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Structure and bonding in three-coordinate N-heterocyclic carbene adducts of iron(II) bis(trimethylsilyl)amide†

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The molecular structures, chemical bonding and magnetochemistry of the three-coordinate iron(II) NHC complexes [(NHC)Fe{N(SiMe$_3$)$_2$}$_2$] (NHC = IPr, 2; NHC = IMes, 3) are reported.

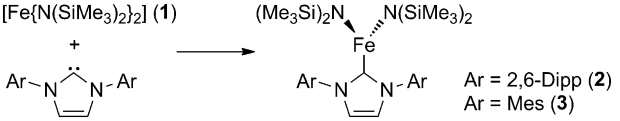
N-Heterocyclic carbene (NHC) complexes of late transition metals such as ruthenium, palladium and gold are an intensely studied class of compound owing to their applications in catalysis.[1–3] In contrast, studies of iron NHC complexes are less widespread. A series of recent reports has, however, shown that NHC complexes of iron do have considerable potential for development in a range of carbon-carbon and carbon-heteroatom bond forming reactions.[4] In most cases, the nature of the active iron NHC complex is not known, but it is probable that low-coordinate iron NHC complexes play an important role.[4d]

The growing importance of iron NHC complexes, combined with our interests in the chemistry of iron silyl-amides,[5] prompted us to investigate the interactions of NHC ligands with the low-coordinate iron(II) amide [Fe{N(SiMe$_3$)$_2$}$_2$] (**1**).[6,7] We selected the bulky NHC ligands 1,3-*bis*(diisopropylphenyl)-imidazol-2-ylidene (IPr) and 1,3-*bis*(2,4,6-trimethylphenyl)-imidazole-2-ylidene (IMes) in order to synthesize the complexes [(NHC)Fe{N(SiMe$_3$)$_2$}$_2$] (NHC = IPr, **2**; NHC = IMes, **3**), which are rare examples of three-coordinate iron NHC complexes.

Compound **1** reacts with either IPr or IMes in toluene to produce brown-coloured solutions. Concentrating the solutions followed by storage at −28 °C produced air-sensitive, light-green crystals of [(IPr)Fe{N(SiMe$_3$)$_2$}]·(toluene) and [(IMes)Fe{N(SiMe$_3$)$_2$}$_2$] (**3**) (Scheme 1). Molecules of **2** have an iron(II) centre complexed by the carbene carbon of an IPr ligand and by two nitrogens of the silyl-amide ligands (Fig. 1). The Fe(1)–C(1) bond length in **2** is 2.182(2) Å, and the Fe(1)–N(3) and Fe(1)–N(4) bond distances are 1.982(2) and 1.979(2) Å, respectively. The C(1)–Fe(1)–N(3), C(1)–Fe(1)–N(4) and N(3)–Fe(1)–N(4) bond angles are 117.06(7), 118.64(7) and 124.30(7)°. Compound **3** has a similar molecular structure to that of **2**. The Fe(1)–C(1) bond bond length is 2.184(2) Å, and the Fe(1)–N(1/1A) bond length is 1.9709(13) Å (Fig. S5†). The N–Fe–N and C–Fe–N angles are 122.96(6) and 118.52(4)°, respectively. In **2** and **3**, the Fe centres lie in the planes of the donor atoms.

The steric influence of the diisopropylphenyl and mesityl substituents in **2** and **3** is reflected in the bond angles around iron. The less bulky adduct [(thf)Fe{N(SiMe$_3$)$_2$}$_2$] (**4**)[6a] has a much larger N–Fe–N angle of 144.0(3)° and a much more acute N–Fe–O angle of 108.0(1)° than the analogous angles in **2** and **3**, suggesting that the aryl substituents on the NHC ligands in **2** and **3** 'squeeze' the silyl-amide ligands closer together. Particularly notable features in the structures of **2** and **3** are the lengths of the Fe–C bonds, which are approximately 0.2 Å longer than the mean average Fe–C(NHC) bond according to the Cambridge Structural Database,[8] and are in fact the longest Fe–(NHC) bonds of any iron complex of a monodentate NHC ligand.[9] The origin of the long Fe–C bonds in **2** and **3** is likely to be the steric repulsion between the bulky aryl and trimethylsilyl substituents, which prevent closer approach of the carbene carbon to the iron centre. The dihedral angles formed between the FeN$_2$ planes and the planes of the carbene five-membered ring are 41.7° and 62.3° in **2** and **3**, respectively, which reveals significant twisting about the Fe–C bonds. This structural motif has been observed in the Group 2 complexes [(NHC)M{N(SiMe$_3$)$_2$}$_2$],[10] and is reminiscent of the Y-shaped platinum(II)-NHC complex [(IPr)Pt(SiMe$_2$Ph)$_2$].[11]

After washing the complexes with cold pentane and drying *in vacuo*, polycrystalline samples of **2** and **3** were obtained, and were then measured in a SQUID magnetometer. The plots of magnetic susceptibility, χ_M, *versus* temperature, and $\chi_M T$ *versus* temperature, of **2** and **3** are very similar, and the Fe(II) centre in each complex can be assigned a spin quintet



Scheme 1 Synthesis of complexes **2** and **3**.

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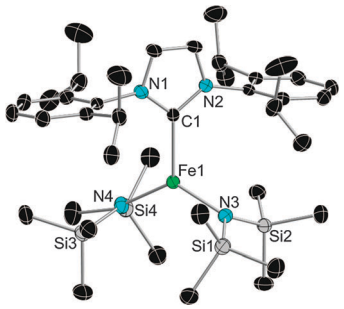


Fig. 1 Thermal ellipsoid plot (50% probability) of complex **2**. Hydrogen atoms not shown.

($S = 2$) ground state. For **2**, a zero-field splitting of $D = -18.2$ cm^{-1} was determined, with $g = 2.27$, and the analogous values for **3** are $D = -23.3$ cm^{-1} and $g = 2.24$ (Fig. S4 and S8†). The D and g values for **2** and **3** indicate significant orbital contributions to the magnetic susceptibility. The likely origin of this effect is second-order spin–orbit coupling involving low-lying excited states, an observation with precedent for planar three-coordinate iron(II) environments in which the bond angles deviate from 120°.[5,12]

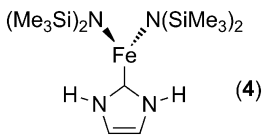
The ^{1}H NMR spectrum of **2** in toluene has a strong temperature dependence (Fig. S2 and S3†). As the temperature is lowered to from 298 K to 228 K, a resonance at $\delta \approx 63$ ppm grows in intensity, which is assignable to the $SiMe_3$ protons in **1**,[6a] and resonances characteristic of uncoordinated IPr also increase in intensity.[13] These observations imply facile dissociation of the IPr ligand from **2** at room temperature. The remaining resonances therefore correspond to intact **2**. Notably, a broad resonance at $\delta = -13.97$ ppm observed at 298 K decoalesces on cooling, producing resonances at $\delta = -19.57$, –36.61, and –65.37 ppm at 228 K, with intensities in an approximate ratio of 6 : 12 : 6. These resonances can be assigned to the isopropyl methyl groups in **2**, implying isopropyl rotation at higher temperatures.

The ^{1}H NMR spectrum of **3** at 353 K shows resonances that can be assigned to uncoordinated IMes: these resonances shift slightly to lower field on cooling to 193 K (Fig. S6 and S7†). Although a resonance due to **1** was not observed at $\delta \approx 63$ ppm, a broad resonance occurring at 23.08 ppm and 353 K undergoes significant line-broadening on cooling, followed by decoalescence to produce two very broad peaks at 51.32 and 24.52 ppm at 193 K. The resonance at 51.32 ppm and the temperature dependence of the IMes resonances suggest that coordination of IMes to **1** to give **3** is more facile than the analogous process involving IPr, which is presumably due to steric over-crowding by the IPr ligand (see below).

Two- and three-coordinate NHC complexes of d^8 and d^{10} metals form a vast series.[1–3] Although many iron NHC complexes have been crystallographically characterized, most contain six- or five-coordinate iron with 18- or 16-electron configurations, respectively.[14] Several examples of four-coordinate iron carbenes are also known.[15] Only one example of a three-coordinate iron carbene has been previously reported.[16]

To obtain deeper insight into the structure and bonding in **2** and **3**, a computational analysis was carried out. Our aim was to quantify the strengths of the Fe–C bonds, and to determine the orbital interactions that contribute towards (de)stabilization of these bonds. The influence of NHC ligand steric bulk was investigated via calculations on the unsubstituted model complex[$(H_2Im)Fe\{N(SiMe_3)_2\}$] (**4**), in which the NHC ligand is imidazole-2-ylidene.

The calculations on **2**, **3** and **4**, using the ORCA electronic structure programme,[17] involved full geometry optimization at the B3LYP/Def2-SVP[18] level (Fig. S7–S9†) followed by single point energy calculations at the B3LYP/Def2-TZVP level.[19] Toluene solvation was modeled using the conductor-like screening model (COSMO).[20] The $S = 2$ configuration for the Fe centres, as determined by magnetometry, was used in each case. Comparing the crystallographically determined Fe–C distances in **2** and **3** with the computations shows that the DFT-COSMO overestimates the distances by 0.127 Å (**2**) and 0.044 Å (**3**) (Table 1). The gas phase calculation on **3** reveals that the Fe–C bond is 2.233 Å, so the solvent does not have a significant role in determining this bond length (or the equivalent in **2**). The calculated trend in the Fe–C bond lengths is reflected in the corresponding bond dissociation energies, which show a significant decrease for the series **4** (26.6 kcal mol^{-1}) > **3** (14.7 kcal mol^{-1}) > **2** (3.9 kcal mol^{-1}) with B3LYP/Def2-SVP. Calculating the dissociation energies using the larger Def2-TZVP basis set but with geometries obtained with the Def2-SVP basis set shows significant lowering of the dissociation energies to: **4** (20.9 kcal mol^{-1}) > **3** (5.3 kcal mol^{-1}) > **2** (–3.9 kcal mol^{-1}). Within this level of approximation **2** is predicted to be unbound in toluene solution. Repeating the calculation in the gas phase also predicts **2** to be unbound (–2.5 kcal mol^{-1}). These are relatively small energy differences, and optimization with the larger basis could yield a positive binding energy. However, there is no evidence to suggest that the binding will be large, hence **2** should either be non-coordinated or only weakly coordinated in toluene.



(4)

These results are broadly consistent with the ^{1}H NMR spectra of **2** and **3**, *i.e.* the Fe–C bond energies are sufficiently small in both complexes to allow for some dissociation of the NHC ligand, but that the dissociation should occur to a greater extent in **2** than in **3**. These observations can be interpreted in terms of the steric repulsion between the diisopropylphenyl and trimethylsilyl substituents in **2**, which is greater than the repulsion between the mesityl and trimethysilyl substituents in **3**.

Further support for the conclusion that steric factors play a dominant role was obtained from a COSMO calculation of the

Table 1 Fe–C bond lengths and N–Fe–C–N dihedral angles. Calculated Fe–C bond dissociation energies

	Fe–C/Å	N–Fe–C–N/°	E(Fe–C)/kcal mol^{-1}
2	2.182(2)[a]; 2.309[b]	41.7[a]; 44[b]	3.9[b]; –3.9[c]
3	2.184(2); 2.228	62.3; 59	14.7; 5.3
4	2.167	17, 19	26.6; 20.9

[a] X-ray crystallography. [b] B3LYP/Def2-SVP + COSMO(toluene). [c] B3LYP/Def2-TZVP + COSMO(toluene) energies using geometries from *b*.

Fe–C distance and the associated dissociation energy in the model complex **4**. The calculated Fe–C distance of 2.167 Å for **4** in toluene is very similar to the crystallographically determined Fe–C bond lengths in **2** and **3**, but is 0.142 and 0.061 Å shorter than the Fe–C distances calculated for **2** and **3**, respectively, in toluene. The Fe–C dissociation energy in **4** was calculated to be 20.9 kcal mol^{-1} in toluene, which is 24.5 kcal mol^{-1} greater than the analogous value for **2**, and 15.6 kcal mol^{-1} greater than that calculated for **3**. The results of these calculations strongly suggest that the negligible steric demands of the H_2Im ligand enable more effective spatial overlap of the NHC and Fe orbitals, and hence the formation of a considerably stronger Fe–C bond in **4**. The substantial spatial requirements of the IPr ligands in **2** are such that steric clashes are readily relieved by dissociation of the NHC ligand as a result of a long, weak Fe–C bond.

Although π-contributions to transition metal-carbene bonds are now regarded as being small but significant,[3] the large dihedral angles between the carbene and FeN_2 planes in the molecular structures of **2** and **3**, which are also found in their calculated structures and in that of **4**, suggests that π-type overlap between iron d-orbitals and the NHC π-orbitals cannot be presumed. Our calculations of the quasi-restricted orbitals for **2**, **3** and **4** reveal that the iron d-orbitals are entirely metal-based, and that the NHC orbitals that could conceivably be involved in metal-NHC π-bonding are entirely ligand-based. These orbitals are shown for the most strongly bound example (**4**) in Table S3. The Fe–C bonding in **2**, **3** and **4** arises entirely from one σ-molecular orbital (Table S3). The extent of the σ-overlap in these molecular orbitals should be the least for the longest Fe–C bond, hence in **2** the considerable bulk of the aryl substituents leads to a long Fe–C bond and hence a weak interaction. The same effect is seen in **3** but not to the same extent, whereas a relatively strong Fe–C bond is found in the unhindered model complex **4**.

In summary, we have reported the three-coordinate iron NHC complexes **2** and **3**. SQUID magnetometry revealed that the Fe(II) centres in each complex possess an $S = 2$ ground-state and large zero-field splittings. Solution-phase lability of the NHC ligands in **2** and **3** was shown by ^{1}H NMR spectroscopy. A DFT study of **2**, **3** and **4**, revealed that the Fe–C bonds are composed entirely of σ-type orbitals, and that this bonding weakens considerably with increasing NHC bulk.

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