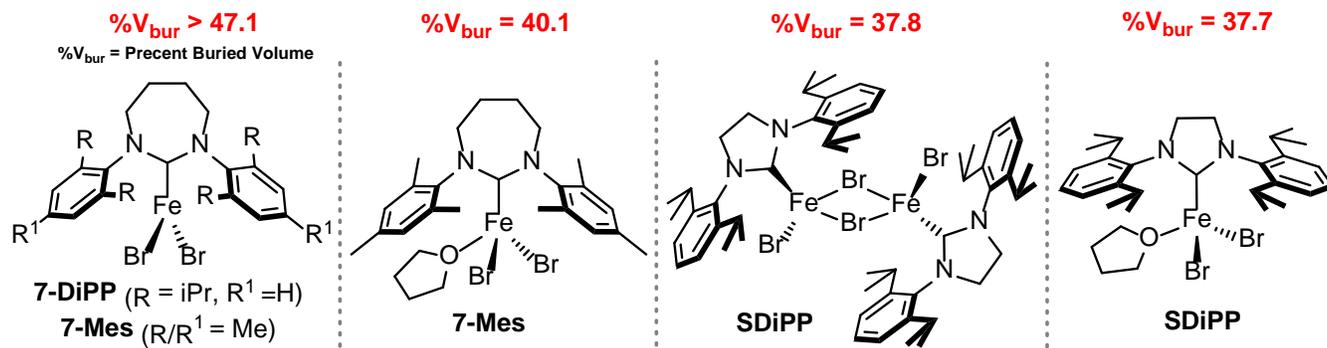
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REFERENCES

- [1] For recent reviews see: a) Ingleson, M. J.; Layfield, R. A. *Chem. Commun.*, **2012**, *48*, 3579–3589. b) Riener, K.; Haslinger, S.; Raba, A.; Högerl, M. P.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. *Chem. Rev.*, **2014**, *14*, 5215–5272. c) Bzier, D.; Sortais, J.-B.; Darcel, C. *Adv. Synth. Catal.* **2013**, *355*, 19–33.
- [2] For recent examples of low-coordinate iron(II)-NHC compounds see: a) Louie, J.; Grubbs, R. H. *Chem. Commun.* **2000**, 1479–1480. b) Grohmann, C.; Hashimoto, T.; Fröhlich, R.; Ohki, Y.; Tatsumi, K.; Glorius F. *Organometallics* **2012**, *31*, 8047–8050. c) Przyojski, J. A.; Arman, H. D.; Tonzetich, Z. *Organometallics* **2012**, *31*, 3264. d) Zlatogorsky, S.; Mury, C. A.; Tuna, F.; Evans, D. J.; Ingleson, M. J. *Organometallics* **2011**, *30*, 4974–4982. e) Ouyang, Z.; Deng, L. *Organometallics* **2013**, *32*, 7268–7271. f) Wu, J.; Dai, W.; Farnaby, J. H.; Hazari, N.; Le Roy, J. J.; Mereacre, V.; Murugesu, M.; Powell, A. K.; Takase, M. K. *Dalton Trans.*, **2013**, *42*, 7404–7413. g) Blom, B.; Tan, G.; Enthaler, S.; Inoue, S.; Epping, J. D.; Driess, M. *J. Am. Chem. Soc.* **2013**, *135*, 18108–1812.
- [3] For a recent example of iron-NHC complexes in homogeneous catalysis see: Liu, Y.; Wang, L.; Deng, L. *J. Am. Chem. Soc.* **2016**, *138*, 112–115.
- [4] a) Xiang, L.; Xiao, J.; Deng, L. *Organometallics* **2011**, *30*, 2018–2025. b) Fillman, K. L.; Przyojski, J. A.; Al-Afyouni, M. H.; Tonzetich, Z. J.; Neidig, M. L. *Chem. Sci.*, **2015**, *6*, 1178–1188. c) Przyojski, J. A.; Veggeberg, K. P.; Arman, H. D.; Tonzetich, Z. J. *ACS Catal.* **2015**, *5*, 5938–5946.
- [5] Danopoulos, A. A.; Braunstein, P.; Wesolek, M.; Monakhov, K. Y.; Rabu, P.; Robert, V. *Organometallics* **2012**, *31*, 4102–4105.
- [6] a) Layfield, R. A.; McDouall, J. J. W.; Scheer, M.; Schwarzmaier, C.; Tuna, F. *Chem. Commun.* **2011**, *47*, 10623–10625. b) Day, B. M.; Pugh, T.; Hendriks, D.; Guerra, C. F.; Evans, D. J.; Bickelhaupt, F. M.; Layfield, R. A. *J. Am. Chem. Soc.* **2013**, *135*, 13338–13341.

- [7] Danopoulos, A. A.; Braunstein, P.; Stylianides, N.; Wesolek, M. *Organometallics* **2011**, *30*, 6514–6517.
- [8] Wang, X.; Mo, Z.; Xiao, J.; Deng, L. *Inorg. Chem.* **2013**, *52*, 59–65.
- [9] Pugh, T.; Layfield, R. A.; *Dalton Trans.*, **2014**, *43*, 4251–4254.
- [10] Liu, Y.; Wang, L.; Deng, L. *Organometallics* **2015**, *34*, 4401–4407.
- [11] (a) Zhang, H.; Ouyang, Z.; Liu, Y.; Zhang, Q.; Wang, L.; Deng, L. *Angew. Chem. Int. Ed.* **2014**, *53*, 8432–8436. (b) Liu, Y.; Wang, L.; Deng, L., *Organometallics*, **2015**, *34*, 4401.
- [12] For an example of a three-coordinate iron(II)-bis-NHC complex see: Lee, W.-T.; Jeon, I.-R.; Xu, S.; Dickie, D. A.; Smith, J. M. *Organometallics*, **2014**, *33*, 5654–5659.
- [13] For examples of three-coordinate iron(I)-NHC complexes see: a) Mo, Z.; Ouyang, Z.; Wang, L.; Fillman, K. L.; Neidig, M. L.; Deng, L. *Org. Chem. Front.*, **2014**, *1*, 1040–1044. b) Ouyang, Z.; Du, J.; Wang, L.; Kneebone, J. L.; Neidig, M. L.; Deng, L. *Inorg. Chem.* **2015**, *54*, 8808–8816.
- [14] Dunsford, J. J.; Cade, I. A.; Fillman, K. L.; Neidig, M. L.; Ingleson, M. J. *Organometallics* **2014**, *33*, 370–377.
- [15] Pranckevicius, C.; Stephan, D. W. *Organometallics* **2013**, *32*, 2693–2697.
- [16] Poater, A.; Cozenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 1759–1766.
- [17] Parameters applied for SambVca calculations: 3.50 Å was selected as the value for sphere radius, 2.10 Å was used as the distance for the metal-ligand bond, hydrogen atoms were omitted and bond radii were scaled by 1.17
- [18] Iglesias, M.; Beetstra, D. J.; Knight, J. C.; Ooi, L.; Stasch, A.; Coles, S.; Male, L.; Hursthouse, M. B.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Organometallics* **2008**, *27*, 3279–3289.
- [19] For recent examples of sterically demanding expanded ring NHC complexes see: a) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 1256–1266. b) Herrmann, W. A.; Schneider, S. K.; Ofele, K.; Sakamoto, M.; Herdtweck, E. *J. Organomet. Chem.* **2004**, *689*, 2441–2449. c) Dunsford, J. J.; Cavell, K. J. *Dalton Trans.* **2011**, *40*, 9131–9135. d) Davies, C. J. E.; Page, M. J.; Ellul, C. E.; Mahon, M. F.; Whittlesey, M. K. *Chem. Commun.* **2010**, *46*, 5151–5153. e) Newman, P. D.; Cavell, K. J.; Kariuki, B. M. *Organometallics* **2010**, *29*, 2724–2734. f) Dunsford, J. J.; Tromp, D. S.; Cavell, K. J.; Elsevier, C. J.; Kariuki, B. M. *Dalton Trans.* **2013**, *42*, 7318–7329. g) Dunsford, J. J.; Cavell, K. J. *Organometallics* **2014**, *33*, 2902–2905.
- [20] For a comprehensive review on NHC %Vbur values see: Clavier, H.; Nolan, S. P. *Chem. Commun.*, **2010**, *46*, 841–861.
- [21] Dunsford, J. J.; Cavell, K. J.; Kariuki, B. M. *Organometallics* **2012**, *31*, 4118–4121.
- [22] a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. b) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.
- [23] Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
- [24] Dihedral angle defined as the angle between the N-C_{NHC}-N and X-Fe-X planes.
- [25] Dierick, S.; Dewez, D. F.; Markó, I. E. *Organometallics*, **2014**, *33*, 677–683
- [26] Organ, M. G.; Çalimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. J. *Angew. Chem.* **2009**, *121*, 2419–2423.
- [27] Meiries, S.; Le Duc, G.; Chartoire, A.; Collado, A.; Speck, K.; Athukorala Arachchige, K. S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Eur. J.* **2013**, *19*, 17358–17368.
- [28] For examples of the discrepancy between the use of 5-DiPP and SDiPP in iron catalyzed Kumada-type Csp²-Csp² cross-coupling see: a) Hatakeyama, T.; Nakamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 9844–9845; (b) Hatakeyama, T.; Hashimoto, S.; Ishizuka, K.; Nakamura, M. *J. Am. Chem. Soc.* **2009**, *131*, 11949–11963. c) Chua, Y.-Y.; Duong, H. A. *Chem. Commun.* **2014**, *50*, 8424
- [29] Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. *J. Comp. Chem.* **2013**, *34*, 1164–1175.
- [30] Gomez-Coca, S.; Cremades, E.; Aliaga-Alcalde, N.; Ruiz, E. *J. Am. Chem. Soc.* **2013**, *135*, 7010–7018.
- [31] Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534.
- [32] Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.; Fdez. Galván, I.; Ferré, N.; Frutos, L. M.; Gagliardi, L.; Garavelli, M.; Giussani, A.; Hoyer, C. E.; Manni, G.; Lischka, H.; Ma, D.; Malmqvist, P. Å.; Müller, T.; Nenov, A.; Olivucci, M.; Pedersen, T. B.; Peng, D.; Plasser, F.; Pritchard, B.; Reiher, M.; Rivalta, I.; Schapiro, I.; Segarra-Martí, J.; Stenrup, M.; Truhlar, D. G.; Ungur, L.; Valentini, A.; Vancoillie, S.; Veryazov, V.; Vysotskiy, V. P.; Weingart, O.; Zapata, F.; Lindh, R. *J. Comp. Chem.*, **2015**, doi:10.1002/jcc.24221.
- [33] a) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A*, **2004**, *108*, 2851–2858. b) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O.; *J. Phys. Chem. A*, **2005**, *109*, 6575–6579.



Structural variation in [Fe(NHC)X₂] complexes dependent upon NHC steric environment and solvent of recrystallization