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Reactivity of three-coordinate iron–NHC complexes towards phenylselenol and lithium phenylselenide†

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The three-coordinate iron(II) NHC complexes [(IPr)Fe(N″)$_2$] (1) and [(I^{t}Bu)Fe(N″)$_2$] (3) (N″ = N(SiMe$_3$)$_2$) react with PhSeH or LiSePh to give the iron(II) selenolates [(IPr)Fe(N″)(SePh)] (6) and [I^{t}Bu(H)]-[(*a*I^{t}Bu)Fe(SePh)$_3$], [I^{t}Bu(H)][7], with complex 7 containing an abnormal NHC ligand.

N-heterocyclic carbene (NHC) complexes of iron have been known for over 40 years,[1] yet, despite these early studies, iron–NHC chemistry has evolved at slow pace relative to the NHC chemistry of late transition metals.[2] However, in the last five years, iron–NHC chemistry has grown at a more rapid rate,[3] which is due largely to the increasing number of applications of iron–NHC complexes in homogeneous catalysis.[4] In addition to catalytic applications of iron–NHC complexes, their chemistry has also been used to develop structural and/or functional models of iron coordination environments of relevance to biological systems, such as nitrogenase enzymes[5] and iron nitrosyl complexes.[6] Tripodal NHC ligands have also enabled the detailed structural characterization of iron coordination environments that were otherwise difficult or impossible to stabilize, such as a terminal nitride complex of iron(V).[7] Reflecting on this emerging field as a whole, it is apparent that many significant advances in iron chemistry have been achieved through the use of NHC ligands.

Three-coordinate iron complexes have provided a source of intrigue for many years.[8] Although several examples of three-coordinate iron NHC complexes have been structurally characterized,[9] their reactivity has not yet been studied to any great extent. Our own work has focused on the bulky three-coordinate complexes [(NHC)Fe(N″)$_2$] (N″ = N(SiMe$_3$)$_2$), in which the NHC ligands are 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr, complex 1), 1,3-bis(mesityl)imidazole-2-ylidene (IMes, complex 2) and 1,3-bis(*tert*-butyl)imidazole-2-ylidene (I^{t}Bu, complex 3) (Chart 1).[10] In a recent study, we have shown that the NHC ligands in **1** and **3** are thermally unstable.[11] In the case of the sterically hindered complex [(IPr)Fe(N″)$_2$] (**1**), refluxing in toluene for 2–3 hours results in a rearrangement of the normal IPr ligand to its abnormal/*meso*-ionic isomer [(*a*IPr)Fe(N″)$_2$] (**4**) in order to relieve steric pressure. In contrast, refluxing [(I^{t}Bu)Fe(N″)$_2$] (**3**) in toluene for prolonged periods results in one *tert*-butyl substituent per NHC ligand being eliminated as isobutene, in what appears to be a consecutive C–H/C–N bond activation process, and which results in the formation of the tetrahedral iron(II) bis(imidazole) complex [(^{t}BuIm)$_2$Fe(N″)$_2$] (**5**).

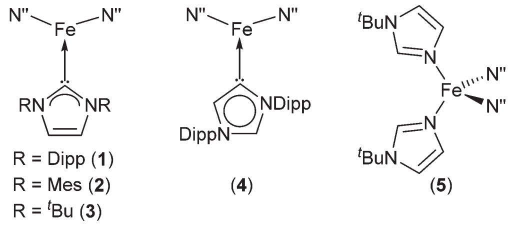

Chart 1 N″ = N(SiMe$_3$)$_2$.

Having established that **1** and **3** are sensitive to heat, we have now begun to explore their chemical reactivity, particularly towards Brønsted acids and organolithium reagents. The reactions of iron–NHC complexes towards thiols are well established, especially in the context of bio-mimetic chemistry,[5,6,12] however analogous chemistry with selenium is not well developed. Our initial reactivity studies have therefore focused on the reactions of **1** and **3** with phenylselenol, PhSeH, and lithium phenylselenide, PhSeLi (Scheme 1).

The reaction of **1** with two stoichiometric equivalents of PhSeH or PhSeLi in toluene solvent was undertaken in order to synthesize the three-coordinate iron bis(selenolate) complex [(IPr)Fe(SePh)$_2$] (**5**). However, the product of these reactions was the mono-substituted complex [(IPr)Fe(N″)(SePh)] (**6**), which was isolated as colourless crystals. Compound **6** can also be obtained from the reaction of **1** with one equivalent of PhSeE (E = H, Li). The molecular structure of **6** (Fig. 1) was

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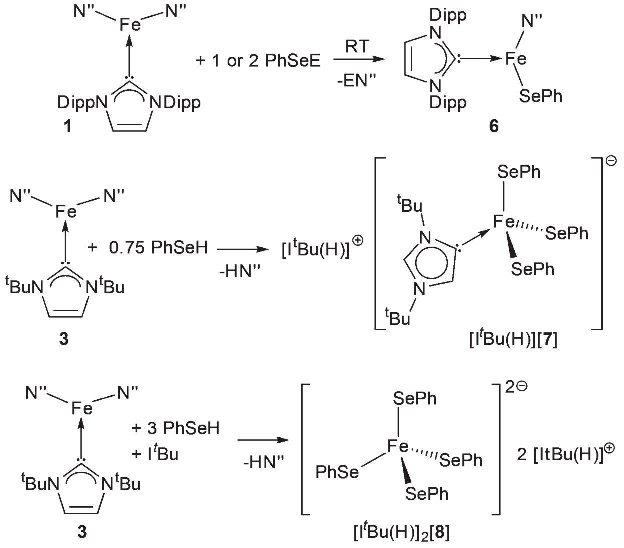

Scheme 1 E = H or Li.

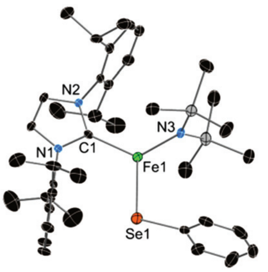

Fig. 1 Molecular structure of **6** (50% thermal ellipsoids). Hydrogen atoms not shown. Unlabelled atoms are silicon (grey) and carbon (black).

determined by X-ray crystallography (Table S1†), and features an iron centre in a distorted trigonal planar environment, with Fe(1)–C(1), Fe(1)–N(3) and Fe(1)–Se(1) bond distances of 2.124(3), 1.926(2), and 2.4351(3) Å, respectively, and C–Fe–N, N–Fe–Se and Se–Fe–C bond angles of 125.53(11), 119.99(8) and 114.52(8)°, respectively (sum of 360°). Although the Fe–C bond in **6** is approximately 0.06 Å shorter than that in **1**, it is still relatively long for an iron–NHC complex, according to the average distance of 1.994 Å in the Cambridge Structural Database (CSD).[13]

The ^{1}H NMR spectrum of **6** in toluene-d_8 at room temperature reflects the low-symmetry of the molecule (Fig. S1†). A series of broad, overlapping resonances occur in the range $\delta(^1H)$ = 0.29–9.69 ppm, in addition to a very broad, weak downfield resonance at $\delta(^1H)$ = 51.97 ppm and three sharper upfield resonances at $\delta(^1H)$ = −16.25, −19.12 and −42.12 ppm. The solution-phase effective magnetic moment of **6** was determined by the Evans method to be $\mu_{eff} = 5.2(6)\mu_B$,[14] which indicates that the iron(II) centre has a high-spin S = 2 configuration, with a contribution from spin–orbit coupling. Complex **6** extends the relatively small family of three-coordinate iron–NHC complexes, and it is the first example to contain a selenium donor ligand. The structures of two dimetallic iron–NHC complexes with additional selenium ligation have been reported previously, both of which contain five-coordinate iron and an iron–iron bond.[15]

The observation that double substitution of the amido ligands in **1** to give [(IPr)Fe(SePh)$_2$] (**5**) does not occur is intriguing. To investigate the possibility that the extreme steric bulk imparted by the IPr ligand influences the reactivity of **1** towards phenylselenol, the analogous reaction with another bulky NHC, I^{t}Bu, was carried out.[16] Surprisingly, the reaction of **3** with 0.75 equivalents of phenylselenol in toluene solvent, followed by work-up in thf, resulted in the formation of [I^{t}Bu(H)][(*a*I^{t}Bu)Fe(SePh)$_3$]·thf, [I^{t}Bu(H)][**7**]·thf, as light-yellow crystals (Scheme 1, Fig. 2 and Table S1†). In the monoanion **7**, the iron centre is complexed by an abnormal, or *meso*-ionic, *a*I^{t}Bu ligand in addition to three phenylselenolate ligands. The iron centre occupies a distorted tetrahedral environment, with an Fe(1)–C(1) distance of 2.099(5) Å and Fe–Se distances in the range 2.4812(8)–2.4995(8) Å. The angles formed by the ligand donor atoms and iron are 88.96(3) and 107.39(11)–115.89(13)° (average 109.1°).

The ^{1}H NMR spectrum of [I^{t}Bu(H)][**7**] in acetonitrile-d_3 features a series of resonances in the range $\delta(^1H)$ = +33.99 to −17.25 ppm, including several very broad, low-intensity resonances. The *ortho*- and *meta*- ^{1}H environments on the PhSe ligands in **7** occur at $\delta(^1H)$ = 17.86, 16.83, −16.29 and −17.25 ppm, with the resonances due to the *para* ^{1}H environments probably occurring at $\delta(^1H)$ = −9.17 and −11.23 ppm (the rationale for these assignments is provided by observations on complex **8** – see below). The resonances due to [I^{t}Bu(H)]$^+$ cation occur at 1.58, 6.70 and 7.46 ppm, suggesting that the other resonances in the spectrum should be due to the *a*I^{t}Bu ligand. We tentatively assign the resonance at $\delta(^1H)$ = 33.99 ppm to the imidazolylidene ^{1}H bonded to the carbon that is adjacent to the carbene donor atom, which is in agreement with our previous studies on iron(II) NHC complexes.[10,11] The two inequivalent *tert*-butyl groups in **7** occur at $\delta(^1H)$ = 11.60 and 4.26 ppm, on the basis that they have relatively high intensity and are broad, which indicates that the methyl groups are magnetically inequivalent on the NMR timescale at room temperature; these features were also observed in the ^{1}H NMR spectrum of **3**. The only remaining resonance is the backbone imidazolylidene ^{1}H at $\delta(^1H)$ = −2.39 ppm. The solution-

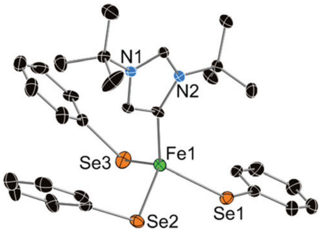

Fig. 2 Molecular structure of **7** (50% thermal ellipsoids). Hydrogen atoms are not shown. Unlabelled atoms are silicon (grey) and carbon (black).

phase effective magnetic moment for [I^{t}Bu(H)][**7**] is μ_{eff} = 5.9(6)μ_B, which is consistent with high-spin tetrahedral iron(II).[17]

In contrast to the deprotonation of the *tert*-butyl substituents by the $[(Me_3Si)_2N]^-$ ligands in **3** upon heating, the substituents on the I^{t}Bu ligands in **3** are retained in complex **7**. This suggests that deprotonation of PhSeH by the $[(Me_3Si)_2N]^-$ ligands is relatively rapid, and also that the $[PhSe]^-$ ligands in **7** are too weakly basic to deprotonate the *tert*-butyl substituents and, hence, initiate elimination of isobutene. The normal-to-abnormal rearrangement of the I^{t}Bu ligand probably occurs in order to reduce steric congestion around the iron coordination environment, which is consistent with observations made on the 2,6-dipp-substituted normal NHC complex **1** and its abnormal isomer **4**.[11] Although a reduction in steric bulk is likely to initiate the normal-to-abnormal rearrangement of **3** to **7**, the Fe–C bond in **7** is approximately 0.05 Å shorter than that of 2.151(2) Å in **3**, which, coupled with the stronger Lewis basicity of the abnormal I^{t}Bu ligand relative to its normal isomer, should also produce a stronger Fe–C bond.

Although transition metal complexes of abnormal, or *meso*-ionic, NHC ligands are well known in late transition metal chemistry,[18] abnormal iron–NHC complexes are uncommon.[9h,19,20] The abnormal I^{t}Bu ligand has not previously been observed for iron, however it is known in late transition metal chemistry, with examples including osmium and ruthenium carbonyl clusters[21] and the square-planar platinum(II) complex [(I^{t}Bu)(*a*I^{t}Bu)PtMe$_2$].[22] Examples of the *a*I^{t}Bu ligand in main group chemistry include the tetrahedral aluminium complex [(*a*I^{t}Bu)AlMe$_3$],[23] and a sulphide-bridged dimetallic tin(IV) cation ligated by two *a*I^{t}Bu ligands.[24]

The composition of [I^{t}Bu(H)][**7**] suggested that the synthesis of this compound could be achieved by combining complex **3** with I^{t}Bu and PhSeH in the 'correct' stoichiometric ratio of 1 : 1 : 3. However, yet another surprising outcome was observed, in which the only isolable product of the reaction was [I^{t}Bu(H)]$_2$[Fe(SePh)$_4$]·(2MeCN), the structure of which was determined by X-ray crystallography (Fig. S3 and Table S1†). Upon reaction with phenylselenol, all the amido and NHC ligands in **3** are replaced by phenylselenolate ligands to give the tetrahedral complex anion $[Fe(SePh)_4]^{2-}$ (**8**) (Scheme 1). Complex **8** has no remarkable structural features (Fig. S3†), with the Fe(1)–Se(1/1A) and Fe(1)–Se(2/2A) bond lengths of 2.4559(5) Å and 2.4522(5) Å, respectively, being very similar to those in the only other examples of [Q][Fe(SePh)$_4$] compounds in the CSD, where Q = $[(NEt_4)^+]_2$ or $[Fe^{II}(1,10\text{-phen})_3]^{2+}$.[25] The ^{1}H NMR spectrum of [I^{t}Bu(H)]$_2$[**8**] in acetonitrile-d_3 is relatively straightforward to interpret (Fig. S4†), with the resonances due to the $[I^tBu(H)]^+$ cation being observed at $\delta(^1H)$ = 8.31, 7.44 and 1.56 ppm, and the resonances due to **8** occurring at $\delta(^1H)$ = 17.85 and −16.29 ppm (*ortho* and *meta* Ph), and $\delta(^1H)$ = −9.16 ppm (*para* Ph). The solution-phase effective magnetic moment of **8** is μ_{eff} = 5.4(2)μ_B, which is similar to that of **7**.

The formation of [I^{t}Bu(H)]$_2$[**8**] suggests that phenylselenol is deprotonated by the amido ligands in **3**, and also by I^{t}Bu, at a rapid rate relative to the rate of the rearrangement of I^{t}Bu to *a*I^{t}Bu. In attempting to relate complexes **6**–**8**, complex **8** can, in a thermodynamic sense, be regarded as the end product of a sequence of reactions in which the amido and NHC ligands are sequentially replaced by selenolate ligands. The mono-selenolate complex **6** can therefore be regarded as the first step in the formation of **8**, and the tris(selenolate) complex **7** can be regarded as an intermediate species. The missing link for this chemistry is therefore a bis(selenolate) complex of iron(II), which has yet to reveal itself to us, although our on-going studies will attempt to identify such a species.

Conclusions

Our initial studies on the chemistry of the three-coordinate iron(II) complexes [(NHC)Fe(N″)$_2$] have provided evidence of complicated reactivity towards phenylselenol and lithium phenylselenide. In addition to the tendency of the NHC ligands to undergo normal-to-abnormal rearrangements, it is also apparent that the relatively weak Fe–C bonds can be cleaved by the Brønsted acid PhSeH. Future work will study the reactivity of [(NHC)Fe(N″)$_2$] with a range of other substrates.

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