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Iron(II) complexes of ditopic carbanionic carbenes†

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Rebecca A. Musgrave,[a] Robert S. P. Turbervill,[a] Mark Irwin,[a] Radovan Herchel[b] and Jose M. Goicoechea*[a]

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Reaction of dimesityliron(II) ($Fe_2(mes)_4$) with the N-heterocyclic carbenes 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) and 1,3-bis(2,6-dimethylphenyl)hexahydropyrimidin-2-ylidene (6-Xyl) afforded the novel trigonal planar complexes [Fe(IPr)(mes)$_2$] (**1**) and [Fe(6-Xyl)(mes)$_2$] (**2**), respectively. Both species were structurally characterized by single crystal X-ray diffraction and display structures and magnetic responses consistent with a quintet ground state (S = 2). Reaction of **1** with KC_8 in THF afforded K^+ salts of the anionic complex $[\{:C[N(2,6\text{-}^iPr_2C_6H_3)]_2(CH)C\}_2Fe(mes)]^-$ (**3**) and the homoleptic organometallic anion $[Fe(mes)_3]^-$ (**4**). By contrast, reduction of **2** resulted in extensive decomposition and intractable product mixtures. Complex **3** is coordinated by two ditopic carbanionic carbenes *via* the C4/C5 position while the C2 position retains unquenched carbenic character and remains vacant for further coordination. This was corroborated by reacting solutions of **3** with one and two equivalents of triethylaluminium ($AlEt_3$) which resulted in the formation of $[\{Et_3Al:C[N(2,6\text{-}^iPr_2C_6H_3)]_2(CH)C\}\{:C[N(2,6\text{-}^iPr_2C_6H_3)]_2(CH)C\}Fe(mes)]^-$ (**5**) and $[\{Et_3Al:C[N(2,6\text{-}^iPr_2C_6H_3)]_2(CH)C\}_2Fe(mes)]^-$ (**6**), respectively. Both of these species were structurally characterized as $[K(2,2,2\text{-crypt})]^+$ salts.

1. Introduction

Despite their extensive use as supporting ligands in catalysis,[1] it is well established that N-heterocyclic carbenes (NHCs) can undergo a variety of bond activation reactions (C–H, C–C and C–N) at the nitrogen atom functionalities when in the presence of transition metals.[2–4] By contrast, chemical activation of the ligand backbone is much rarer and, to the best of our knowledge, limited to systems with unsaturated alkenic backbones. The first example of such a transformation was reported by Whittlesey and co-workers who isolated a complex of an activated ditopic carbanionic carbene capable of bridging two metal centres *via* the C4 and C5 positions simultaneously (Fig. 1, Type A).[5] Similar reactions affording formally anionic activated NHC ligands capable of bridging metal centres *via* the C2 and C4/C5 positions were reported soon thereafter (Fig. 1, Type B).[6] The latter species can also be accessed in the absence of a transition metal; direct chemical reduction of lanthanide NHC complexes or of the ligands themselves has been found to yield alkali metal salts of the activated ligand.[7,8]

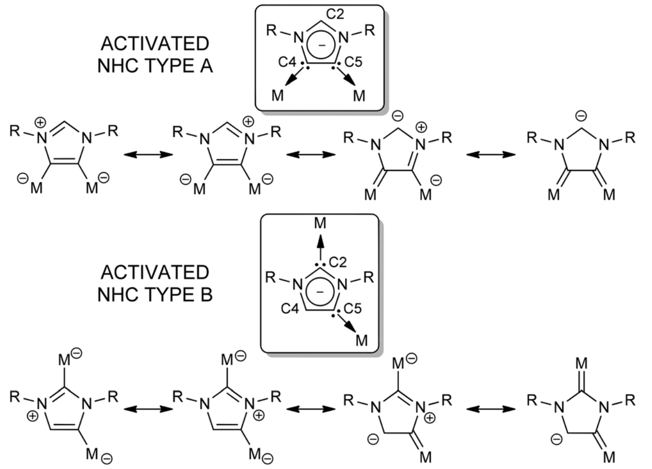

Fig. 1 Bimetallic ditopic carbanionic carbenes (anionic dicarbenes) and their resonance canonicals: derived from the activation of alkenic C–H bonds in unsaturated imidazolylidene N-heterocyclic carbene complexes.

More recently, the synthesis of bimetallic complexes of such ligands has become possible *via* the alkali–metal-mediated zincation of a carbene (IPr).[9] These carbanionic carbenes can be represented using a variety of resonance structures some of which imply a significant degree of carbenic character at both of the metallated positions. This has led to such species also being discussed as "dicarbenes".[8] As such they are reminiscent of the neutral 1,2,4-triazole-3,5-diylidenes first identified in silver(I) coordination polymers.[10]

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[a] *Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, UK. E-mail: jose.goicoechea@chem.ox.ac.uk*

[b] *Department of Inorganic Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, 77146 Olomouc, Czech Republic*

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In both kinds of backbone-activated imidazol-2-ylidene ligands, one of the metal atoms is bonded to the carbanionic C4 position (which has significant vinylic character). This bonding mode is similar to that observed for transition metal complexes of abnormally-bonded carbenes, first reported by Crabtree and co-workers (these species are also termed mesoionic because they cannot be represented by a Lewis structure without invoking two opposing charges on the ligand).[11] While the number of transition metal complexes of such ligands has steadily increased since they were first reported,[12] the first metal-free mesoionic carbene was not reported until 2009.[13]

We have recently observed that chemical reduction of transition metal NHC complexes, *e.g.* [Mn(IPr)(mes)$_2$] (mes = 2,4,6-trimethylphenyl), can be used to access complexes of anionic backbone-activated ligands such as K[{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Mn(mes)(THF)]·THF.[14] This reaction can be extended to other post-transition metal compounds such as [M(IPr)(mes)$_2$] (M = Zn, Cd) affording complexes which also contain carbanionic carbenes (or dicarbenes).[15] Herein we expand on these findings by demonstrating that chemical reduction of the trigonal planar iron complex [Fe(IPr)(mes)$_2$] (**1**) can be used to access an iron(II) complex bearing two carbanionic carbene ligands, [{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Fe(mes)]$^-$ (**3**), alongside the previously reported anion [Fe(mes)$_3$]$^-$ (**4**). By contrast, attempts to chemically reduce the saturated ring-expanded carbene complex [Fe(6-Xyl)(mes)$_2$] (**2**) resulted in extensive decomposition and did not result in ligand activation nor in the generation of an isolable iron(I) complex. The unquenched carbenic properties of the two carbanionic carbene ligands in **3** were established by reacting the complex with one and two equivalents of triethylaluminium resulting in the formation of the novel complexes [{Et$_3$Al:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}Fe(mes)]$^-$ (**5**) and [{Et$_3$Al:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Fe(mes)]$^-$ (**6**), respectively. The relative ease with which metal complexes of backbone-activated carbenes can be accessed is surprising considering the significant role imidazol-2-ylidenes have played in the isolation of low oxidation state main-group compounds (similarly accessed by chemical reduction of preformed NHC compounds).[16–22]

2. Results and discussion

2.1. Formation of neutral carbene complexes

Reaction of Fe(mes)$_2$ with one equivalent of the N-heterocyclic carbenes IPr or 6-Xyl yields the trigonal planar Lewis acid–base adducts [M(L)(mes)$_2$] (L = IPr (**1**), 6-Xyl (**2**)), respectively. The resulting white solids display poor solubility in the majority of common laboratory solvents. **1** and **2** are sparingly soluble in THF and highly soluble in pyridine giving rise to clear red solutions (presumably a result of pyridine coordination to the metal centre and metal–ligand charge transfer transitions). Single crystal X-ray diffraction quality colourless crystals of **1** and **2** could be obtained by slow diffusion of hexane into solutions of the solids. Elemental analyses and powder X-ray diffraction (PXRD) were used to confirm the compositional purity of the solids (see ESI†).

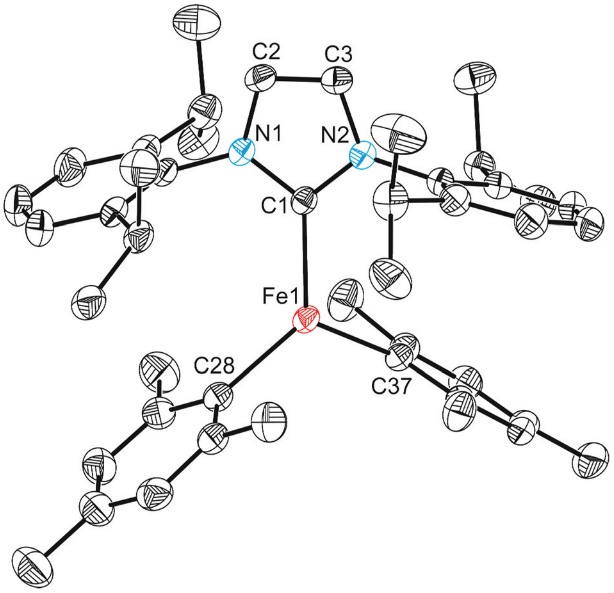


Fig. 2 Molecular structure of **1** (anisotropic displacement ellipsoids pictured at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe1–C1: 2.115(1); Fe1–C28: 2.076(2); Fe1–C37: 2.059(1); C1–N1: 1.362(2); C1–N2: 1.361(2); N1–C2: 1.387(2); N2–C3: 1.389(2); C2–C3: 1.346(2); N1–C4: 1.447(2); N2–C16: 1.447(2); C1–Fe1–C28: 122.6(1); C1–Fe1–C37: 117.8(1); C28–Fe1–C37: 119.6(1); N1–C1–N2: 103.3(1).

The single crystal X-ray structures of **1** and **2** (Fig. 2 and 3) confirm their trigonal planar geometries (selected data collection and refinement parameters for all of the structures described in the manuscript are provided in Table 1). The sum of C–Fe–C bond angles is 360.0° for both **1** and **2** (the deviation from planarity of the iron centre and bonded carbon atoms is 0.005 and 0.000 Å, respectively). Trigonal planar iron complexes of N-heterocyclic carbenes are rare and only a handful of structurally authenticated species are reported in the chemical literature (all of them containing imidazole based NHC systems).[4d,23] No structurally authenticated trigonal planar iron systems are known for expanded ring carbene systems; in fact, of all of the transition metals, the only examples of such complexes reported to date are limited to nickel(I).[24]

The structure of **1** is closely related to the isomorphous manganese(II) complex previously reported by our research group, [Mn(IPr)(mes)$_2$],[14] with some notable differences in bond metric parameters. The Fe–C$_{\mathrm{NHC}}$ bond in **1** (2.115(1) Å) is significantly shorter (Δd = 0.08 Å) than that of its manganese homologue (2.195(2) Å). This observation is consistent with the different covalent radii published by Alvarez and co-workers for high-spin compounds of manganese and iron, reported to be 1.61(8) and 1.52(6) Å, respectively.[25] The metal–mesityl bonds are also shorter for **1** (2.059(1) and 2.076(2) Å) than for the manganese analogue (2.122(2) and 2.125(2) Å). Geometric parameters for **1** are consistent with other previously reported trigonal planar iron(II) NHC complexes such as [Fe(IPr$_2$Me$_2$)-

(mes)$_2$] (IPr$_2$Me$_2$ = 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene).[23a] Both complexes display trigonal planar geometries with similar bond metrics. The Fe–C$_{NHC}$ distances are very similar: 2.115(1) Å in **1** compared to 2.125(3) Å in [Fe(IPr$_2$Me$_2$)(mes)$_2$]. The same is true of the Fe–C$_{mes}$ distances which are 2.059(1) and 2.076(2) Å in **1** (*cf.* 2.074(3) and 2.072(3) Å in [Fe(IPr$_2$Me$_2$)(mes)$_2$]).

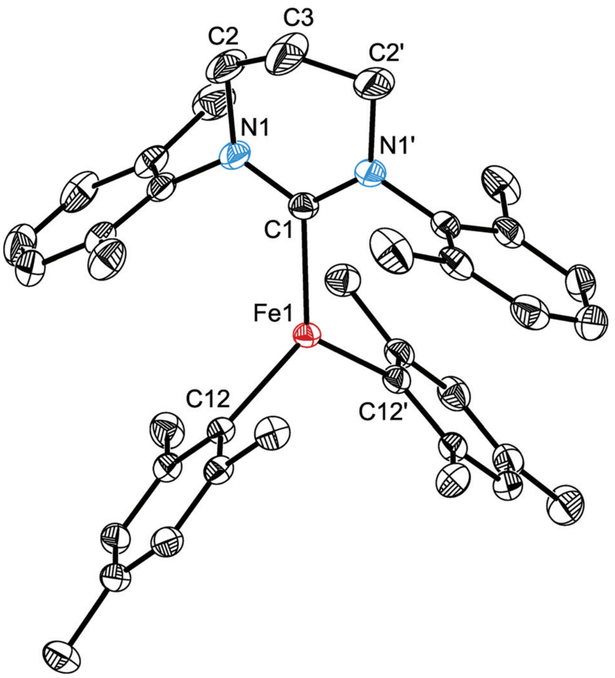


Fig. 3 Molecular structure of **2** (anisotropic displacement ellipsoids pictured at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe1–C1: 2.139(2); Fe1–C12: 2.062(1); C1–N1: 1.341(2); N1–C2: 1.479(2); C2–C3: 1.530(5); C2′–C3: 1.469(5); N1–C4: 1.442(2); C1–Fe1–C12: 124.4(1); C12–Fe1–C12′: 111.3(1); N1–C1–N1′: 117.08(18). Symmetry operation ′: 1 – *x*, +*y*, 0.5 – *z*.

A comparison of the structural features of **1** and **2** (Table 2) confirms previous observations on the steric requirements of expanded ring carbenes with respect to their five-membered ring analogues.[26,27] The greater N–C$_{NHC}$–N angle of 6-Xyl relative to IPr (117.1(2) *vs.* 103.3(1)°) makes the former significantly more sterically demanding, pushing the 2,6-dimethylphenyl substituents towards the iron centre. This is manifested in a longer Fe–C$_{NHC}$ bond, more obtuse C$_{NHC}$–Fe–C$_{mes}$ angles and a more acute angle between the mesityl substituents.

According to our density functional theory (DFT) studies, the aforementioned structural parameters are consistent with an S = 2 ground state for both **1** and **2**. The optimized computed geometries for both complexes with singlet (S = 0), triplet (S = 1) and quintet (S = 2) electronic configurations were calculated at the DFT level of theory (see ESI† for full details). For both complexes, the lowest energy electronic configuration is S = 2. Moreover, the optimized geometries for the quintet states have the greatest similarity to those determined by single crystal X-ray diffraction (M–C bond distances and C–M–C bond angles are strongly affected by the electronic configuration of the metal centre). Our calculations show that M–C bond distances lengthen substantially on increasing the number of unpaired electrons at the metal centre as might be expected. Moreover, the singlet and triplet structures display a more "T-shaped" geometry than that of the S = 2 system. These observations were reported previously for the manganese(II)

Table 1 Selected X-ray data collection and refinement parameters for **1**, **2**, K[**3**]·C$_6$H$_{14}$·0.5THF, [K(2,2,2-crypt)][**5**]·0.5THF and [K(2,2,2-crypt)][**6**]

	1	**2**	K[**3**]·C$_6$H$_{14}$·0.5THF	[K(2,2,2-crypt)][**5**]·0.5THF	[K(2,2,2-crypt)][**6**]
Formula	$C_{45}H_{58}FeN_2$	$C_{38}H_{46}FeN_2$	$C_{71}H_{99}FeKN_4O_{0.5}$	$C_{89}H_{136}AlFeKN_6O_{6.5}$	$C_{93}H_{147}Al_2FeKN_6O_6$
Fw [g mol^{-1}]	682.78	586.62	1111.49	1515.97	1594.08
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	*P*2(1)/*c*	*C*2/*c*	$P\bar{1}$	*P*2(1)/*n*	*Pna*2(1)
a (Å)	12.3163(1)	21.1298(3)	12.7856(3)	10.8094(1)	23.1194(5)
b (Å)	17.9494(1)	9.8555(1)	14.2917(5)	25.7657(4)	37.1470(12)
c (Å)	18.0222(1)	17.0866(3)	19.9211(7)	31.1703(4)	11.0300(3)
α (°)			71.953(3)		
β (°)	98.365(1)	116.231(2)	85.004(2)	94.291(1)	
γ (°)			74.811(2)		
V (Å^3)	3941.79(4)	3191.77(8)	3340.08(18)	8656.96(19)	9472.7(4)
Z	4	4	2	4	4
Radiation, *λ* (Å)	Cu K$_\alpha$, 1.54178				
T (K)	150(2)				
ρ_{calc} (g cm^{-3})	1.151	1.221	1.105	1.163	1.118
μ (mm^{-1})	3.291	3.984	2.676	2.344	2.245
Reflections collected	82 827	8080	31 883	42 401	48 896
Independent reflections	8283	3317	11 766	15 228	15 442
Parameters	441	208	724	964	1000
R(int)	0.0473	0.0207	0.0546	0.0364	0.0502
R_1/wR_2,[a] $I \geq 2\sigma_I$ (%)	3.56/9.36	3.29/8.88	6.33/17.22	4.83/12.76	7.06/13.63
R_1/wR_2,[a] all data (%)	4.04/9.74	3.52/9.09	7.72/18.56	6.57/13.65	8.30/14.05
GOF	1.022	1.022	1.060	1.060	1.105

[a] $R_1 = [\sum||F_o| - |F_c||]/\sum|F_o|$; $wR_2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the *A* and *B* values are 0.0539 and 1.19 for **1**, 0.0567 and 1.73 for **2**·THF, 0.1204 and 0.16 for K[**3**]·C$_6$H$_{14}$·0.5THF, 0.0789 and 0.80 for [K(2,2,2-crypt)][**5**]·0.5THF and 0.0041 and 20.88 for [K(2,2,2-crypt)][**6**].

Table 2 Selected bond distances (Å) and angles (°) for **1** and **2**

	1	**2**
Fe–C_{NHC}	2.115(1)	2.139(2)
Fe–C_{mes}	2.076(2), 2.059(1)	2.062(1)
N–C_{NHC}–N	103.3(1)	117.1(2)
C_{NHC}–Fe–C_{mes}	122.6(1), 117.8(1)	124.4(1)
C_{mes}–Fe–C_{mes}	119.6(1)	111.3(1)

complex [Mn(IPr)$(mes)_2$] which has a sextet (S = 5/2) ground state.[14]

The paramagnetic character of **1** and **2** is manifested in the broad paramagnetically shifted resonances observed in their ^{1}H NMR spectra. Due to the dynamic behaviour of these species in pyridine (presumably involving the formation of a Lewis acid–base adduct between the solvent and the metal centre) attempts to determine the magnetic moment of the samples using the Evans method were unsuccessful. The chemical shift differences ($\Delta\delta$) between the residual protic solvent and the internal reference are not meaningful as each solvent resonance experiences a different absolute shift (due to variations in pseudo contact shifts). Attempts to use any (or an average), of these values to determine magnetic moments led to unphysically large values of μ_{eff}. SQUID magnetometry measurements on solid samples of **1** and **2** were also complicated by the presence of trace amounts of a paramagnetic contaminant and were thus run using a ferrosubtract protocol at high fields to saturate the contaminant (this procedure is described in the Experimental section). The results obtained are consistent with a quintet ground state for both samples with μ_{eff} values found to be moderately larger than the calculated spin-only value of 4.89 μ_B. The effect of trigonal symmetry and spin–orbit coupling is manifested by substantial values for the axial zero-field splitting parameters, $D = -11.5$ cm^{-1} for **1** and $D = -18.9$ cm^{-1} for **2**, which resulted from the magnetic analysis (see ESI† for more details). These values are comparable to others reported in the chemical literature for trigonal planar iron(II) complexes.[23b]

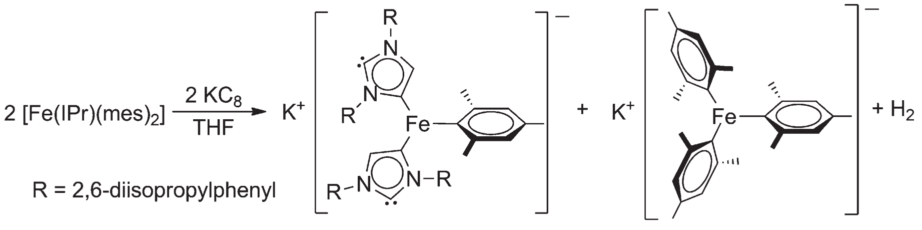
2.2. Synthesis of complexes containing ditopic carbanionic carbene ligands

A 1 : 1 stoichiometric mixture of [Fe(IPr)$(mes)_2$] and KC_8 was stirred overnight in THF after which the black suspension was filtered to remove graphite from the reaction mixture. Slow diffusion of hexane into the resulting brown solution yielded off-white crystalline blocks suitable for single crystal X-ray diffraction. The crystals were identified as a K^+ salt of [{:C[N-(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Fe(mes)]$^-$ (**3**), which contains two C4/C5 bonded carbanionic carbenes. The formation of **3** involves the chemical reduction of one of the imidazolium protons of the alkenic backbone to yield dihydrogen. The deprotonation of an NHC complex followed by migration of the C2 substituent to the C4 (or "abnormal" position) has previously been demonstrated by Bertrand and co-workers.[28]

A balanced equation for the synthesis of **3** can be written by invoking the formation of [Fe$(mes)_3$]$^-$ as a side-product (see Scheme 1). Addition of half of an equivalent of 2,2,2-crypt to the mother liquor that afforded crystals of **3** allowed for the crystallization of [K(2,2,2-crypt)][Fe$(mes)_3$] ([K(2,2,2-crypt)][**4**]; this species has previously been reported by our research group).[29] Similarly, addition of 18-crown-6 affords the novel salt [K(18-crown-6)THF][**4**] (see ESI† for structural data). It is worth noting that the reaction mixtures that give rise to species **3** and **4** are highly reactive and that the presence of other species in solution, such as cation sequestering agents (18-crown-6) or polydimethylsiloxane grease, can give rise to products resulting from the chemical activation of C–O or Si–O bonds, respectively. During the course of our studies we were able to isolate and crystallographically characterize two such products [{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}Fe(κ^2,μ^1,μ^2-O(C$_2$H$_4$O)$_4$-C$_2$H$_4$O)K]$_2$ (**7**) and [K(2,2,2-crypt)]$_2${Fe[Fe{κ^2-O$_4$(SiMe$_2$)$_3$}]$_2$-[κ^2,μ^2,μ^2-O$_3$(SiMe$_2$)$_2$]$_2$} ([K(2,2,2-crypt)]$_2$[**8**]). Due to the small quantities of samples obtained the structures of these two novel species are presented in the ESI† solely for reference purposes.

The lack of alkenic protons in the carbene backbone of **2** led us to hypothesize that ligand activation might be circumvented on reduction allowing access to an iron(I) complex. However, all attempts to reduce **2** using the methodology described above gave rise to oily, intractable solids that could not be satisfactorily identified.

The crystal structure of K[**3**]·C$_6$H$_{14}$·0.5THF (Fig. 4) contains a single crystallographically unique anionic iron(II) complex in the asymmetric unit (accompanied by a potassium cation and solvent of crystallization). Species **3** is closely related to a manganese(II) complex previously reported by our research group, K[{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Mn(mes)(THF)]·THF.[14] The most notable difference is that the manganese species adopts a distorted tetrahedral geometry due to the presence of a THF molecule in the coordination sphere of the metal. No such solvent is observed for **3**, which is consistent with the smaller covalent radius of iron relative to manganese (a result



Scheme 1 Synthesis of **3** and **4** by chemical reduction of **1**.

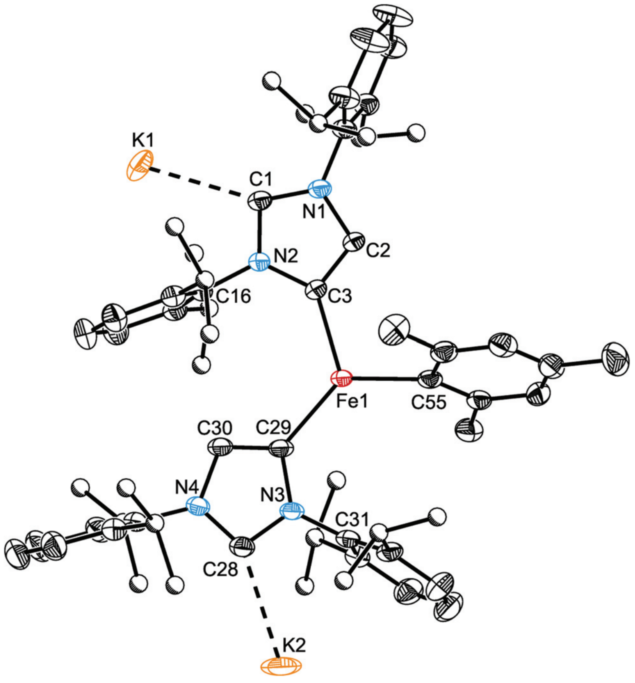


Fig. 4 Molecular structure of K[**3**]·C_6H_{14}·0.5THF (anisotropic displacement ellipsoids pictured at 50% probability level). Solvent of crystallization and hydrogen atoms have been omitted for clarity. Atoms of ^{i}Pr groups are pictured as spheres of arbitrary radii. Selected bond distances (Å) and angles (°): Fe1–C3: 2.071(2); Fe1–C29: 2.064(2); Fe1–C55: 2.065(3); K1–C1: 2.811(3); C1–N1: 1.354(4); C1–N2: 1.359(3); N1–C2: 1.400(3); N2–C3: 1.406(3); C2–C3: 1.359(4); K2–C28: 2.824(3); C28–N3: 1.372(3); C28–N4: 1.350(4); N3–C29: 1.416(3); N4–C30: 1.403(3); C29–C30: 1.369(4); C3–Fe1–C29: 122.5(1); C3–Fe1–C55: 108.4(1); C29–Fe1–C55: 128.4(1).

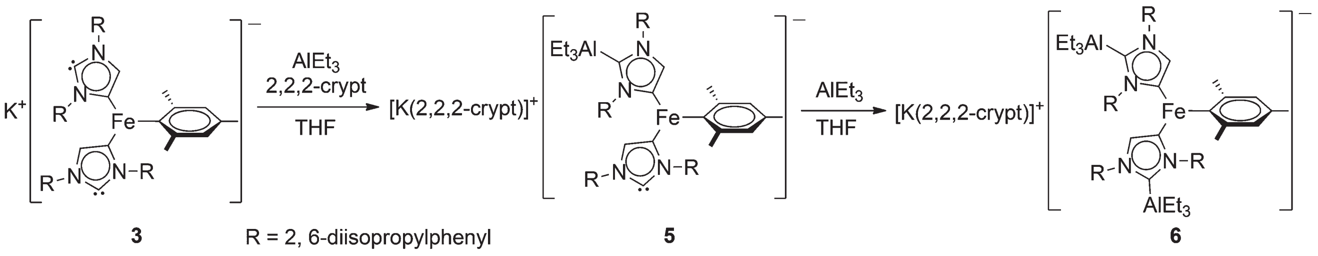
of an increase in effective nuclear charge on moving from left to right along the first transition metal series). This is also manifested in the M–C bond lengths which are on average 0.11 Å shorter for **3** than for the manganese complex (see ESI† for a comparison of bond metric data). The iron metal center in **3** is coordinated by two ditopic carbanionic carbenes, in each case through the C4/C5 position. The remaining carbenic C2 sites are stabilized by electrostatic contacts with charge-balancing potassium cations ($d_{C\text{–}K}$: 2.811(3) and 2.824(3) Å). The Fe–C distances in **3** are comparable to one another, Fe–C_{NHC}: 2.071(2) and 2.064(2) Å; Fe–C_{mes}: 2.065(3). This is contrary to what was observed for **1** where the iron–mesityl distances were notably shorter than the iron–carbene distance (by approximately 0.05 Å), and is consistent with the vinylic character of the iron–carbene bonds in **3**.

Compositionally pure solid samples of K[**3**]·C_6H_{14}·0.5THF could be obtained by successive recrystallizations from THF/hexane. The presence of **3** in solution was confirmed by electrospray mass-spectrometry of a THF solution of K[**3**]·C_6H_{14}·0.5THF which showed the molecular ion at an *m/z* value of 950.2 in the negative ion mode spectrum. The mass spectrum shows no evidence of other reaction side-products although some decomposition of the anion was observed during ionization.

Elemental analyses for K[**3**]·C_6H_{14}·0.5THF were consistently (and reproducibly) found to give low carbon values (as previously observed for related manganese and zinc complexes of carbanionic carbenes) presumably due to the formation of metal carbides.[14,15] A powder X-ray diffraction pattern collected on a solid sample of K[**3**]·C_6H_{14}·0.5THF confirmed that the crystalline material was compositionally pure (see ESI†). Due to the high sensitivity of the compound and the presence of decomposition products with a strong magnetic response (colloidal iron resulting from the reduction of **1** is ferromagnetic), we were unable to collect satisfactory magnetic data for K[**3**]·C_6H_{14}·0.5THF. Calculations at the DFT level are consistent with an $S = 2$ or quintet ground state. The lowest energy configuration gives rise to an $S = 2$ state which is lower in energy than the singlet ($S = 0$) and triplet ($S = 1$) states by 74.4 and 23.1 KJ mol^{-1}, respectively. Bond metric data for the $S = 2$ optimized computed geometry ($^5\mathbf{3}_{\mathbf{DFT}}$) are also the most closely related to the experimentally determined values and shows Fe–C bond distances and C–Fe–C bond angles that are comparable to the values as determined by single crystal X-ray diffraction.

2.2. Complexation of Lewis acids to vacant carbenic sites

THF solutions of K[**3**] were reacted with one and two equivalents of triethylaluminium in the presence of an equivalent of a cation sequestering agent (2,2,2-crypt) yielding the Lewis acid–base adducts [{Et_3Al:C[N(2,6-^{i}$Pr_2C_6H_3$)]$_2$(CH)C}{:C[N(2,6-^{i}$Pr_2C_6H_3$)]$_2$(CH)C}Fe(mes)]$^-$ (**5**) and [{Et_3Al:C[N(2,6-^{i}$Pr_2C_6H_3$)]$_2$(CH)C}$_2$Fe(mes)]$^-$ (**6**), respectively. A schematic representation of the synthesis of these two novel compounds is provided in Scheme 2. Formation of these species serves to highlight the carbenic nature of the two C2 positions in **3** as neutral NHCs



Scheme 2 Synthesis of **5** and **6** by reaction of K[**3**] with one and two equivalents of triethylaluminium, respectively.

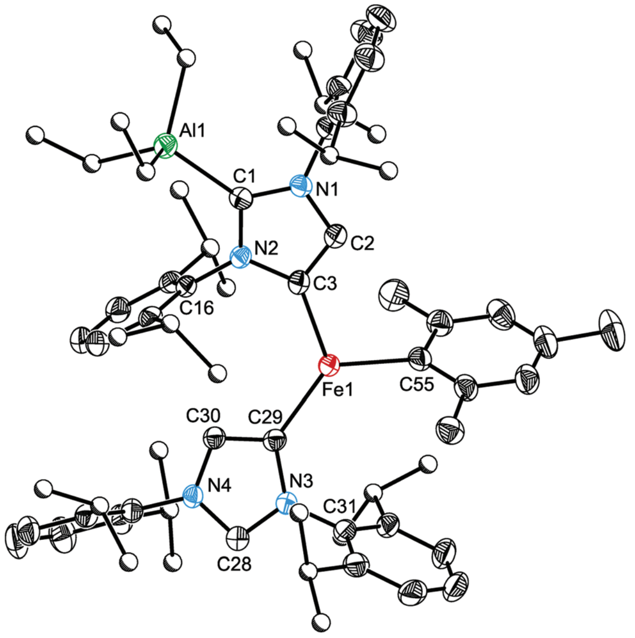


Fig. 5 Molecular structure of [K(2,2,2-crypt)][**5**]·0.5THF (anisotropic displacement ellipsoids pictured at 50% probability level). $[K(2,2,2\text{-crypt})]^+$, solvent of crystallization and hydrogen atoms have been omitted for clarity. Atoms of the ^{i}Pr and Et groups are pictured as spheres of arbitrary radii. Selected bond distances (Å) and angles (°): Fe1–C3: 2.110(2); Fe1–C29: 2.074(2); Fe1–C55: 2.071(2); Al1–C1: 2.123(2); C1–N1: 1.358(3); C1–N2: 1.364(3); N1–C2: 1.398(3); N2–C3: 1.418(3); C2–C3: 1.358(4); C28–N3: 1.367(3); C28–N4: 1.366(3); N3–C29: 1.426(3); N4–C30: 1.399(3); C29–C30: 1.359(3); C3–Fe1–C29: 124.9(1); C3–Fe1–C55: 109.6(1); C29–Fe1–C55: 125.4(1).

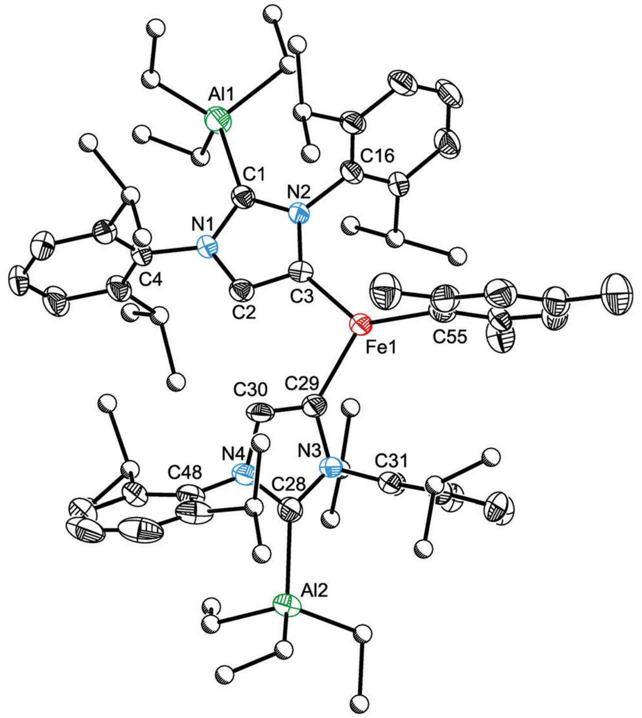


Fig. 6 Molecular structure of [K(2,2,2-crypt)][**6**] (anisotropic displacement ellipsoids pictured at 50% probability level). $[K(2,2,2\text{-crypt})]^+$ and hydrogen atoms have been omitted for clarity. Atoms of the ^{i}Pr and Et groups are pictured as spheres of arbitrary radii. Two of the Et groups bonded to Al1 exhibit positional disorder, only the major components are shown for clarity. Selected bond distances (Å) and angles (°): Fe1–C3: 2.085(5); Fe1–C29: 2.085(5); Fe1–C55: 2.049(5); Al1–C1: 2.092(5); C1–N1: 1.371(6); C1–N2: 1.365(6); N1–C2: 1.391(6); N2–C3: 1.414(6); C2–C3: 1.359(7); Al2–C28: 2.105(5); C28–N3: 1.359(6); C28–N4: 1.369(6); N3–C29: 1.423(6); N4–C30: 1.396(6); C29–C30: 1.339(7); C3–Fe1–C29: 106.4(2); C3–Fe1–C55: 136.1(2); C29–Fe1–C55: 116.5(2).

Table 3 Selected bond distances (Å) and angles (°) for **3**, **5** and **6**

	3	**5**	**6**
Fe–C3	2.071(2)	2.110(2)	2.085(5)
Fe–C29	2.064(2)	2.074(2)	2.085(5)
Fe–C55	2.065(3)	2.071(2)	2.049(5)
C1–Al1	N/A	2.123(2)	2.092(5)
C28–Al2	N/A	N/A	2.105(5)
C3–Fe–C29	122.5(1)	124.9(1)	106.4(2)
C3–Fe–C55	108.4(1)	109.6(1)	136.1(2)
C29–Fe–C55	128.4(1)	125.4(1)	116.5(2)

are known to react with a variety of main-group based Lewis acids such as $AlEt_3$.[30] Both anionic complexes could be isolated as crystallographically pure samples by slow diffusion of hexane into THF solutions of the crude reaction mixtures.

Complexes **5** and **6** were characterized by single crystal X-ray diffraction in [K(2,2,2-crypt)][**5**]·0.5THF and [K(2,2,2-crypt)][**6**], respectively (Fig. 5 and 6). Each species displays a trigonal planar moiety consisting of an iron(II) centre coordinated by two ditopic carbanionic carbenes (*via* the C4/C5 positions) and a mesityl substituent. These cores are identical to those observed for **3**. Bond metric data for these complexes are very similar and summarized in Table 3. One of the two vacant C2 carbene positions present in **3** is bonded to a triethylaluminium moiety in the case of **5** ($d_{\text{C–Al}}$ = 2.123(2) Å) while both of the available sites form carbene–$AlEt_3$ adducts in the case of **6** ($d_{\text{C–Al}}$ = 2.095(5) and 2.105(5) Å). The remaining bond metric data for the complexes are generally very similar and do not merit a detailed analysis. Perhaps the most interesting observation is the relative orientation of the two carbanionic carbenes in **6**. While in **3** and **5** these two ligands are oriented in the same manner (with the imidazolium protons pointing away from one another), in **6** these two protons point directly at one another (conferring greater C_{2v} character to the anion). However, while this observation is structurally noteworthy, it presumably arises due to crystal packing effects and is not meaningful with regard to the behaviour of the anion in solution. Analogous zinc species have been shown by multi-element NMR spectroscopy to exhibit free rotation about the Zn–C_{NHC} bonds.[15]

Species **5** and **6** were further characterized in solution by means of electrospray mass-spectrometry. The negative ion mode spectra of THF solutions of the samples show the anions as the molecular ions at 1063.0 and 1177.7 Da. In the positive ion mode ion-coupled peaks for $[K_2(\mathbf{5})]^+$ and $[K\{K(2,2,2\text{-crypt})\}_2(\mathbf{6})]^+$ were also observed at *m*/*z* values of 1141.1 and 2049.2.

3. Conclusions

We have shown that the reaction of Fe(mes)$_2$ with one equivalent of the NHC ligands IPr and 6-Xyl can be used to access the trigonal planar iron(II) complexes [Fe(IPr)(mes)$_2$] (**1**) and [Fe(6-Xyl)(mes)$_2$] (**2**). Chemical reduction of the imidazol-2-ylidene complex, **1**, affords an iron(II) compound containing carbanionic carbenes, $[\{:C[N(2,6\text{-}^{i}Pr_2C_6H_3)]_2(CH)C\}_2Fe(mes)]^-$ (**3**). This reaction mixture gives rise to the known side-product $[Fe(mes)_3]^-$ (**4**), but was also found to activate 18-crown-6 and polydimethylsiloxane grease when present, highlighting the highly reactive nature of these mixtures. By contrast, chemical reduction of **2** was found to give rise to complex and intractable product mixtures. The unquenched Lewis basic character of the coordinated carbanionic carbene ligands in **3** was demonstrated by reacting the anion with one and two equivalents of triethylaluminium affording the novel complexes $[\{Et_3Al:C[N(2,6\text{-}^{i}Pr_2C_6H_3)]_2(CH)C\}\{:C[N(2,6\text{-}^{i}Pr_2C_6H_3)]_2(CH)C\}Fe(mes)]^-$ (**5**) and $[\{Et_3Al:C[N(2,6\text{-}^{i}Pr_2C_6H_3)]_2(CH)C\}_2Fe(mes)]^-$ (**6**). These findings show that formation of carbanionic carbenes is a common result on reduction of organometallic complexes of imidazol-2-ylidene type ligands and expand the increasing number of backbone activated NHC complexes capable of acting as ditopic donors between metal centers.

Experimental section

General synthetic methods

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at <0.1 ppm H_2O and <0.1 ppm O_2). Fe$_2$(mes)$_4$ (mes = trimethylphenyl), 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene (IPr) and 1,3-bis(2,6-dimethylphenyl)hexahydropyrimidin-2-ylidene (6-Xyl) were prepared according to previously reported literature procedures.[31,32,27a] KC$_8$ was prepared by heating a stoichiometric mixture of K (99.95%, Strem) and graphite (99.99+%, Sigma-Aldrich) at 200 °C under an inert atmosphere over the course of several days. 2,2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]-hexacosane; VWR, 99%) and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane; 99%, Alfa Aesar) were used as received after careful drying under vacuum. Hexane (hex; HPLC grade, Sigma-Aldrich) and diethylether (Et$_2$O; pesticide residue grade, Fisher) were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (THF; HPLC grade, Sigma-Aldrich) was distilled over a sodium metal–benzophenone mixture. 1,2-Difluorobenzene (DFB; 98%, Fluorochem) and pyridine (py; 99%, Alfa Aesar) were distilled over CaH$_2$. d_5-Pyridine (99.5%, Cambridge Isotope Laboratories, Inc.) was dried over CaH$_2$ and vacuum distilled. All dry solvents were stored under argon in gas-tight ampoules. Additionally hexanes, Et$_2$O, diflurorobenzene and THF were stored over activated 3 Å molecular sieves. Celite 545 (Sigma-Aldrich) was used as received after careful drying under a dynamic vacuum.

Fe(IPr)(mes)$_2$ (1). Fe$_2$(mes)$_4$ (500 mg, 0.85 mmol) and IPr (660 mg, 1.70 mmol) were dissolved in diethyl ether (15 mL) and the reaction mixture allowed to stir for 3 hours. A grey-white solid was found to immediately precipitate from the dark brown solution. The solid was isolated by filtration, washed with 1,2-difluorobenzene (2 mL) and subsequently dried under vacuum, affording 1.04 g of a grey-white powder Fe(IPr)(mes)$_2$ (89% yield). Off-white crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of hexanes into a THF solution of the product (CCDC 962247). A powder X-ray diffraction pattern was obtained which matched the simulated diffraction pattern based on the single crystal X-ray diffraction data (see ESI† for details). Anal. Calcd for $C_{45}H_{58}FeN_2$ (Fw = 682.31): C 79.14%, H 8.57%, N 4.10%. Found: C 78.94%, H 8.44%, N 3.97%.

Fe(6-Xyl)(mes)$_2$ (2). Fe$_2$(mes)$_4$ (150 mg, 0.51 mmol) and 6-Xyl (150 mg, 0.26 mmol) were dissolved in THF (5 mL). A grey-white solid immediately precipitated from the dark brown solution and the resulting mixture was stirred for 24 hours at room temperature. The solid was isolated by filtration and dried under vacuum, affording 59 mg of a grey-white powder identified as Fe(6-Xyl)(mes)$_2$ (58% yield). Colourless crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of hexanes into a red solution of the product in a 1 : 1 mixture (by volume) of THF–pyridine (CCDC 962248). A powder X-ray diffraction pattern was obtained which matched the simulated diffraction pattern based on the single crystal X-ray diffraction data (see ESI† for details). Anal. Calcd for $C_{38}H_{46}FeN_2$ (Fw = 586.21): C, 77.79%; H, 7.91%; N, 4.78%. Found: C, 76.87%; H, 7.94%; N, 4.70%. The % C values obtained for this sample were found to be consistently higher than anticipated, perhaps due to the presence of a solvate containing THF in the lattice.

$K[\{:C[N(2,6\text{-}^{i}Pr_2C_6H_3)]_2(CH)C\}_2Fe(mes)]$ (K[3]) and K[Fe(mes)$_3$] (K[4]). A mixture of **1** (100 mg, 0.15 mmol) and KC$_8$ (20 mg, 0.15 mmol) was weighed into a glass vial under dinitrogen inside a glovebox. THF (5 mL) was added and the resulting black mixture stirred for 48 hours. The mixture was filtered through a Celite plug and layered with hexane to yield off-white crystals of K[**3**]·C_6H_{14}·0.5THF suitable for single crystal X-ray diffraction (26% crystalline yield; CCDC 962249). Samples of K[**3**]·C_6H_{14}·0.5THF suitable for powder X-ray diffraction were obtained by multiple recrystallizations from THF–benzene mixtures, and a final recrystallization from THF–hexane. ESI (–ve ion mode): m/z 950.2 $[M]^-$. Anal. Calcd for $C_{63}H_{81}FeKN_4$ (Fw = 988.59): C, 76.47%; H, 8.26%; N, 5.67%. Found: C, 69.38%; H, 8.14%; N, 5.86%. The sample was found to consistently burn low for carbon as previously observed for the manganese analogue.

The mother liquor that afforded K[**3**]·C_6H_{14}·0.5THF was isolated and reduced to dryness under a dynamic vacuum. The resulting dark solid was redissolved in THF and 2,2,2-crypt (28 mg, 0.075 mmol) was added. Filtration of the THF solution followed by its slow diffusion into hexane afforded crystals of the previously-reported compound [K(2,2,2-crypt)][**4**]. A similar procedure, employing 18-crown-6 as a cation sequestering in place of 2,2,2-crypt, yielded the [K(18-crown-6)THF][**4**] salt (CCDC 962250).

[K(2,2,2-crypt)][{Et_3Al:C[N(2,6-$^iPr_2C_6H_3$)]$_2$(CH)C}{:C[N(2,6-$^iPr_2C_6H_3$)]$_2$(CH)C}Fe(mes)] ([K(2,2,2-crypt)][5]). A mixture of K[**3**] (44 mg, 0.04 mmol) and 2,2,2-crypt (15 mg, 0.04 mmol) was weighed into a glass vial in a glovebox. $AlEt_3$ (5 μL, 0.04 mmol) and THF (5 mL) were added and the resulting mixture stirred for 24 hours at room temperature. The mixture was filtered through a Celite plug and layered with hexane to yield colourless crystals of [K(2,2,2-crypt)][**5**]·0.5THF suitable for single crystal X-ray diffraction (CCDC 962251). After the SXRD experiment a small number of crystals (~5 mg) were able to be isolated for mass spectrometric analysis. ESI (−ve ion mode): *m*/*z* 1063.0 $[M]^-$; (+ve ion mode): *m*/*z* 1141.1 $[K_2M]^+$.

[K(2,2,2-crypt)][{Et_3Al:C[N(2,6-$^iPr_2C_6H_3$)]$_2$(CH)C}Fe(mes)] ([K(2,2,2-crypt)][6]). A mixture of K[**3**] (100 mg, 0.09 mmol) and 2,2,2-crypt (34 mg, 0.09 mmol) was weighed into a glass vial in a glovebox under dinitrogen. $AlEt_3$ (24 μL, 0.18 mmol) and THF (5 mL) were added and the resulting mixture stirred for 24 hours at room temperature. The mixture was filtered through a Celite plug and layered with hexane to yield colourless crystals of [K(2,2,2-crypt)][**6**] suitable for single crystal X-ray diffraction (56% crystalline yield; CCDC 962252). ESI (−ve ion mode): *m*/*z* 1177.7 $[M]^-$. ESI (+ve ion mode): *m*/*z* 2049.2 $\{K[K(2,2,2\text{-crypt})]_2[\mathbf{6}]\}^+$.

Single crystal X-ray structure determination

Single crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[33] Data were collected at 150 K using mirror monochromated CuKα radiation ($\lambda = 1.5418$ Å) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[34] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using direct methods, and refined on F^2 using the SHELXL 97-2 package.[35]

Other characterization techniques

Positive and negative ion mode electrospray mass spectra were recorded on THF solutions of the compounds (10–20 mM) on a Masslynx LCT Time of Flight mass spectrometer with a Z-spray source (150 °C source temperature, 200 °C desolvation temperature, 2.4 kV capillary voltage and 25 V cone voltage). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe. Samples were introduced directly with a 1 mL SGE syringe and a syringe pump at 0.6 mL h^{-1}.

^{1}H NMR spectra were acquired at 500 MHz on a Varian Unity 500 MHz NMR spectrometer and referenced to the most downfield residual solvent resonance (d_5-pyridine: 8.74 ppm).

The magnetic properties of all complexes were measured on unanchored polycrystalline samples with a Quantum Design MPMS 5 or MPMS XL SQUID magnetometer. Due to the high air- and moisture-sensitivity of the complexes they were flame-sealed under vacuum in Suprasil tubes. In order to distinguish the intrinsic susceptibility of **1** and **2** from that of ferromagnetic impurities, the magnetization was measured at five applied fields between 4 and 5 T after an initial zero-field cooling to 2 K. The sample was warmed to 302 K in small increments and the magnetization measured at each step at the same five fields. The slope of the resulting linear plot of the molar magnetization as a function of applied field was used to obtain the molar magnetic susceptibility at each temperature. Diamagnetic corrections, obtained from tables of Pascal's constants,[36] have been applied to the measured molar magnetic susceptibilities.

Computational methods

All calculations described in this paper were performed with the Amsterdam Density Functional package (ADF2013.01).[37] The TZ2P Slater-type basis set of triple-ζ quality, extended with two polarization functions, was used to describe Fe (the DZP basis set was employed for Al, C and N and the DZ basis set used for H). Electrons in orbitals up to and including 2p for Fe were considered part of the core and treated in accordance with the frozen core approximation (Fe 2p). All calculations employed the local density approximation (LDA)[38] to the exchange potential, along with the local exchange-correlation potential of Vosko, Wilk and Nusair (VWN)[39] and gradient corrections to non-local exchange and correlation proposed by Becke and Perdew (BP86).[40] All calculations were unrestricted (the doublet, quartet and sextet states were computed for **1** and **2**). Relativistic effects were incorporated using the zeroth order relativistic approximation (ZORA).[41] The presence of cations in the crystal lattice was modelled by surrounding the clusters with a continuum dielectric model (COSMO).[42] The chosen dielectric constant $\varepsilon = 7.58$ corresponds to tetrahydrofuran, although structural parameters are not strongly dependent on this choice. All structures were optimized using the gradient algorithm of Versluis and Ziegler.[43]

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