Electronic Supplementary Information

Iron (II) complexes of ditopic carbanionic carbenes

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

† Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, U.K.

‡ Department of Inorganic Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, 77146 Olomouc, Czech Republic

1. Powder X-ray diffraction patterns

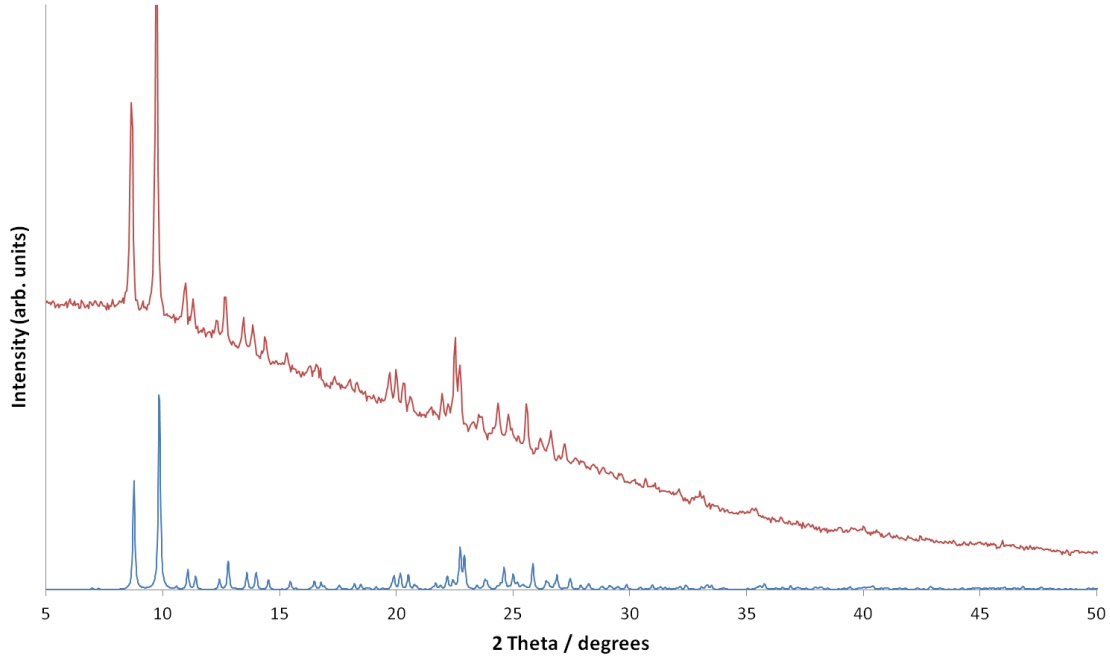

Figure S1. Comparison of experimental (red) and calculated (blue) powder X-ray diffraction (PXRD) patterns for sample **1**. Experimental PXRD was collected at room temperature.

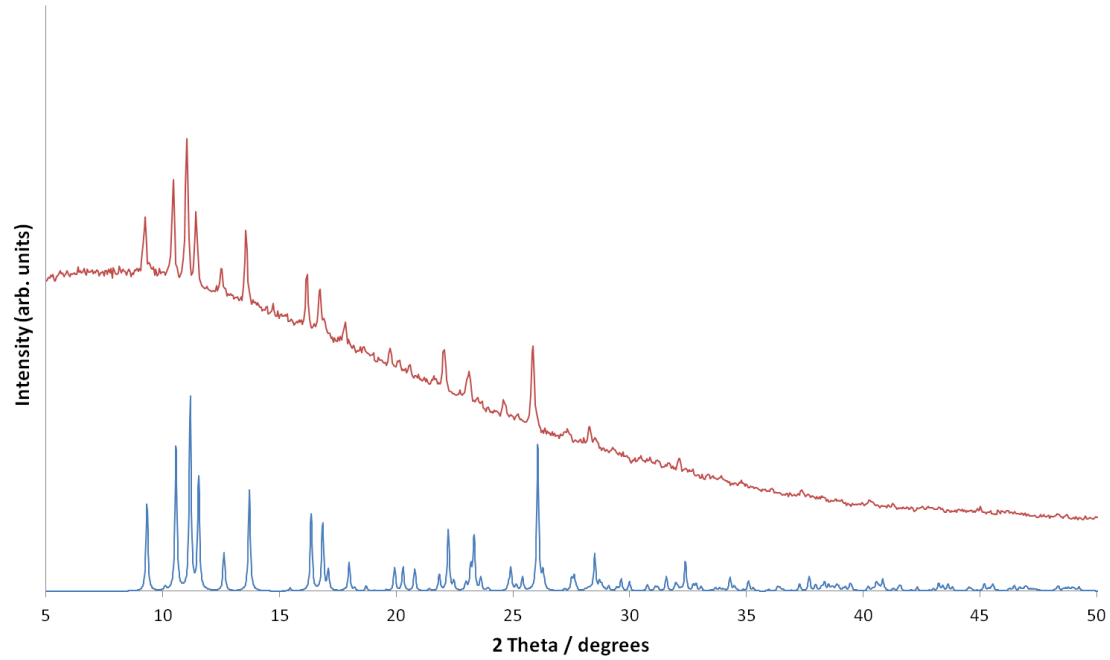

Figure S2. Comparison of experimental (red) and calculated (blue) powder X-ray diffraction (PXRD) patterns for sample **2**. Experimental PXRD was collected at room temperature.

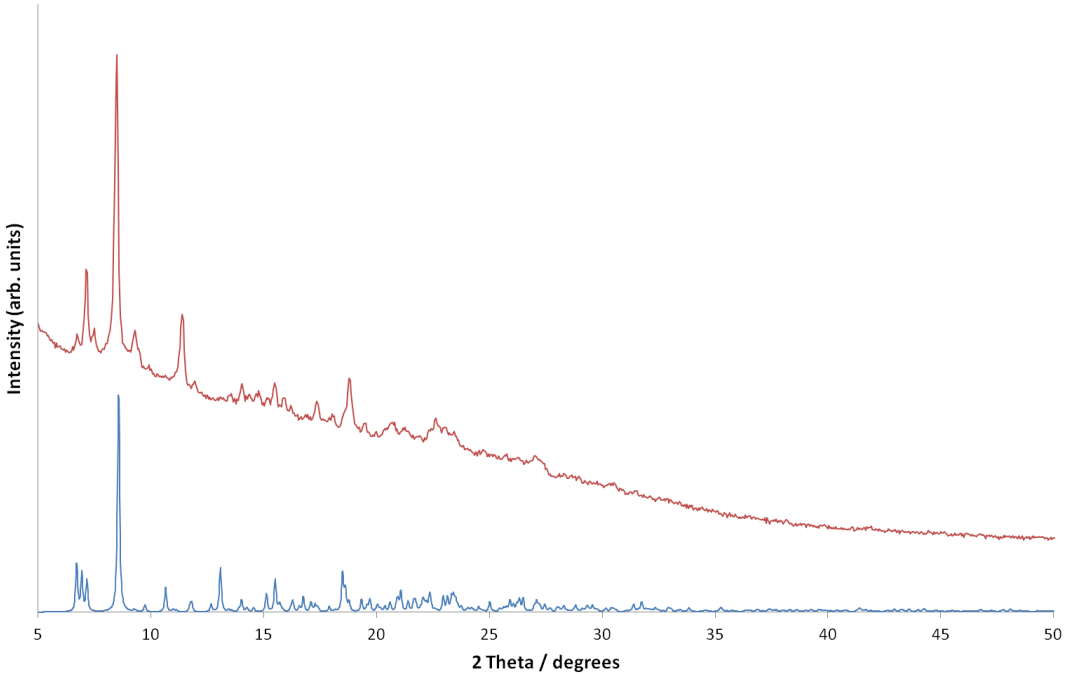

Figure S3. Comparison of experimental (red) and calculated (blue) powder X-ray diffraction (PXRD) patterns for sample K[**3**]·C_6H_{14}·0.5THF. Experimental PXRD was collected at room temperature.

2. Single crystal X-ray diffraction

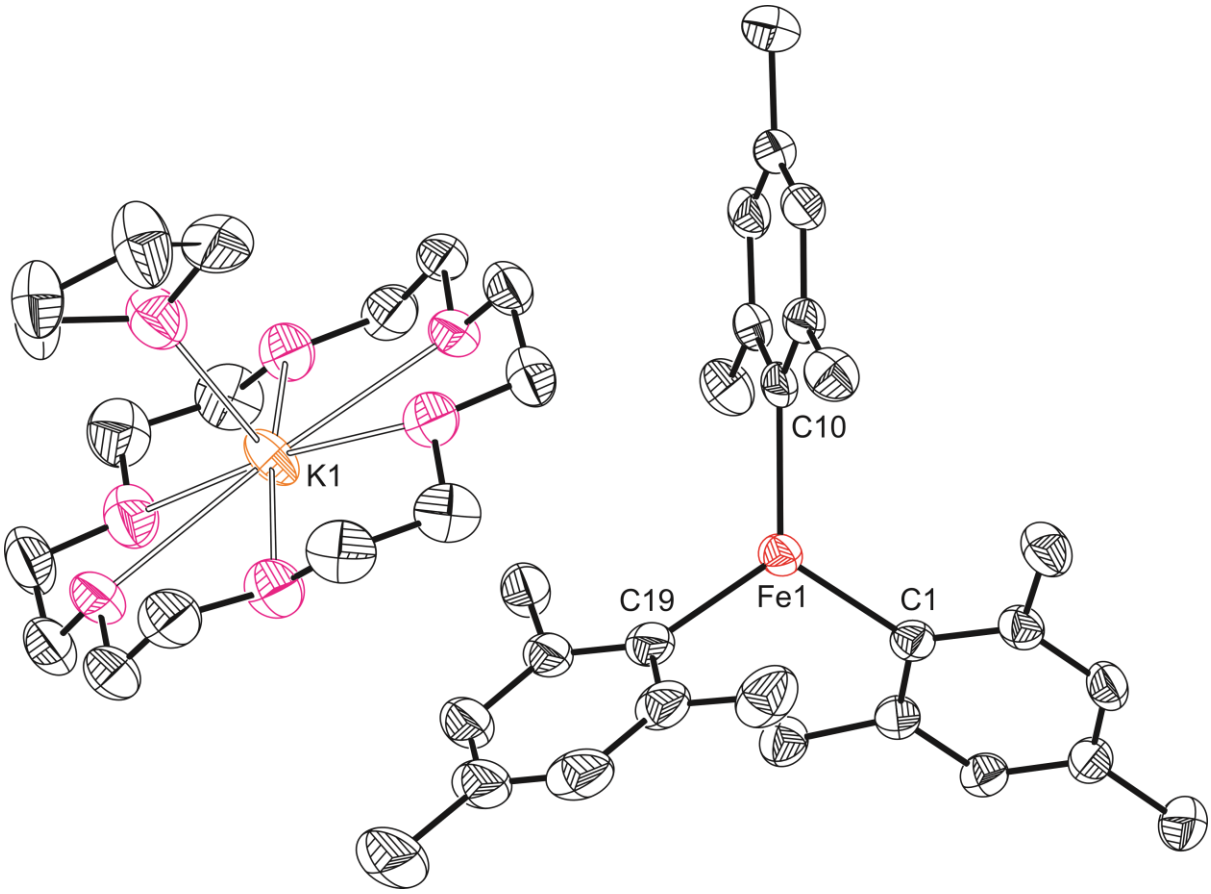

Figure S4. Molecular structure of [K(18-crown-6)THF)][**4**] (anisotropic displacement ellipsoids pictured at 50% probability level). CCDC 962250. Hydrogen atoms have been omitted for clarity. The THF model exhibits positional disorder, for clarity only the major component (59% occupancy) is shown. Selected bond distances (Å) and angles (°): Fe1−C1: 2.088(3); Fe1−C10: 2.089(3); Fe1−C19: 2.089(3); C1−Fe1−C10: 120.0(1); C1−Fe1−C19: 118.1(1); C10−Fe1−C19: 121.9(1).

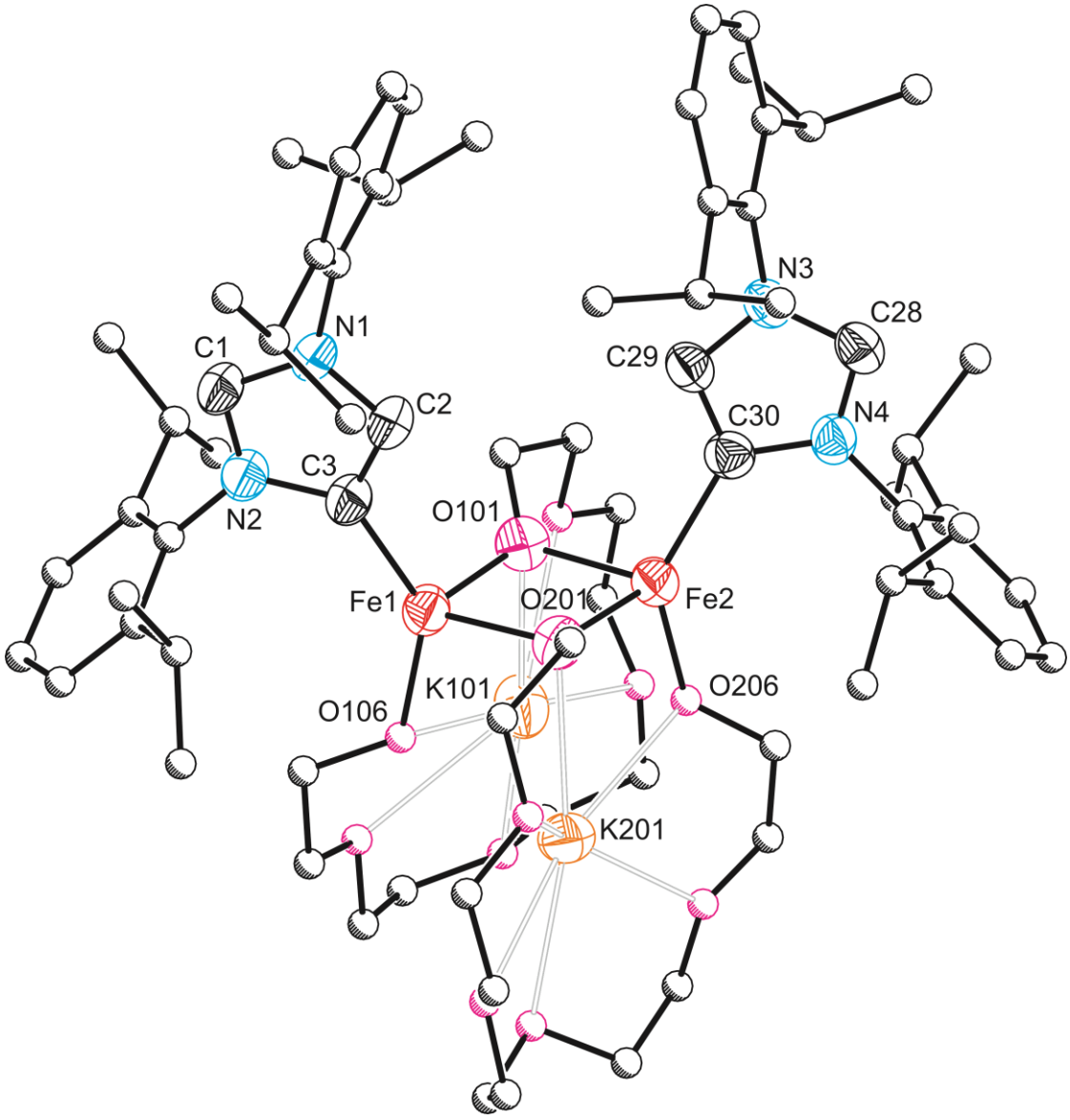

Figure S5. Molecular structure of [{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}Fe(κ^2,μ^1,μ^2-O(C$_2$H$_4$O)$_4$C$_2$H$_4$O)K]$_2$ (**7**) (anisotropic displacement ellipsoids for selected atoms pictured at 50% probability level). CCDC 962253. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe1−C3: 2.053(5); Fe1−O106: 1.916(3); Fe1−O101: 2.045(3); Fe1−O201: 2.048(3); Fe2−O101: 2.051(3); Fe2−O201: 2.046(3); Fe2−O206: 1.910(4); Fe2−C30: 2.055(4); C1−N1: 1.365(6); C1−N2: 1.365(6); N1−C2: 1.399(6); N2−C3: 1.416(6); C2−C3: 1.350(7); C28−N3: 1.360(6); C28−N4: 1.364(6); N3−C29: 1.402(6); N4−C30: 1.408(6); C29−C30: 1.351(6); O101−Fe1−O201: 82.4(1); Fe1−O101−Fe2: 97.5(1); Fe1−O201−Fe2: 97.7(1); O101−Fe2−O201: 82.3(1).

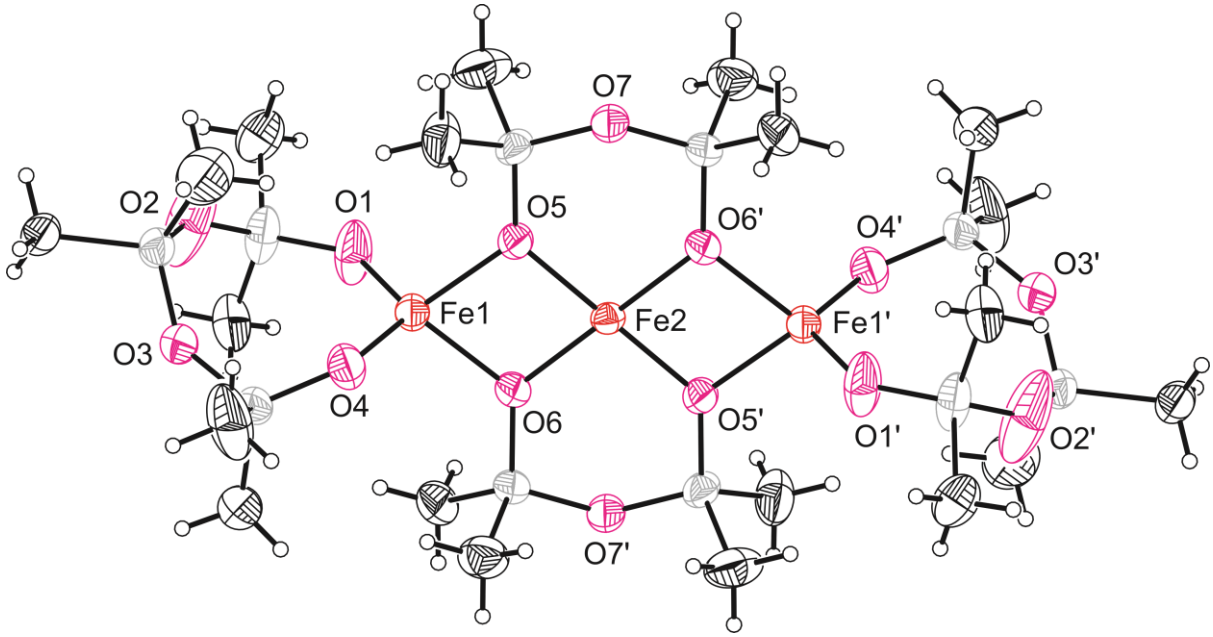

Figure S6. Molecular structure of the dianionic moiety in $[K(2,2,2\text{-crypt})]_2\{Fe[Fe\{\kappa^2\text{-}O_4(SiMe_2)_3\}]_2[\kappa^2,\mu^2,\mu^2\text{-}O_3(SiMe_2)_2]_2\}$ ($[K(2,2,2\text{-crypt})]_2$[**8**]) (anisotropic displacement ellipsoids pictured at 50% probability level). CCDC 962254. Hydrogen atoms were assigned idealized coordinates and are pictured as spheres of arbitrary radii. There is some substitutional crystallographic disorder at the site of the $\kappa^2\text{-}O_4(SiMe_2)_3$ ligand with a shorter chelate, $\kappa^2\text{-}O_3(SiMe_2)_2$, occupying the same position in 11% occupancy (not shown for clarity). Selected bond distances (Å) and angles (°): Fe1−O1: 1.889(3); Fe1−O4: 1.904(2); Fe1−O5: 2.076(2); Fe1−O6: 2.087(2); Fe2−O5: 1.980(2); Fe2−O6: 1.985(2); O1−Fe1−O4: 117.2(1); O1−Fe1−O5: 108.9(1); O1−Fe1−O6: 118.6(1); O4−Fe1−O5: 117.9(1); O4−Fe1−O6: 78.4(1); O5−Fe1−O6: 78.4(1); O5−Fe2−O6: 83.1(1); O5−Fe2−O6′: 96.9(1). Symmetry operation ′: –x, –y, –z.

Table S1. Selected X–ray data collection and refinement parameters for [K(18-crown-6)THF][**4**], **7** and [K(2,2,2-crypt)]$_2$[**8**].

	[K(18-crown-6)THF][**4**]	**7**	[K(2,2,2-crypt)]$_2$[**8**]
Formula	$C_{43}H_{65}FeKO_7$	$C_{74}H_{110}Fe_2K_2N_4O_{12}$	$C_{55.54}H_{130.62}Fe_3K_2N_4O_{25.77}Si_{9.77}$
Fw [g mol^{-1}]	788.90	1437.56	1787.25
crystal system	orthorhombic	orthorhombic	triclinic
space group	*Pbcn*	*Pbca*	*P*−1
a (Å)	33.7821(5)	23.4906(7)	10.6110(2)
b (Å)	10.77070(10)	20.2128(7)	13.5342(2)
c (Å)	24.2239(3)	33.1958(8)	16.7124(3)
α (°)			102.789(2)
β (°)			95.550(2)
γ (°)			102.524(2)
V (Å^3)	8814.03(19)	15761.7(8)	2258.30(7)
Z	8	8	1
radiation, λ (Å)	Cu K$_\alpha$, 1.54178		
T (K)	150(2)		
ρ_{calc} (g cm^{-3})	1.189	1.212	1.326
μ (mm^{-1})	3.942	4.358	6.475
reflections collected	118437	48423	42915
independent reflections	7773	13877	7970
parameters	506	899	485
R(int)	0.1174	0.0934	0.0473
R1/wR2,[a] $I \geq 2\sigma I$ (%)	5.75/12.09	7.51/17.87	4.80/12.27
R1/wR2,[a] all data (%)	8.08/12.09	13.38/20.35	5.44/12.63
GOF	1.046	1.012	1.036

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0499 and 9.44 for [K(18-crown-6)THF][**4**], 0.1057 and 0.00 for **7** and 0.0598 and 2.66 for [K(2,2,2-crypt)]$_2$[**8**].

Table S2. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **1** and the analogous manganese(II) (**Mn_{NHC}**: [Mn(IPr)$(mes)_2$]) and zinc(II) (**Zn_{NHC}**: [Zn(IPr)$(mes)_2$]) complexes previously reported in the literature.[S1, S2]

	Mn_{NHC}	**1**	**Zn_{NHC}**
M1–C1	2.195(2)	2.115(1)	2.097(2)
M1–C28	2.122(2)	2.076(2)	2.008(2)
M1–C37	2.125(2)	2.059(1)	2.016(3)
C1–N1	1.364(2)	1.362(2)	1.361(3)
C1–N2	1.359(2)	1.361(2)	1.361(3)
N1–C2	1.390(2)	1.387(2)	1.392(3)
N2–C3	1.389(2)	1.389(2)	1.389(3)
C2–C3	1.347(3)	1.346(2)	1.340(4)
N1–C4	1.446(2)	1.447(2)	1.452(3)
N2–C16	1.446(2)	1.447(2)	1.448(3)
C1–M1–C28	116.5(1)	122.6(1)	116.4(1)
C1–M1–C37	122.6(1)	117.8(1)	120.2(1)
C28–M1–C37	120.9(1)	119.6(1)	123.4(1)
M1−C1−N1	129.8(1)	127.3(1)	116.4(1)
M1−C1−N2	126.9(1)	129.5(1)	120.2(1)
N1–C1–N2	103.3(2)	103.3(1)	123.4(1)
C1–N1–C4	125.2(2)	124.6(1)	129.0(2)
C1–N2–C16	124.2(2)	125.5(1)	127.7(2)

Table S3. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **3** and the related manganese(II) (**Mn$_{aNHDC}$**: [{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Mn(mes)(THF)]$^-$) and zinc(II) complexes (**Zn$_{aNHDC}$**: [{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Zn(mes)]$^-$) previously reported in the literature. [S1, S2]

	Mn$_{aNHDC}$	**3**	**Zn$_{aNHDC}$**
M−C3	2.183(3)	2.071(2)	2.023(2)
M−C29	2.157(3)	2.064(2)	2.009(2)
M−C55	2.188(3)	2.065(3)	2.015(2)
C1−N1	1.363(3)	1.354(4)	1.357(3)
C1−N2	1.361(3)	1.359(3)	1.369(2)
N1−C2	1.391(4)	1.400(3)	1.398(2)
N2−C3	1.423(3)	1.406(3)	1.413(2)
C2−C3	1.362(4)	1.359(4)	1.361(3)
N1−C4	1.437(3)	1.445(3)	1.438(2)
N2−C16	1.447(3)	1.440(3)	1.430(2)
C28−N3	1.363(4)	1.372(3)	1.370(2)
C28−N4	1.361(4)	1.350(4)	1.355(3)
N3−C29	1.418(3)	1.416(3)	1.416(2)
N4−C30	1.397(4)	1.403(3)	1.394(2)
C29−C30	1.367(4)	1.369(4)	1.363(3)
N3−C31	1.451(3)	1.432(3)	1.437(2)
N4−C43	1.438(4)	1.445(3)	1.445(3)
C3−M−C29	117.2(1)	122.5(1)	121.2(1)
C3−M−C55	109.9(1)	108.4(1)	109.0(1)
C29−M−C55	125.0(1)	128.4(1)	129.2(1)
M−C3−N2	137.6(2)	132.4(2)	133.5(1)
M−C3−C2	121.1(2)	125.2(2)	124.3(1)
N2−C3−C2	101.0(2)	102.0(2)	101.9(2)
C1−N1−C4	118.8(2)	123.4(2)	122.8(2)
C1−N2−C16	118.5(2)	118.1(2)	118.2(2)
N1−C1−N2	101.5(2)	101.6(2)	101.7(2)
M−C29−N3	128.7(2)	129.4(2)	128.5(1)
M−C29−C30	130.7(2)	128.5(2)	129.4(1)
N3−C29−C30	100.4(2)	101.8(2)	101.7(2)
C28−N3−C31	116.7(2)	118.3(2)	118.2(2)
C28−N4−C43	121.9(2)	123.6(2)	123.6(2)
N3−C28−N4	101.4(2)	102.2(2)	101.8(2)

Table S4. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structures of **3, 5** and **6**.

	3	**5**	**6**
M−C3	2.071(2)	2.110(2)	2.085(5)
M−C29	2.064(2)	2.074(2)	2.085(5)
M−C55	2.065(3)	2.071(2)	2.049(5)
C1−N1	1.354(4)	1.358(3)	1.371(6)
C1−N2	1.359(3)	1.364(3)	1.365(6)
C1−Al1	N/A	2.123(2)	2.092(5)
N1−C2	1.400(3)	1.358(3)	1.391(6)
N2−C3	1.406(3)	1.418(3)	1.414(6)
C2−C3	1.359(4)	1.358(4)	1.359(7)
N1−C4	1.445(3)	1.444(3)	1.445(6)
N2−C16	1.440(3)	1.437(3)	1.462(6)
C28−N3	1.372(3)	1.367(3)	1.359(6)
C28−N4	1.350(4)	1.366(3)	1.369(6)
C28−Al2	N/A	N/A	2.105(5)
N3−C29	1.416(3)	1.426(3)	1.423(6)
N4−C30	1.403(3)	1.399(3)	1.396(6)
C29−C30	1.369(4)	1.359(3)	1.339(7)
N3−C31	1.432(3)	1.440(3)	1.441(6)
N4−C43	1.445(3)	1.440(3)	1.442(6)
C3−M−C29	122.5(1)	124.9(1)	106.4(2)
C3−M−C55	108.4(1)	109.6(1)	136.1(2)
C29−M−C55	128.4(1)	125.4(1)	116.5(2)
M−C3−N2	132.4(2)	133.1(2)	139.3(4)
M−C3−C2	125.2(2)	124.6(2)	118.6(3)
N2−C3−C2	102.0(2)	102.0(2)	101.6(4)
C1−N1−C4	123.4(2)	126.6(2)	128.9(4)
C1−N2−C16	118.1(2)	122.2(2)	122.3(4)
N1−C1−N2	101.6(2)	103.0(2)	102.3(4)
M−C29−N3	129.4(2)	133.4(2)	129.3(3)
M−C29−C30	128.5(2)	124.9(2)	128.3(4)
N3−C29−C30	101.8(2)	101.6(2)	102.4(4)
C28−N3−C31	118.3(2)	119.7(2)	123.6(4)
C28−N4−C43	123.6(2)	122.8(2)	127.5(4)
N3−C28−N4	102.2(2)	101.3(2)	103.1(4)

3. Magnetic data

The magnetic properties of compounds **1** and **2** were treated with following spin Hamiltonian

$$\hat{H} = D(\hat{S}_z^2 - \hat{S}^2/3) + \mu_B B g_i \hat{S}_{i,a} \qquad \text{(eq. S1)}$$

where the zero-field splitting (ZFS) and Zeeman terms are incorporated. The magnetic anisotropy due to ZFS is quantitatively characterized with single-ion axial parameter *D*. In order to properly treat magnetic susceptibility data acquired with ferrosubtract protocol at high fields, the differential susceptibility was calculated as

$$\chi_{\mathrm{mol},a} = \mu_0 N_A kT \frac{\partial^2 \ln Z}{\partial B_a^2} \qquad \text{(eq. S2)}$$

both for parallel ($a = z$) and perpendicular ($a = x$) direction of applied magnetic field (B = 4.5 T), where Z is the partition function. Finally, the powder average was obtained as

$$\chi_{\mathrm{mol},a} = (2\chi_{\mathrm{mol},x} + \chi_{\mathrm{mol},z})/3 + \chi_{\mathrm{TIM}} \qquad \text{(eq. S3)}$$

where χ_{TIM} is the temperature-independent magnetism term, which mainly serves as a correction to the uncompensated contribution of traces of ferromagnetic impurities. The fitting procedure was based on the error functional F defined as

$$F = \sum_{i=1}^{N} \left| (\chi_{\mathrm{mol}} T)_i^o - (\chi_{\mathrm{mol}} T)_i^c \right| \qquad \text{(eq. S4)}$$

where upper indexes *o* and *c* means observed and calculated data, respectively.

The found parameters *D* and *g* (Figure S7) are similar to other trigonal organometallic Fe(II) complexes.[S3] The higher g-factor in case of compound **1** is ascribed to the complicated experimental protocol used to acquire the magnetic data.

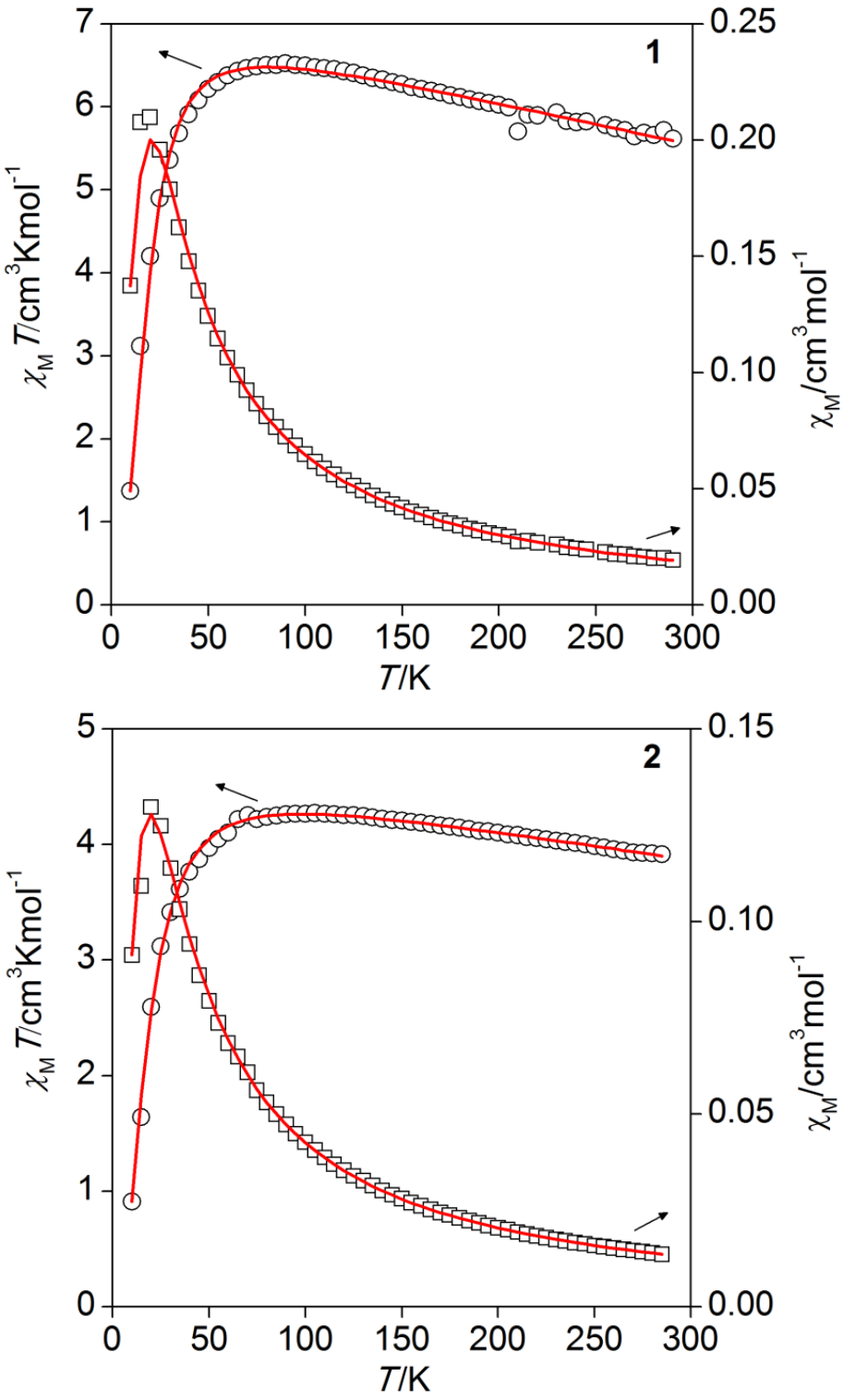

Figure S7. The magnetic data of **1** (top) and **2** (bottom). The full lines are the best fits calculated using eqns. eq. S1−S3 with following parameters: g = 3.07, D = −11.5 cm^{-1}, χ_{TIM} = −64×10^{-4} cm^{3}mol^{-1} for **1** and g = 2.48, D = −18.9 cm^{-1}, χ_{TIM} = −25×10^{-4} cm^{3}mol^{-1} for **2**.

4. Computational analysis

Cartesian coordinates [Å] for the optimized computed geometry of 1 (*S* = 2).

Atom	x	y	z
1. Fe	0.000000	0.000000	0.000000
2. C	0.000870	0.101236	2.028387
3. N	–0.715322	–0.662351	2.928924
4. C	–0.450967	–0.296130	4.242669
5. H	–0.911412	–0.788799	5.090193
6. C	0.442654	0.722977	4.192395
7. H	0.898987	1.300538	4.986683
8. N	0.714008	0.952374	2.849310
9. C	–1.629553	–1.727172	2.580213
10. C	–3.014299	–1.455502	2.559221
11. C	–3.876741	–2.509752	2.226327
12. H	–4.953443	–2.336901	2.191332
13. C	–3.383514	–3.778401	1.936707
14. H	–4.072940	–4.582416	1.669467
15. C	–2.014311	–4.026431	1.997584
16. H	–1.646347	–5.029524	1.778699
17. C	–1.105533	–3.014585	2.332639
18. C	–3.596526	–0.101944	2.944718
19. H	–2.818762	0.661625	2.781942
20. C	–4.829112	0.285483	2.113414
21. H	–4.667195	0.139501	1.036376
22. H	–5.072765	1.345592	2.285498
23. H	–5.714060	–0.300274	2.408633
24. C	–3.974319	–0.081689	4.438923
25. H	–4.742695	–0.845357	4.647274
26. H	–4.387083	0.903707	4.711358
27. H	–3.112919	–0.281867	5.091842
28. C	0.376570	–3.328706	2.489165
29. H	0.938885	–2.446490	2.144626
30. C	0.838411	–4.521693	1.647710
31. H	0.455719	–5.474832	2.049322
32. H	1.938355	–4.577982	1.673621
33. H	0.527776	–4.420992	0.596301
34. C	0.726676	–3.581359	3.968572
35. H	0.520243	–2.708978	4.605770
36. H	1.798367	–3.822909	4.063886
37. H	0.147668	–4.436885	4.357268
38. C	1.634730	1.972559	2.397582
39. C	3.017215	1.688145	2.394685
40. C	3.885831	2.699053	1.959548
41. H	4.961030	2.514316	1.935775
42. C	3.401183	3.939749	1.556248
43. H	4.094464	4.710207	1.211583
44. C	2.034823	4.204669	1.601636
45. H	1.673878	5.186833	1.294794
46. C	1.120274	3.235941	2.034271

47. C	3.590523	0.372256	2.904434
48. H	2.810094	–0.399265	2.805421
49. C	4.827521	–0.093592	2.121476
50. H	5.713601	0.509904	2.374194
51. H	4.676830	–0.039750	1.034387
52. H	5.061758	–1.136495	2.386541
53. C	3.959314	0.484484	4.396920
54. H	4.727369	1.263132	4.541505
55. H	4.368774	–0.473109	4.758887
56. H	3.094110	0.742432	5.023805
57. C	–0.357165	3.579217	2.169134
58. H	–0.931721	2.670082	1.931002
59. C	–0.816986	4.676987	1.204809
60. H	–0.422048	5.664774	1.495204
61. H	–1.916226	4.747361	1.231982
62. H	–0.515698	4.457763	0.168785
63. C	–0.686753	3.998119	3.615327
64. H	–0.477429	3.200467	4.343082
65. H	–1.755423	4.257961	3.696191
66. H	–0.096314	4.886410	3.899373
67. C	0.376673	–1.771446	–0.923248
68. C	–0.660611	–2.552961	–1.504764
69. C	–0.379131	–3.770968	–2.132767
70. H	–1.200863	–4.355177	–2.564073
71. C	0.930793	–4.268298	–2.226634
72. C	1.954450	–3.504092	–1.663952
73. H	2.986410	–3.872505	–1.713298
74. C	1.690939	–2.284463	–1.017353
75. C	–2.092987	–2.081574	–1.432738
76. H	–2.766705	–2.734458	–2.010208
77. H	–2.191569	–1.058368	–1.829624
78. H	–2.450894	–2.077243	–0.388033
79. C	1.211646	–5.577910	–2.918598
80. H	2.243724	–5.912446	–2.738429
81. H	1.075283	–5.488865	–4.009935
82. H	0.530196	–6.369931	–2.569551
83. C	2.859758	–1.545338	–0.411623
84. H	2.518536	–0.730725	0.245022
85. H	3.510093	–1.103144	–1.185410
86. H	3.486948	–2.220214	0.193027
87. C	–0.375656	1.672760	–1.093139
88. C	0.656775	2.387967	–1.759381
89. C	0.371673	3.539208	–2.503871
90. H	1.190583	4.075661	–2.997383
91. C	–0.936468	4.030421	–2.632219
92. C	–1.956780	3.330443	–1.983461
93. H	–2.987696	3.698881	–2.054825
94. C	–1.690038	2.181035	–1.222632
95. C	2.089213	1.923020	–1.652944
96. H	2.757761	2.509492	–2.302666

97. H	2.182040	0.863862	–1.941133
98. H	2.457477	2.027225	–0.617279
99. C	–1.230747	5.258812	–3.456603
100. H	–0.369563	5.943973	–3.476555
101. H	–2.098592	5.809284	–3.061758
102. H	–1.460280	4.988109	–4.502240
103. C	–2.853164	1.511761	–0.530902
104. H	–3.466926	2.245610	0.016196
105. H	–2.506305	0.761148	0.195472
106. H	–3.518093	1.002390	–1.249029

Table S5. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **1** and its optimized computed geometries in different spin states: $^{1}\mathbf{1}_{\mathbf{DFT}}$ (S = 0), $^{3}\mathbf{1}_{\mathbf{DFT}}$ (S = 1) and $^{5}\mathbf{1}_{\mathbf{DFT}}$ (S = 2).

	1	$^{1}\mathbf{1}_{\mathbf{DFT}}$	$^{3}\mathbf{1}_{\mathbf{DFT}}$	$^{5}\mathbf{1}_{\mathbf{DFT}}$
Fe1–C1	2.115(1)	1.962	1.988	2.031
Fe1–C28	2.076(2)	1.923	1.949	2.033
Fe1–C37	2.059(1)	1.944	1.944	2.033
C1–Fe1–C28	122.6(1)	110.9	138.0	119.8
C1–Fe1–C37	117.8(1)	136.6	112.6	119.7
C28–Fe1–C37	119.6(1)	109.3	106.8	120.5
Total Bonding Energy (kJ/mol)		–60310.94	–60351.52	–60384.10

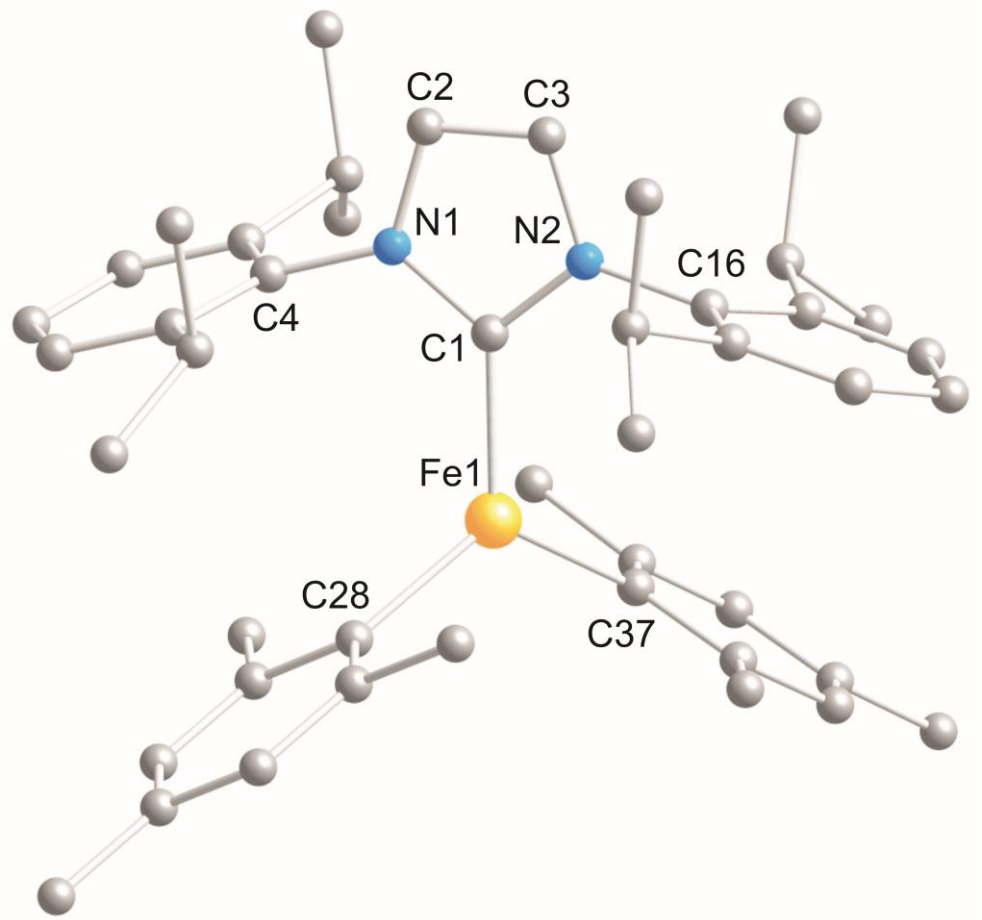

Figure S8. Optimized computed geometry for $^{5}\mathbf{1}_{\mathbf{DFT}}$. All hydrogen atoms have been omitted for clarity.

Table S6. Comparison of bond metric data (distances: Å; angles: °) for the crystallographically determined and computed (S = 2) structures of **1**.

	1	^{5}**1**$_{DFT}$
Fe1–C1	2.115(1)	2.031
Fe1–C28	2.076(2)	2.033
Fe1–C37	2.059(1)	2.033
C1–N1	1.362(2)	1.381
C1–N2	1.361(2)	1.381
N1–C2	1.387(2)	1.389
N2–C3	1.389(2)	1.389
C2–C3	1.346(2)	1.356
N1–C4	1.447(2)	1.446
N2–C16	1.447(2)	1.447
C1–Fe1–C28	122.6(1)	119.8
C1–Fe1–C37	117.8(1)	119.7
C28–Fe1–C37	119.6(1)	120.5
C1–N1–C4	124.6(1)	125.3
C1–N2–C16	125.5(1)	125.3
N1–C1–N2	103.3(1)	102.8

Cartesian coordinates [Å] for the optimized computed geometry of 2 (*S* = 2).

Atom	x	y	z
1. Fe	0.000000	0.000000	0.000000
2. C	–0.074918	0.043491	2.066756
3. N	–0.854813	–0.821558	2.767748
4. C	–0.901701	–0.956134	4.242087
5. H	–0.995550	–2.028008	4.477592
6. H	–1.803754	–0.449910	4.626366
7. C	0.342386	–0.363865	4.874697
8. H	0.207283	–0.291422	5.963233
9. H	1.212518	–1.012598	4.683092
10. N	0.661028	0.912913	2.808594
11. C	0.588088	1.011535	4.281961
12. H	–0.221047	1.710402	4.564644
13. H	1.534115	1.440131	4.641027
14. C	–1.750509	–1.709806	2.068319
15. C	–1.289166	–2.974618	1.654243
16. C	–2.205930	–3.847260	1.050960
17. H	–1.857576	–4.825427	0.709381
18. C	–3.540807	–3.487229	0.885977
19. H	–4.239716	–4.180299	0.412817
20. C	–3.987212	–2.243840	1.333768
21. H	–5.039269	–1.969511	1.222340
22. C	–3.107231	–1.340795	1.944054
23. C	0.122212	–3.438434	1.885533
24. H	0.786651	–2.617362	2.178230
25. H	0.528562	–3.889291	0.966596
26. H	0.142103	–4.204984	2.680651
27. C	–3.641120	–0.048802	2.505248
28. H	–2.880010	0.740514	2.534921
29. H	–4.007239	–0.202022	3.535296
30. H	–4.491304	0.313520	1.910188
31. C	0.641417	–1.672425	–0.959227
32. C	1.959767	–2.167728	–0.815703
33. C	2.346102	–3.387051	–1.393186
34. H	3.371969	–3.748928	–1.246885
35. C	1.453532	–4.156890	–2.146140
36. C	0.155660	–3.655506	–2.323979
37. H	–0.560246	–4.233007	–2.921440
38. C	–0.249546	–2.439683	–1.756333
39. C	2.999030	–1.404904	–0.029037
40. H	2.549681	–0.554330	0.501988
41. H	3.785380	–1.001981	–0.691129
42. H	3.498139	–2.047967	0.714778
43. C	1.886569	–5.458388	–2.774305
44. H	1.021827	–6.083646	–3.041654
45. H	2.529195	–6.038868	–2.094663
46. H	2.464355	–5.280902	–3.697839
47. C	–1.658563	–1.955630	–2.002031
48. H	–2.239567	–1.925461	–1.064488

49. H	–2.195543	–2.615587	–2.701326
50. H	–1.656249	–0.937589	–2.425498
51. C	1.501186	1.892201	2.166069
52. C	0.930018	3.074476	1.655370
53. C	1.785897	4.029211	1.087653
54. H	1.353686	4.941205	0.668042
55. C	3.163626	3.832536	1.053926
56. H	3.812995	4.587306	0.604861
57. C	3.715824	2.675667	1.604177
58. H	4.799096	2.528429	1.594835
59. C	2.899250	1.691768	2.175361
60. C	–0.539451	3.380728	1.755331
61. H	–1.136523	2.494908	1.997493
62. H	–0.907440	3.785000	0.800279
63. H	–0.712900	4.138848	2.539418
64. C	3.533616	0.495219	2.834361
65. H	2.852689	–0.363102	2.888057
66. H	3.842351	0.745509	3.864463
67. H	4.439221	0.186592	2.294170
68. C	–0.489570	1.593609	–1.161406
69. C	–1.810515	2.091494	–1.268765
70. C	–2.091635	3.256197	–1.999961
71. H	–3.125613	3.621529	–2.051432
72. C	–1.083409	3.968294	–2.657674
73. C	0.222892	3.463354	–2.585062
74. H	1.028380	3.997185	–3.102780
75. C	0.523217	2.300070	–1.862476
76. C	–2.966002	1.391881	–0.595204
77. H	–2.623433	0.543041	0.013158
78. H	–3.682176	0.995308	–1.335654
79. H	–3.524792	2.079004	0.061504
80. C	–1.402246	5.217687	–3.440740
81. H	–0.487217	5.754936	–3.730960
82. H	–2.029512	5.907753	–2.853914
83. H	–1.957213	4.979531	–4.363925
84. C	1.949850	1.805378	–1.831490
85. H	2.376382	1.893621	–0.818047
86. H	2.595494	2.382466	–2.512138
87. H	2.003153	0.743626	–2.124077

Table S7. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **2** and its optimized computed geometries in different spin–states: $^{3}\mathbf{2}_{\mathbf{DFT}}$ (S = 1) and $^{5}\mathbf{2}_{\mathbf{DFT}}$ (S = 2). The geometry for $^{1}\mathbf{2}_{\mathbf{DFT}}$ failed to converge.

	2	$^{3}\mathbf{2}_{\mathbf{DFT}}$	$^{5}\mathbf{2}_{\mathbf{DFT}}$
Fe1–C1	2.139(2)	2.023	2.069
Fe1–C12	2.062(1)	1.936	2.032
Fe1–C12′	2.062(1)	1.952	2.032
C1–Fe1–C12	124.4(1)	109.6	120.0
C1–Fe1–C12′	124.4(1)	143.5	123.1
C12–Fe1–C12′	111.3(1)	104.0	116.9
Total Bonding Energy (kJ/mol)		−50204.47	−50227.58

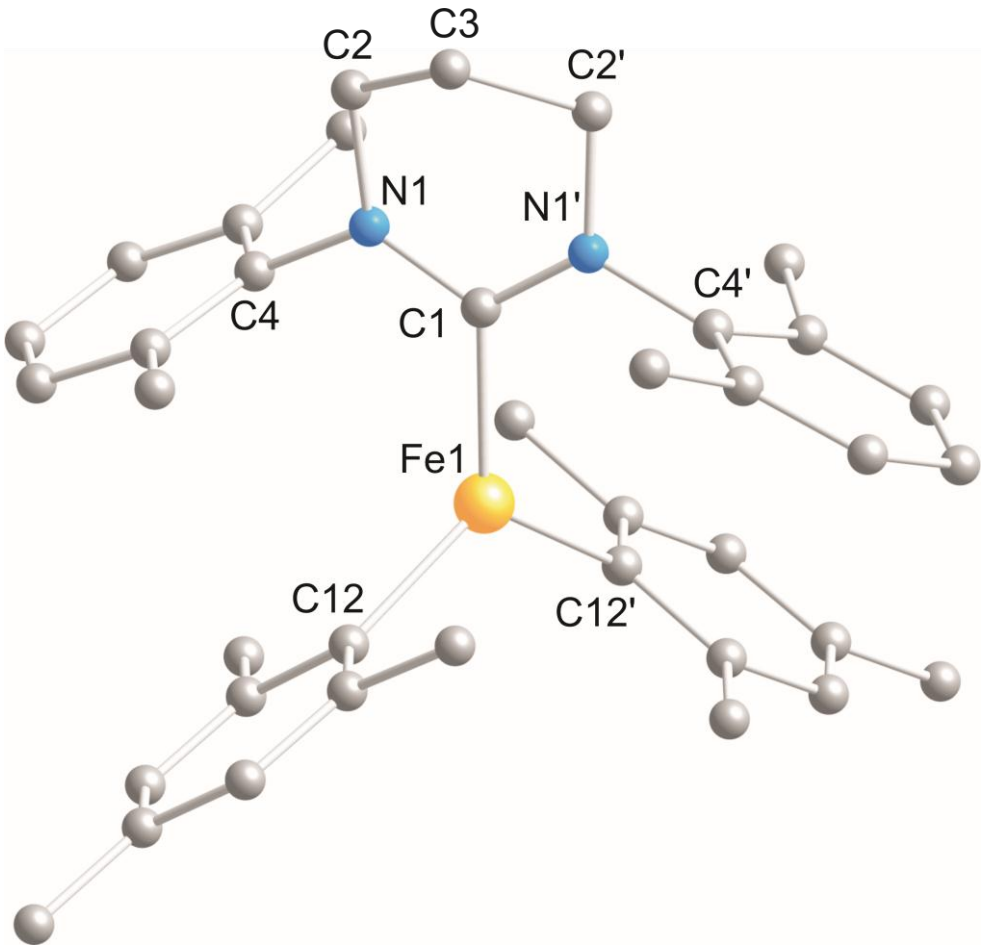

Figure S9. Optimized computed geometry for $^{5}\mathbf{2}_{\mathbf{DFT}}$. All hydrogen atoms have been omitted for clarity.

Table S8. Comparison of bond metric data (distances: Å; angles: °) for the crystallographically determined and computed (S = 2) structures of **2**.

	2	^{5}**2**$_{DFT}$
Fe1–C1	2.139(2)	2.069
Fe1–C12	2.062(1)	2.032
Fe1–C12′	2.062(1)	2.032
C1–N1	1.341(2)	1.359
C1–N1′	1.341(2)	1.359
N1–C2	1.479(2)	1.481
N1′–C2′	1.479(2)	1.478
C2–C3	1.530(5)	1.516
C3–C2′	1.469(5)	1.518
N1–C4	1.442(2)	1.442
N1′–C4′	1.442(2)	1.441
C1–Fe1–C12	124.4(1)	120.0
C1–Fe1–C12′	124.4(1)	123.1
C12–Fe1–C12′	111.3(1)	116.9
C1–N1–C2	124.7(1)	126.1
C1–N1′–C2′	124.7(1)	124.0
C1–N1–C4	119.5(1)	119.9
C1–N1′–C4′	119.5(1)	120.5
N1–C1–N1′	117.1(2)	115.9

Cartesian coordinates [Å] for the optimized computed geometry of 3 (*S* = 2).

Atom	x	y	z
1. Fe	0.000000	0.000000	0.000000
2. N	–0.770390	–4.130286	–0.070268
3. N	–2.020238	–2.443554	–0.307557
4. C	–2.078524	–3.812889	–0.329131
5. C	0.033934	–3.006482	0.093639
6. H	1.108146	–3.079029	0.275712
7. C	–0.752144	–1.881229	–0.056695
8. C	–0.278281	–5.455225	–0.075363
9. C	–0.011210	–6.104629	1.150630
10. C	0.519067	–7.400801	1.115565
11. H	0.732278	–7.925849	2.051303
12. C	0.778032	–8.039506	–0.099959
13. H	1.196319	–9.053421	–0.108501
14. C	0.506719	–7.384320	–1.301523
15. H	0.717399	–7.891595	–2.248486
16. C	–0.019674	–6.084312	–1.312316
17. C	–0.366890	–5.448333	2.474782
18. H	–0.315773	–4.355688	2.335477
19. C	–1.822870	–5.812818	2.835613
20. H	–2.112750	–5.316362	3.780065
21. H	–1.910978	–6.910156	2.958924
22. H	–2.499026	–5.478046	2.030816
23. C	0.589554	–5.823492	3.617787
24. H	0.344391	–5.213737	4.507129
25. H	1.640063	–5.627651	3.331283
26. H	0.484653	–6.887411	3.897113
27. C	–0.270775	–5.388833	–2.640628
28. H	–0.753782	–4.427011	–2.428508
29. C	1.057070	–5.111211	–3.372629
30. H	0.855060	–4.575705	–4.319080
31. H	1.579510	–6.058361	–3.605689
32. H	1.714656	–4.483968	–2.743784
33. C	–1.237323	–6.201265	–3.522207
34. H	–2.188153	–6.364374	–2.982466
35. H	–0.801301	–7.181048	–3.792390
36. H	–1.447001	–5.641723	–4.451451
37. C	–3.154865	–1.658161	–0.630601
38. C	–3.981437	–1.165527	0.400188
39. C	–5.075309	–0.367843	0.048971
40. H	–5.708297	0.053048	0.830665
41. C	–5.343686	–0.056218	–1.284583
42. H	–6.171499	0.617191	–1.534193
43. C	–4.515699	–0.550618	–2.289591
44. H	–4.717615	–0.283290	–3.330483
45. C	–3.407207	–1.351185	–1.981507
46. C	–3.679735	–1.491390	1.853334
47. H	–2.581488	–1.541229	1.945377
48. C	–4.182593	–0.417813	2.827915

49. H	–3.844752	0.578574	2.503218
50. H	–3.772996	–0.622254	3.833415
51. H	–5.285663	–0.425179	2.900256
52. C	–4.262684	–2.874150	2.211064
53. H	–3.845455	–3.637124	1.531880
54. H	–5.365864	–2.848172	2.106763
55. H	–4.003851	–3.134008	3.254326
56. C	–2.490140	–1.820552	–3.099293
57. H	–1.666252	–2.381034	–2.640413
58. C	–1.885735	–0.621149	–3.852482
59. H	–1.387602	0.055506	–3.139404
60. H	–2.670463	–0.056789	–4.385826
61. H	–1.143294	–0.978579	–4.590175
62. C	–3.232173	–2.774215	–4.053784
63. H	–2.544051	–3.120269	–4.846587
64. H	–4.090652	–2.261812	–4.527951
65. H	–3.600073	–3.650819	–3.490421
66. N	–0.946712	2.987511	0.498542
67. N	–2.857021	3.061043	–0.412129
68. C	–1.963160	3.870510	0.239873
69. C	–1.150959	1.664474	0.044945
70. C	–2.396887	1.753481	–0.542712
71. H	–3.009070	0.982112	–1.008683
72. C	0.199552	3.392315	1.228494
73. C	1.403082	3.654753	0.541432
74. C	2.527870	4.025618	1.287493
75. H	3.475958	4.210511	0.776222
76. C	2.461572	4.152188	2.674631
77. H	3.354083	4.441401	3.243394
78. C	1.260911	3.904164	3.337799
79. H	1.218710	4.003755	4.426708
80. C	0.114856	3.516912	2.631778
81. C	1.458415	3.589138	–0.976612
82. H	0.816453	2.747966	–1.284174
83. C	0.877680	4.891858	–1.565799
84. H	0.857149	4.828472	–2.669662
85. H	1.513375	5.748744	–1.264873
86. H	–0.149172	5.049058	–1.194942
87. C	2.865778	3.318267	–1.522869
88. H	2.796406	3.169675	–2.616993
89. H	3.280822	2.400528	–1.069887
90. H	3.540259	4.176569	–1.338521
91. C	–1.162721	3.172713	3.380013
92. H	–1.998284	3.325034	2.682428
93. C	–1.409336	4.076738	4.599312
94. H	–2.416075	3.869146	5.005263
95. H	–1.358627	5.143041	4.308318
96. H	–0.672758	3.887092	5.401479
97. C	–1.130685	1.686016	3.792482
98. H	–2.063999	1.421504	4.321609

99. H	–0.267231	1.505180	4.461623
100. H	–1.029315	1.048776	2.898169
101. C	–4.117598	3.483200	–0.900209
102. C	–4.286883	3.692969	–2.286751
103. C	–5.556376	4.049356	–2.760195
104. H	–5.707375	4.220531	–3.829890
105. C	–6.635123	4.194663	–1.887689
106. H	–7.622339	4.473911	–2.275695
107. C	–6.454036	3.981343	–0.520458
108. H	–7.307429	4.092682	0.154822
109. C	–5.203524	3.615593	–0.004400
110. C	–3.112313	3.613592	–3.248732
111. H	–2.356399	2.945702	–2.806679
112. C	–3.497246	3.039528	–4.622416
113. H	–2.579813	2.880150	–5.218204
114. H	–4.151499	3.732384	–5.182305
115. H	–4.013099	2.071808	–4.501370
116. C	–2.487858	5.017072	–3.398161
117. H	–1.611211	4.970757	–4.070371
118. H	–2.163257	5.388662	–2.411226
119. H	–3.235937	5.714573	–3.823764
120. C	–5.027863	3.392620	1.488902
121. H	–4.214598	2.661492	1.613562
122. C	–6.285065	2.819821	2.164458
123. H	–6.037889	2.533007	3.202638
124. H	–6.642563	1.925403	1.626140
125. H	–7.098682	3.566861	2.202655
126. C	–4.595047	4.709554	2.167032
127. H	–4.466735	4.548918	3.253067
128. H	–5.370710	5.483645	2.003774
129. H	–3.635402	5.035330	1.726214
130. C	2.012024	–0.010169	–0.228262
131. C	2.590245	–0.235350	–1.500452
132. C	3.975621	–0.137184	–1.702935
133. H	4.391930	–0.307897	–2.705570
134. C	4.840121	0.191228	–0.654307
135. C	4.284225	0.386203	0.616545
136. H	4.947521	0.638159	1.456299
137. C	2.904582	0.278523	0.834464
138. C	1.702652	–0.559106	–2.686863
139. H	0.991931	–1.358892	–2.417735
140. H	2.301462	–0.878848	–3.559277
141. H	1.112471	0.331720	–2.967346
142. C	6.330823	0.340561	–0.875246
143. H	6.591886	0.113505	–1.923698
144. H	6.898905	–0.341428	–0.213741
145. H	6.649791	1.376612	–0.649278
146. C	2.365871	0.514814	2.231060
147. H	3.167317	0.427701	2.988859
148. H	1.565008	–0.210178	2.457501

149. H	1.936622	1.530510	2.288772

Table S9. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **3** and its optimized computed geometries in different spin–states: $^{1}\mathbf{3}_{\mathbf{DFT}}$ (S = 0), $^{3}\mathbf{3}_{\mathbf{DFT}}$ (S = 1) and $^{5}\mathbf{3}_{\mathbf{DFT}}$ (S = 2).

	3	$^{1}\mathbf{3}_{\mathbf{DFT}}$	$^{3}\mathbf{3}_{\mathbf{DFT}}$	$^{5}\mathbf{3}_{\mathbf{DFT}}$
Fe1–C3	2.071(2)	1.926	1.948	2.027
Fe1–C29	2.064(2)	1.968	1.955	2.024
Fe1–C55	2.065(3)	1.870	1.866	2.025
C3–Fe1–C29	122.5(1)	137.7	146.5	123.6
C3–Fe1–C55	108.4(1)	94.1	94.2	111.2
C29–Fe1–C55	128.4(1)	119.6	113.7	124.9
Total Bonding Energy (kJ/mol)		−86114.82	−86166.13	−86189.25

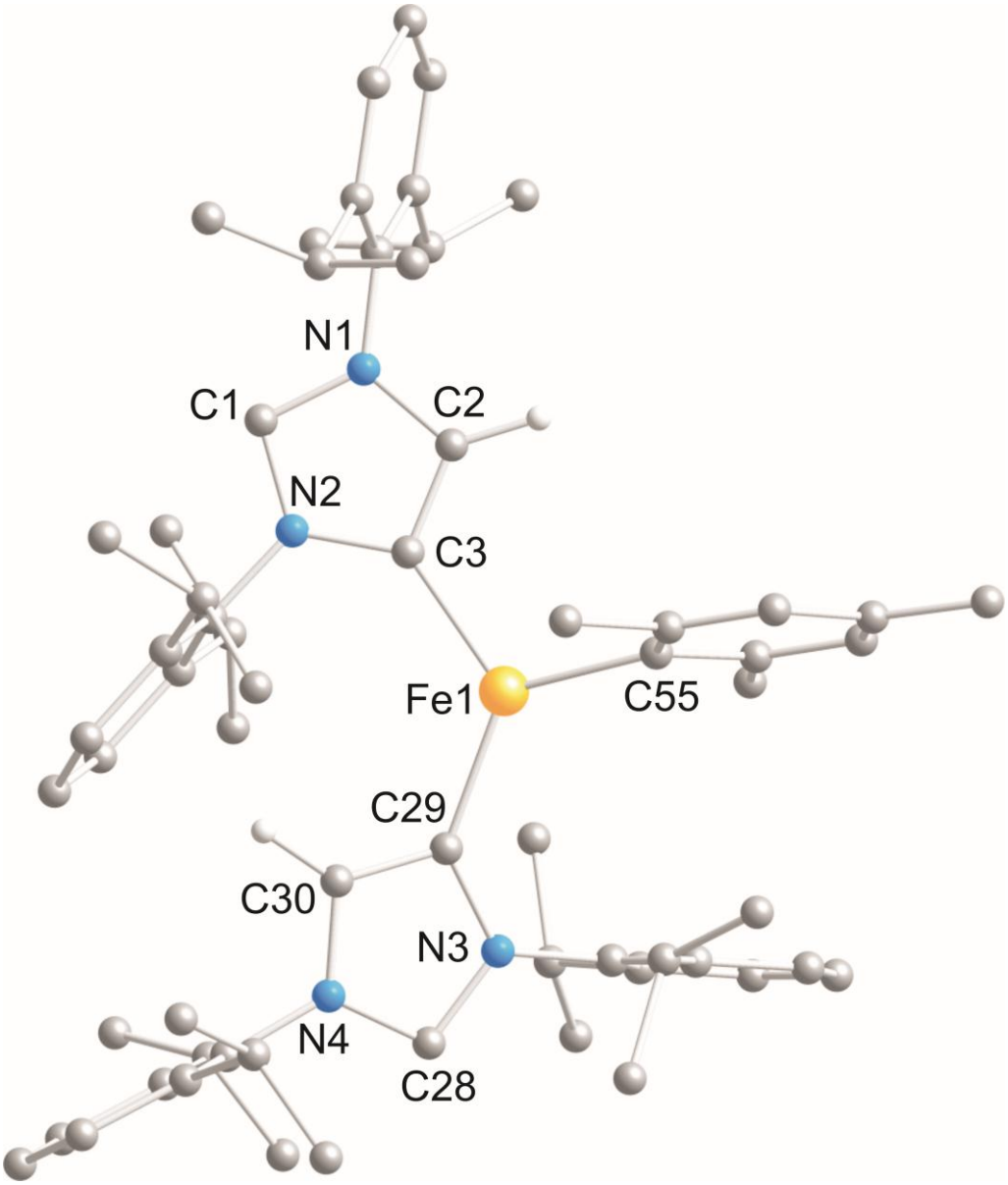

Figure S10. Optimized computed geometry for $^{5}\mathbf{3}_{\mathbf{DFT}}$. All hydrogen atoms, with the exception of those on the imidazol-2-ylidene backbone, have been omitted for clarity.

Table S10. Comparison of bond metric data for the crystallographically determined and computed (S = 2) structures of **3**.

	3	^{5}**3**$_{DFT}$
Fe1–C3	2.070(3)	2.027
Fe1–C29	2.064(2)	2.024
Fe1–C55	2.065(3)	2.025
C1–N1	1.353(4)	1.371
C1–N2	1.360(3)	1.371
N1–C2	1.399(3)	1.392
N2–C3	1.408(3)	1.410
C2–C3	1.360(4)	1.381
N1–C4	1.446(3)	1.413
N2–C16	1.439(3)	1.417
C28–N3	1.375(4)	1.371
C28–N4	1.351(4)	1.371
N3–C29	1.415(3)	1.413
N4–C30	1.403(3)	1.392
C29–C30	1.370(4)	1.380
N3–C31	1.432(4)	1.418
N4–C43	1.445(4)	1.416
C3–Fe1–C29	122.5(1)	123.6
C3–Fe1–C55	108.4(1)	111.2
C29–Fe1–C55	128.3(1)	124.9
Fe1–C3–N2	132.4(2)	135.2
Fe1–C3–C2	125.2(2)	122.8
N2–C3–C2	102.0(2)	101.9
C1–N1–C4	123.4(2)	123.3
C1–N2–C16	118.2(2)	121.1
N1–C1–N2	101.5(2)	100.8
Fe1–C29–N3	129.4(2)	134.0
Fe1–C29–C30	128.5(2)	123.8
N3–C29–C30	101.8(2)	101.9
C28–N3–C31	118.2(2)	120.8
C28–N4–C43	123.6(2)	124.6
N3–C28–N4	102.1(2)	101.1

Cartesian coordinates [Å] for the optimized computed geometry of the anionic moiety present in 5 (*S* = 2).

Atom	x	y	z
1. Fe	0.000000	0.000000	0.000000
2. C	−1.987802	−3.919690	−0.018532
3. N	−0.666604	−4.180232	−0.278619
4. N	−2.009744	−2.550078	0.089547
5. C	0.075486	−3.001078	−0.316060
6. H	1.147167	−3.023313	−0.488315
7. C	−0.748517	−1.926403	−0.081561
8. C	−0.051894	−5.480104	−0.393897
9. C	0.063899	−6.078165	−1.664124
10. C	0.690487	−7.330060	−1.741803
11. H	0.789092	−7.826102	−2.709295
12. C	1.206452	−7.949636	−0.605758
13. H	1.694024	−8.923109	−0.687989
14. C	1.110633	−7.321142	0.633185
15. H	1.530647	−7.812301	1.513063
16. C	0.482494	−6.076271	0.767806
17. C	−0.396910	−5.380639	−2.934232
18. H	−1.126117	−4.609996	−2.647234
19. C	−1.080714	−6.329944	−3.925953
20. H	−1.526584	−5.748594	−4.748627
21. H	−1.880292	−6.909184	−3.443006
22. H	−0.363603	−7.034291	−4.378052
23. C	0.788308	−4.668200	−3.610914
24. H	0.447094	−4.141669	−4.517677
25. H	1.562975	−5.396373	−3.906263
26. H	1.250436	−3.927690	−2.940661
27. C	0.433377	−5.400434	2.130152
28. H	−0.357310	−4.636003	2.096310
29. C	0.087511	−6.373777	3.265703
30. H	−0.099446	−5.809445	4.193250
31. H	0.913764	−7.073321	3.470765
32. H	−0.812564	−6.960059	3.031187
33. C	1.765533	−4.690879	2.434128
34. H	1.718873	−4.205358	3.422911
35. H	1.998700	−3.915690	1.688551
36. H	2.595331	−5.418743	2.449240
37. C	−3.179156	−1.807019	0.490797
38. C	−4.099098	−1.376550	−0.485180
39. C	−5.212504	−0.649802	−0.049475
40. H	−5.944960	−0.299670	−0.777474
41. C	−5.407278	−0.361051	1.299315
42. H	−6.277399	0.219664	1.614245
43. C	−4.482390	−0.796793	2.242011
44. H	−4.642115	−0.559871	3.295584
45. C	−3.345537	−1.519833	1.858552
46. C	−3.889251	−1.657555	−1.966497
47. H	−3.377802	−2.627944	−2.048533

48. C	−5.198754	−1.759963	−2.757924
49. H	−4.987833	−2.142682	−3.768955
50. H	−5.680128	−0.775920	−2.879352
51. H	−5.917706	−2.440852	−2.278938
52. C	−2.977042	−0.595511	−2.602279
53. H	−2.814212	−0.825241	−3.669050
54. H	−1.999582	−0.553023	−2.100013
55. H	−3.435984	0.403677	−2.524190
56. C	−2.347793	−1.962592	2.919480
57. H	−1.459807	−2.351990	2.402054
58. C	−2.917651	−3.092914	3.790153
59. H	−2.167938	−3.416709	4.531330
60. H	−3.203006	−3.959177	3.177900
61. H	−3.812704	−2.754693	4.338889
62. C	−1.885012	−0.786578	3.792261
63. H	−1.075742	−1.113279	4.465649
64. H	−2.703983	−0.404629	4.422705
65. H	−1.508400	0.042513	3.173773
66. C	−1.718605	4.015270	−0.080453
67. N	−0.740121	3.089732	−0.351599
68. N	−2.699146	3.223894	0.462522
69. C	−1.061110	1.738784	−0.008953
70. C	−2.325933	1.873096	0.512473
71. H	−3.012541	1.121620	0.896736
72. C	0.489758	3.493293	−0.976434
73. C	0.520628	3.699468	−2.370705
74. C	1.735570	4.086007	−2.955677
75. H	1.789838	4.246668	−4.034650
76. C	2.880881	4.263685	−2.183882
77. H	3.820453	4.559238	−2.656770
78. C	2.823830	4.073921	−0.804141
79. H	3.726376	4.223215	−0.209562
80. C	1.631433	3.697597	−0.173390
81. C	−0.705527	3.493856	−3.246590
82. H	−1.583131	3.499796	−2.585244
83. C	−0.655147	2.127731	−3.947561
84. H	−1.558662	1.981307	−4.563578
85. H	−0.605153	1.313928	−3.208998
86. H	0.227557	2.055765	−4.606605
87. C	−0.895744	4.626106	−4.266437
88. H	−1.866470	4.513158	−4.775823
89. H	−0.115839	4.617658	−5.045680
90. H	−0.879325	5.612255	−3.773884
91. C	1.554107	3.588432	1.341996
92. H	0.843533	2.778367	1.570794
93. C	2.888867	3.236061	2.004161
94. H	3.345846	2.348256	1.537868
95. H	2.719946	3.015483	3.071479
96. H	3.603068	4.075800	1.957270
97. C	0.990301	4.892772	1.934776

98. H	0.891227	4.803251	3.029824
99. H	0.001929	5.123623	1.507284
100. H	1.672619	5.735368	1.720172
101. C	−3.948905	3.717554	0.967330
102. C	−5.065215	3.778171	0.104605
103. C	−6.285145	4.218120	0.633815
104. H	−7.166789	4.274049	−0.007951
105. C	−6.398178	4.586074	1.975090
106. H	−7.359701	4.922413	2.370146
107. C	−5.283264	4.525895	2.807645
108. H	−5.381899	4.822932	3.854338
109. C	−4.040422	4.091000	2.322096
110. C	−4.939302	3.430152	−1.370416
111. H	−4.144032	2.673014	−1.457540
112. C	−6.217633	2.834566	−1.972386
113. H	−6.006012	2.447431	−2.981944
114. H	−7.015391	3.587756	−2.076864
115. H	−6.605077	2.005387	−1.360629
116. C	−4.496689	4.669492	−2.167497
117. H	−4.377542	4.418331	−3.234280
118. H	−3.537783	5.051315	−1.783529
119. H	−5.255389	5.468123	−2.084668
120. C	−2.840675	4.059446	3.255041
121. H	−1.988847	3.654765	2.690326
122. C	−3.079305	3.137873	4.459832
123. H	−2.163652	3.064867	5.069638
124. H	−3.353450	2.124971	4.128013
125. H	−3.885196	3.518135	5.109207
126. C	−2.465858	5.477622	3.711369
127. H	−1.560138	5.452291	4.339157
128. H	−3.275692	5.934424	4.304819
129. H	−2.267575	6.127462	2.844546
130. C	2.031599	−0.124221	0.238871
131. C	2.919823	0.069533	−0.846481
132. C	4.310751	0.049942	−0.656710
133. H	4.971413	0.230965	−1.513892
134. C	4.878196	−0.187106	0.599571
135. C	4.006485	−0.422224	1.671175
136. H	4.427247	−0.624661	2.664429
137. C	2.615308	−0.387142	1.506376
138. C	2.390358	0.342685	−2.234527
139. H	1.491103	−0.256668	−2.442870
140. H	3.142114	0.118527	−3.009815
141. H	2.110492	1.404668	−2.334944
142. C	6.374883	−0.206727	0.794436
143. H	6.897700	0.165480	−0.099517
144. H	6.744038	−1.227628	0.994092
145. H	6.677421	0.420735	1.648612
146. C	1.740418	−0.600348	2.720288
147. H	0.923454	−1.302604	2.496668

148. H	1.274929	0.347300	3.041998
149. H	2.316318	−0.998248	3.572506
150. Al	−3.617860	−5.293881	−0.082083
151. C	−5.185184	−4.630250	1.006965
152. H	−5.000104	−4.779986	2.089386
153. H	−5.353143	−3.542794	0.888375
154. C	−6.487770	−5.367542	0.632689
155. H	−7.363496	−5.051882	1.237414
156. H	−6.394365	−6.460827	0.759279
157. H	−6.753638	−5.194416	−0.424758
158. C	−4.150535	−5.367007	−2.042486
159. H	−4.934540	−4.599719	−2.202257
160. H	−3.331676	−5.076017	−2.727389
161. C	−4.711770	−6.724960	−2.508446
162. H	−5.057214	−6.715862	−3.563386
163. H	−5.573182	−7.041385	−1.893796
164. H	−3.958953	−7.527481	−2.425370
165. C	−3.054621	−7.112261	0.616055
166. H	−3.529241	−7.869724	−0.042499
167. H	−1.966652	−7.284725	0.504426
168. C	−3.466600	−7.420582	2.069321
169. H	−3.127705	−8.416408	2.423287
170. H	−4.564433	−7.396596	2.187384
171. H	−3.064485	−6.676369	2.777794

Table S11. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **5** and its optimized computed geometries in different spin–states: ^{1}**5**$_{\mathbf{DFT}}$ (*S* = 0), ^{3}**5**$_{\mathbf{DFT}}$ (*S* = 1) and ^{5}**5**$_{\mathbf{DFT}}$ (*S* = 2).

	5	^{1}**5**$_{\mathbf{DFT}}$	^{3}**5**$_{\mathbf{DFT}}$	^{5}**5**$_{\mathbf{DFT}}$
Fe1–C3	2.110(2)	1.979	1.989	2.068
Fe1–C29	2.074(2)	1.965	1.981	2.037
Fe1–C55	2.071(2)	1.888	1.898	2.049
C1–Al1	2.123(2)	2.133	2.115	2.133
C3–Fe1–C29	124.9(1)	143.4	163.3	127.3
C3–Fe1–C55	109.6(1)	97.3	92.3	107.9
C29–Fe1–C55	125.4(1)	112.7	103.7	124.7
Total Bonding Energy (kJ/mol)		−95919.38	−95955.40	−95995.74

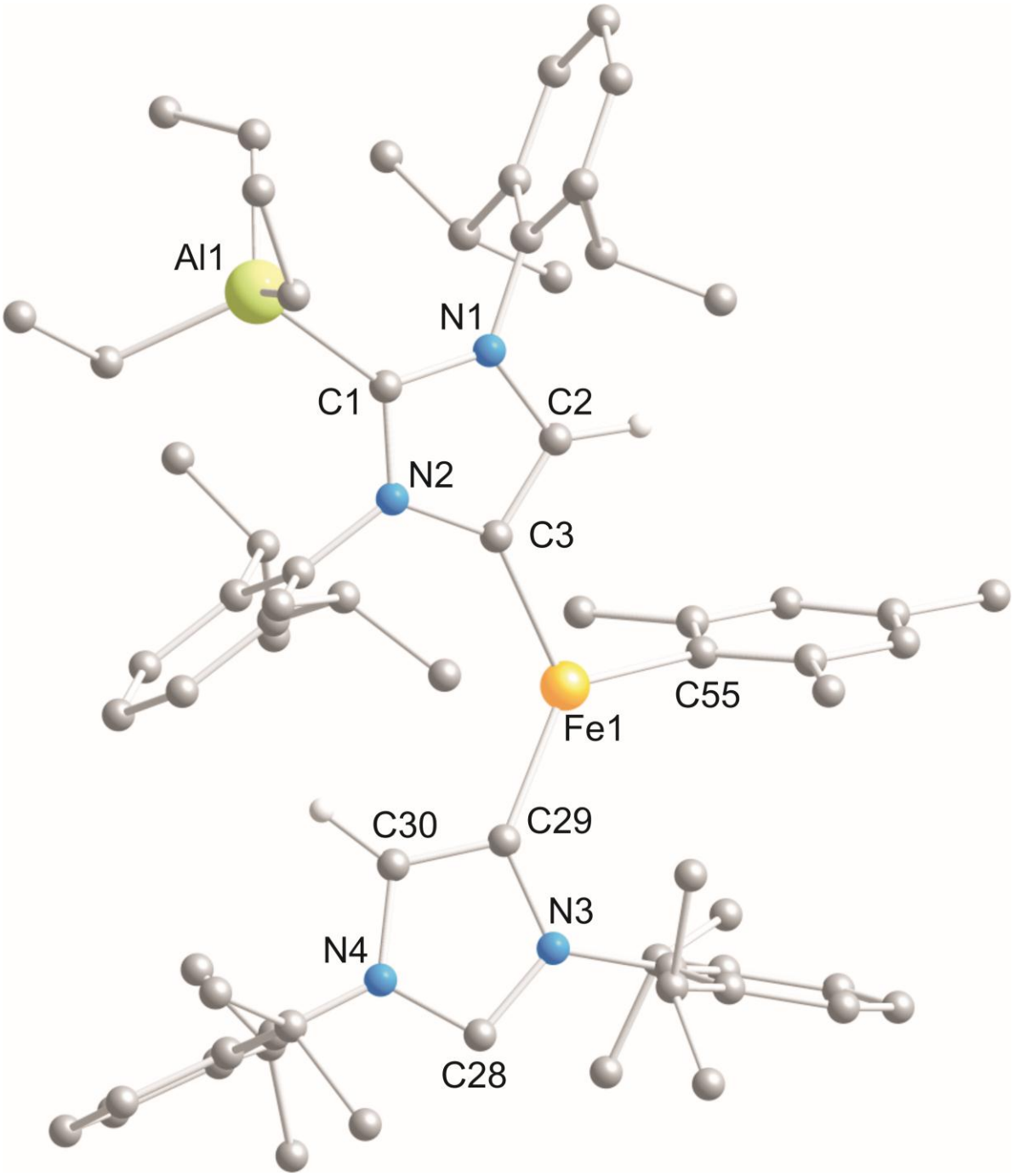

Figure S11. Optimized computed geometry for $^{5}\mathbf{5}_{\mathbf{DFT}}$. All hydrogen atoms, with the exception of those on the imidazol-2-ylidene backbone, have been omitted for clarity.

Table S12. Comparison of bond metric data for the crystallographically determined and computed (S = 2) structures of **5**.

	5	^{5}**5**$_{DFT}$
Fe1–C3	2.110(2)	2.068
Fe1–C29	2.074(2)	2.037
Fe1–C55	2.071(2)	2.049
C1–N1	1.358(3)	1.372
C1–N2	1.364(3)	1.374
N1–C2	1.398(3)	1.394
N2–C3	1.418(3)	1.417
C2–C3	1.358(4)	1.374
N1–C4	1.444(3)	1.443
N2–C16	1.437(3)	1.442
C28–N3	1.367(3)	1.374
C28–N4	1.366(3)	1.372
N3–C29	1.426(3)	1.430
N4–C30	1.399(3)	1.402
C29–C30	1.359(3)	1.375
N3–C31	1.440(3)	1.437
N4–C43	1.440(3)	1.435
C1–Al1	2.123(2)	2.133
C3–Fe1–C29	124.9(1)	127.3
C3–Fe1–C55	109.6(1)	107.9
C29–Fe1–C55	125.4(1)	124.6
Fe1–C3–N2	133.1(2)	136.6
Fe1–C3–C2	124.6(2)	121.2
N2–C3–C2	102.0(2)	102.1
C1–N1–C4	126.6(2)	126.6
C1–N2–C16	122.2(2)	123.3
N1–C1–N2	103.0(2)	102.7
Fe1–C29–N3	133.4(2)	133.7
Fe1–C29–C30	124.9(2)	124.1
N3–C29–C30	101.6(2)	101.8
C28–N3–C31	119.7(2)	120.4
C28–N4–C43	122.8(2)	124.3
N3–C28–N4	101.3(2)	101.5

Cartesian coordinates [Å] for the optimized computed geometry of the anionic moiety present in 6 (*S* = 2).

Atom	x	y	z
1. Fe	0.138457	0.016513	−0.030110
2. C	−1.230442	4.164881	0.606009
3. N	−2.382828	3.479193	0.319860
4. N	−0.276509	3.176936	0.607173
5. C	−2.121563	2.116726	0.166037
6. H	−2.936579	1.431727	−0.041080
7. C	−0.780308	1.869267	0.335092
8. C	−3.715350	4.031794	0.277017
9. C	−4.231859	4.494518	−0.950267
10. C	−5.531174	5.020547	−0.953080
11. H	−5.958426	5.400608	−1.882543
12. C	−6.296525	5.059696	0.210213
13. H	−7.306635	5.474191	0.184895
14. C	−5.778225	4.558360	1.401484
15. H	−6.394642	4.580370	2.302012
16. C	−4.481046	4.034118	1.461770
17. C	−3.461842	4.366051	−2.255660
18. H	−2.390258	4.334202	−2.011365
19. C	−3.697548	5.539067	−3.215864
20. H	−2.981388	5.483388	−4.050933
21. H	−3.564751	6.508673	−2.714696
22. H	−4.708209	5.509305	−3.654477
23. C	−3.818342	3.041714	−2.957029
24. H	−3.258489	2.951202	−3.902578
25. H	−4.896735	3.004116	−3.188672
26. H	−3.569611	2.171660	−2.331195
27. C	−3.966629	3.440504	2.764532
28. H	2.872080	3.361974	2.690384
29. C	−4.286308	4.303800	3.991984
30. H	−3.781921	3.886799	4.878137
31. H	−5.365897	4.321752	4.211536
32. H	−3.942254	5.338688	3.855311
33. C	−4.526820	2.019734	2.956273
34. H	−4.128487	1.573946	3.882507
35. H	−4.252008	1.364388	2.117296
36. H	−5.627196	2.043254	3.029077
37. C	1.108442	3.413634	0.949898
38. C	1.989995	3.914859	−0.029072
39. C	3.339163	4.034400	0.320627
40. H	4.058497	4.386938	−0.419011
41. C	3.787117	3.716836	1.599635
42. H	4.847417	3.812624	1.845978
43. C	2.883980	3.292473	2.568182
44. H	3.246364	3.072329	3.573843
45. C	1.527065	3.125601	2.264547
46. C	1.498153	4.373152	−1.397420
47. H	0.541587	4.890129	−1.233114

48. C	2.433535	5.382958	−2.071696
49. H	1.941203	5.792220	−2.967837
50. H	3.373164	4.911769	−2.403975
51. H	2.681686	6.224401	−1.407053
52. C	1.229248	3.198657	−2.345104
53. H	0.860760	3.574895	−3.315706
54. H	0.477135	2.514408	−1.928718
55. H	2.153045	2.619298	−2.506799
56. C	0.542036	2.695114	3.346586
57. H	−0.238847	2.088810	2.859983
58. C	−0.137149	3.919629	3.985261
59. H	−0.876744	3.595612	4.736479
60. H	−0.646838	4.538492	3.236182
61. H	0.613179	4.551024	4.490139
62. C	1.169483	1.833272	4.449739
63. H	0.374083	1.439362	5.102588
64. H	1.852052	2.419107	5.087085
65. H	1.726358	0.977882	4.039643
66. C	−1.500149	−4.047931	0.278040
67. N	−0.535393	−3.087924	0.471091
68. N	−2.535605	−3.332426	−0.264950
69. C	−0.927026	−1.773031	0.098466
70. C	−2.204249	−1.980623	−0.366043
71. H	−2.926647	−1.276832	−0.766005
72. C	0.729881	−3.384060	1.101548
73. C	0.793435	−3.360467	2.506572
74. C	2.021243	−3.655240	3.112809
75. H	2.104351	−3.643719	4.201611
76. C	3.138594	−3.971149	2.347424
77. H	4.088639	−4.202474	2.835462
78. C	3.048700	−3.987674	0.957638
79. H	3.937730	−4.225149	0.371767
80. C	1.848306	−3.691769	0.300737
81. C	−0.412248	−3.028989	3.372513
82. H	−1.304976	−3.051589	2.731997
83. C	−0.298003	−1.610163	3.949637
84. H	−1.190876	−1.368997	4.550849
85. H	−0.213298	−0.865491	3.143006
86. H	0.588619	−1.521359	4.599106
87. C	−0.625859	−4.061923	4.489114
88. H	−1.578725	−3.863760	5.005850
89. H	0.174428	−4.015921	5.245570
90. H	−0.660081	−5.083049	4.083192
91. C	1.773004	−3.714759	−1.220994
92. H	1.062903	−2.924618	−1.514036
93. C	3.113732	−3.403571	−1.894605
94. H	3.570210	−2.486958	−1.490020
95. H	2.951875	−3.251781	−2.974439
96. H	3.824108	−4.241112	−1.786008
97. C	1.242134	−5.055866	−1.752388

98. H	1.172848	−5.018775	−2.852845
99. H	0.250502	−5.298351	−1.352292
100. H	1.927758	−5.874414	−1.478661
101. C	−3.826360	−3.859727	−0.636263
102. C	−4.908391	−3.686007	0.250152
103. C	−6.145557	−4.237634	−0.112611
104. H	−6.999963	−4.132476	0.558634
105. C	−6.305160	−4.916313	−1.315919
106. H	−7.272574	−5.354086	−1.573102
107. C	−5.237098	−5.014361	−2.206990
108. H	−5.389762	−5.516986	−3.163103
109. C	−3.981781	−4.475920	−1.899283
110. C	−4.814541	−2.855743	1.523948
111. H	−3.763436	−2.566483	1.670156
112. C	−5.638850	−1.565149	1.359239
113. H	−5.494769	−0.905446	2.228854
114. H	−6.715016	−1.797816	1.286262
115. H	−5.353823	−1.011541	0.451028
116. C	−5.269105	−3.606665	2.782564
117. H	−5.170057	−2.947659	3.660855
118. H	−4.657825	−4.502413	2.954619
119. H	−6.324696	−3.915631	2.715940
120. C	−2.864480	−4.487620	−2.935245
121. H	−1.913191	−4.619801	−2.399277
122. C	−2.802584	−3.134007	−3.670722
123. H	−2.010027	−3.159696	−4.437010
124. H	−2.580090	−2.304158	−2.984933
125. H	−3.762587	−2.925838	−4.174153
126. C	−2.984351	−5.614277	−3.968450
127. H	−2.059441	−5.659175	−4.565178
128. H	−3.813371	−5.434101	−4.672184
129. H	−3.130261	−6.595532	−3.494631
130. C	2.001335	−0.047348	−0.853102
131. C	3.140649	−0.016339	−0.011231
132. C	4.430825	0.076436	−0.547099
133. H	5.290949	0.121822	0.131845
134. C	4.649091	0.132901	−1.927396
135. C	3.531508	0.058266	−2.765439
136. H	3.679971	0.083275	−3.852368
137. C	2.230862	−0.040910	−2.250267
138. C	2.983935	−0.123016	1.484352
139. H	2.100642	0.437807	1.823884
140. H	3.862421	0.276148	2.017400
141. H	2.843951	−1.176955	1.783131
142. C	6.040179	0.308278	−2.484204
143. H	6.794360	−0.178150	−1.845620
144. H	6.306576	1.378431	−2.546183
145. H	6.128612	−0.111499	−3.498168
146. C	1.084598	−0.167884	−3.226541
147. H	0.194737	0.378716	−2.880926

148. H	0.784478	−1.224921	−3.337553
149. H	1.360009	0.204446	−4.226951
150. Al	−1.019610	6.304687	0.783534
151. C	0.708549	6.806872	1.702713
152. H	0.623931	6.648935	2.796069
153. H	1.564010	6.180938	1.384599
154. C	1.065220	8.286967	1.449266
155. H	1.990031	8.613325	1.969177
156. H	0.261294	8.968589	1.779507
157. H	1.220830	8.483017	0.373946
158. C	−0.978706	7.018262	−1.123557
159. H	0.086031	7.163915	−1.399641
160. H	−1.364855	6.299062	−1.869420
161. C	−1.706324	8.362928	−1.323376
162. H	−1.611475	8.761728	−2.354888
163. H	−1.314842	9.140771	−0.644026
164. H	−2.785577	8.277892	−1.110340
165. C	−2.561401	7.106584	1.828932
166. H	−2.852697	8.027113	1.281710
167. H	−3.467150	6.472007	1.799321
168. C	−2.263453	7.501379	3.289290
169. H	−3.133650	7.953334	3.809496
170. H	−1.441949	8.237082	3.344923
171. H	−1.943408	6.636705	3.895642
172. Al	−1.493066	−6.150543	0.783965
173. C	−2.046252	−7.198046	−0.855356
174. H	−3.107585	−7.005045	−1.104983
175. H	−1.474131	−6.885107	−1.750973
176. C	0.348644	−6.796618	1.328909
177. H	0.864115	−7.123037	0.402345
178. H	1.001435	−6.014230	1.756765
179. H	−2.174426	−9.303864	−1.570003
180. C	−1.849975	−8.718446	−0.684049
181. H	−0.789222	−8.968853	−0.507650
182. H	−2.415259	−9.112123	0.178616
183. C	0.331412	−7.987346	2.309227
184. H	−0.305719	−8.815729	1.952992
185. H	1.340251	−8.415198	2.486414
186. H	−0.063492	−7.689989	3.295965
187. C	−2.816160	−6.469309	2.286545
188. H	−4.106226	−7.962862	1.331171
189. H	−4.875381	−7.198531	2.739568
190. C	−4.200448	−7.008886	1.878418
191. H	−4.727253	−6.314477	1.202683
192. H	−2.940210	−5.571500	2.922208
193. H	−2.336009	−7.215546	2.953686

Table S13. Comparison of selected bond metric parameters (distances: Å; angles: °) for the crystallographically determined structure of **6** and its optimized computed geometries in different spin–states: $^{1}\mathbf{6}_{\mathbf{DFT}}$ (S = 0), $^{3}\mathbf{6}_{\mathbf{DFT}}$ (S = 1) and $^{5}\mathbf{6}_{\mathbf{DFT}}$ (S = 2).

	6	$^{1}\mathbf{6}_{\mathbf{DFT}}$	$^{3}\mathbf{6}_{\mathbf{DFT}}$	$^{5}\mathbf{6}_{\mathbf{DFT}}$
Fe1–C3	2.085(5)	2.007	2.020	2.100
Fe1–C29	2.085(5)	1.967	1.980	2.087
Fe1–C55	2.049(5)	1.877	1.894	2.038
C1–Al1	2.092(5)	2.149	2.149	2.157
C28–Al2	2.105(5)	2.167	2.145	2.163
C3–Fe1–C29	106.4(2)	135.9	140.8	121.5
C3–Fe1–C55	136.1(2)	110.0	108.2	119.9
C29–Fe1–C55	116.5(2)	104.5	102.1	117.7
Total Bonding Energy (kJ/mol)		−106594.28	−106654.43	−106666.25

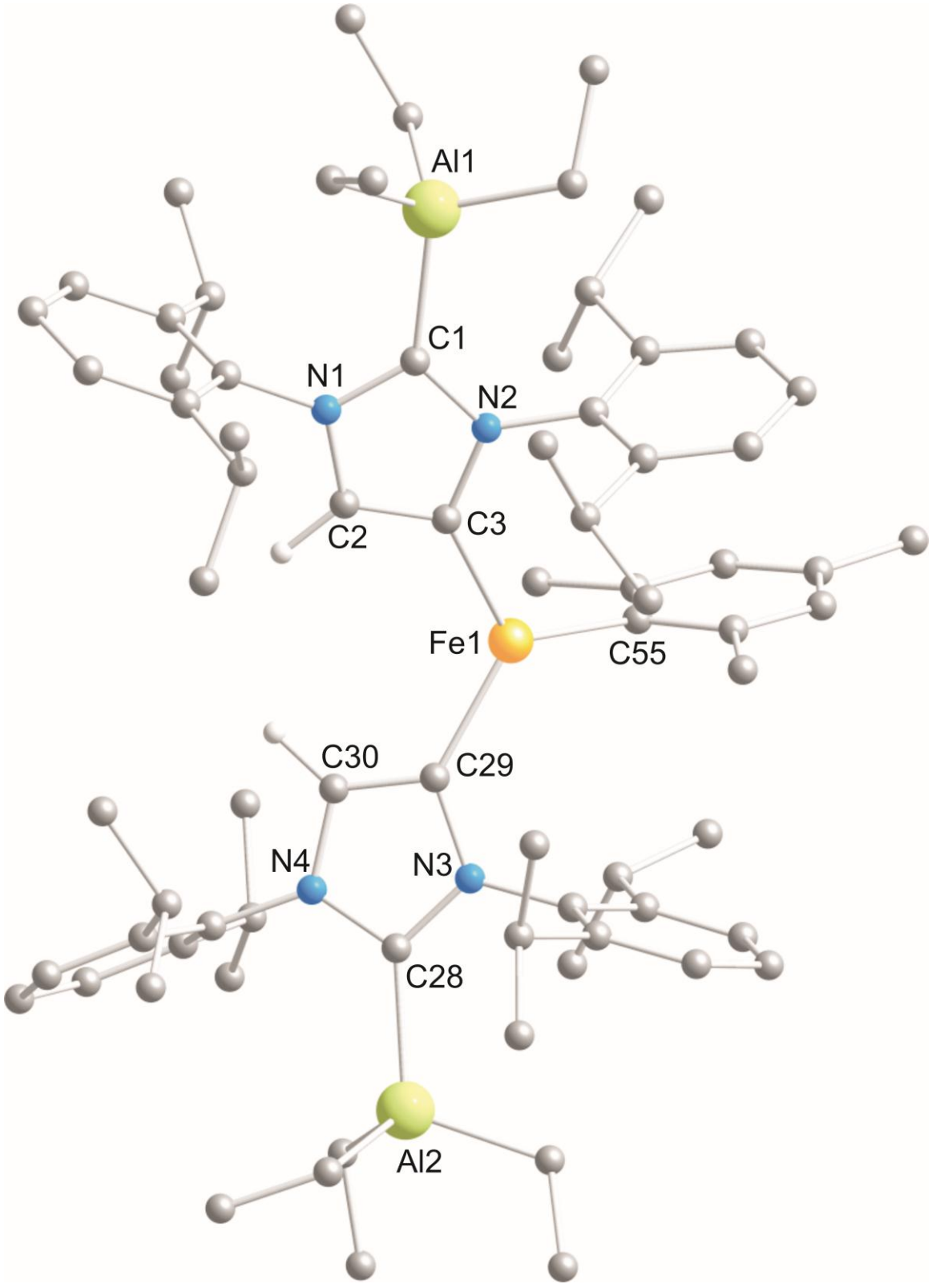

Figure S12. Optimized computed geometry for $^{5}\mathbf{6}_{\mathbf{DFT}}$. All hydrogen atoms, with the exception of those on the imidazol-2-ylidene backbone, have been omitted for clarity.

Table S14. Comparison of bond metric data for the crystallographically determined and computed (S = 2) structures of **6**.

	6	^{5}**6**$_{DFT}$
Fe1–C3	2.085(5)	2.100
Fe1–C29	2.085(5)	2.087
Fe1–C55	2.049(5)	2.038
C1–N1	1.371(6)	1.371
C1–N2	1.365(6)	1.373
N1–C2	1.391(6)	1.396
N2–C3	1.414(6)	1.428
C2–C3	1.359(7)	1.374
N1–C4	1.445(6)	1.443
N2–C16	1.462(6)	1.446
C28–N3	1.359(6)	1.375
C28–N4	1.369(6)	1.371
N3–C29	1.423(6)	1.422
N4–C30	1.396(6)	1.395
C29–C30	1.339(7)	1.375
N3–C31	1.441(6)	1.444
N4–C43	1.442(6)	1.443
C1–Al1	2.092(5)	2.157
C28–Al2	2.105(5)	2.163
C3–Fe1–C29	106.4(2)	121.5
C3–Fe1–C55	136.1(2)	119.9
C29–Fe1–C55	116.5(2)	117.7
Fe1–C3–N2	139.3(4)	133.4
Fe1–C3–C2	118.6(3)	124.4
N2–C3–C2	101.6(4)	101.7
C1–N1–C4	128.9(4)	126.2
C1–N2–C16	122.3(4)	123.2
N1–C1–N2	102.3(4)	103.0
Fe1–C29–N3	129.3(3)	132.0
Fe1–C29–C30	128.3(4)	125.7
N3–C29–C30	102.4(4)	101.8
C28–N3–C31	123.6(4)	122.2
C28–N4–C43	127.5(4)	125.9
N3–C28–N4	103.1(4)	102.8

5. ESI-MS spectra

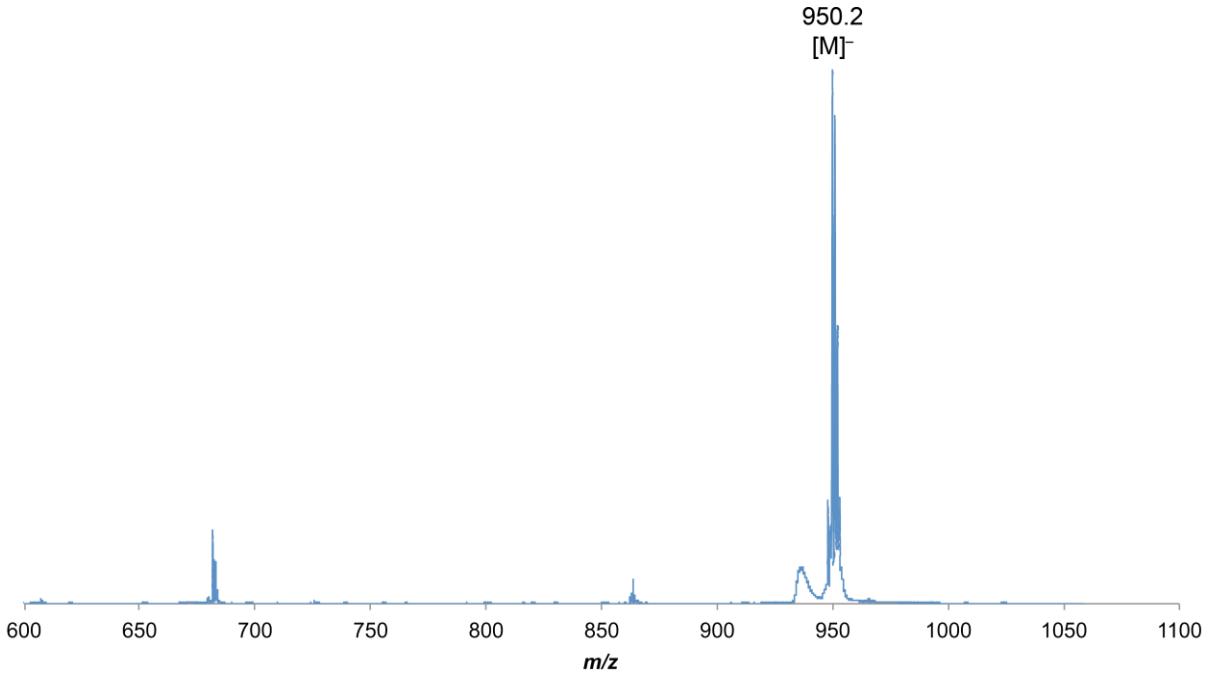

Figure S13. Negative ion mode mass spectrum of a THF solution of [K][**3**].

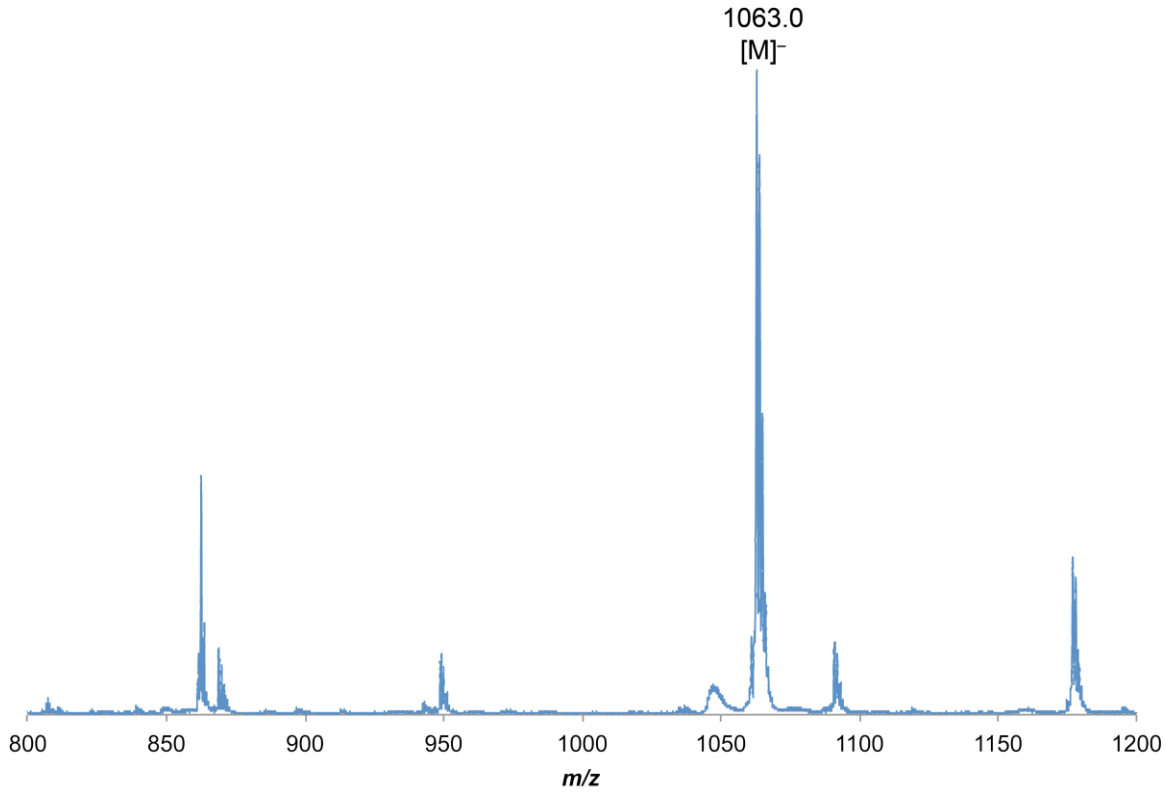

Figure S14. Negative ion mode mass spectrum of a THF solution of [K(2,2,2-crypt)][**5**].

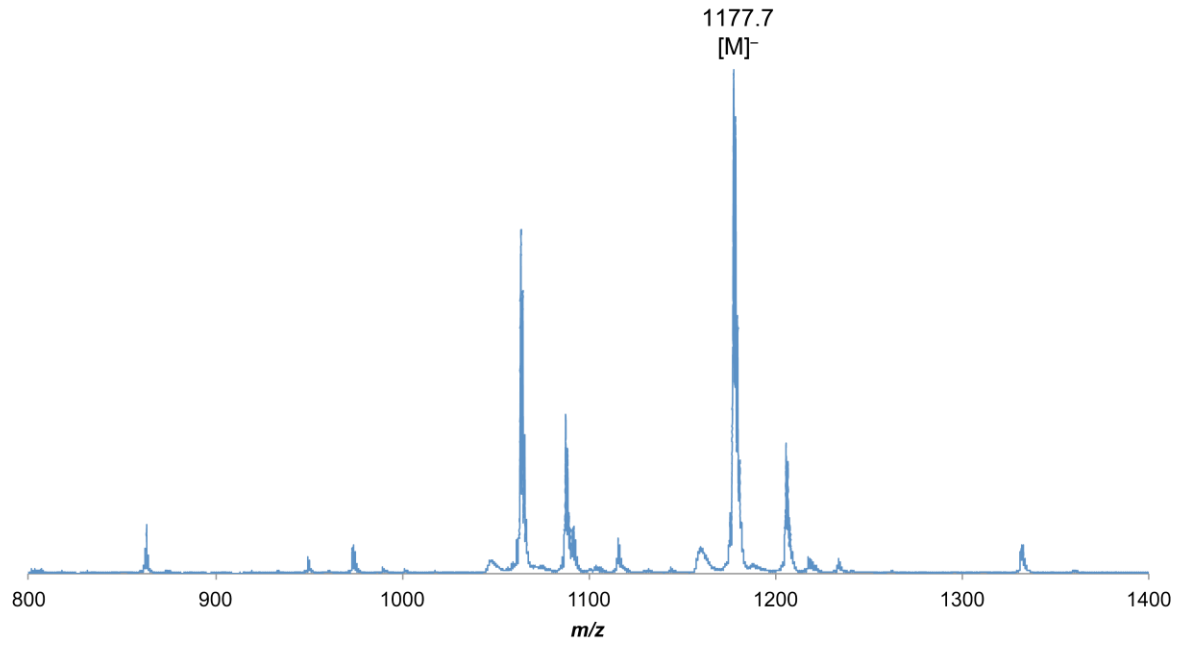

Figure S15. Negative ion mode mass spectrum of a THF solution of [K(2,2,2-crypt)][**6**].

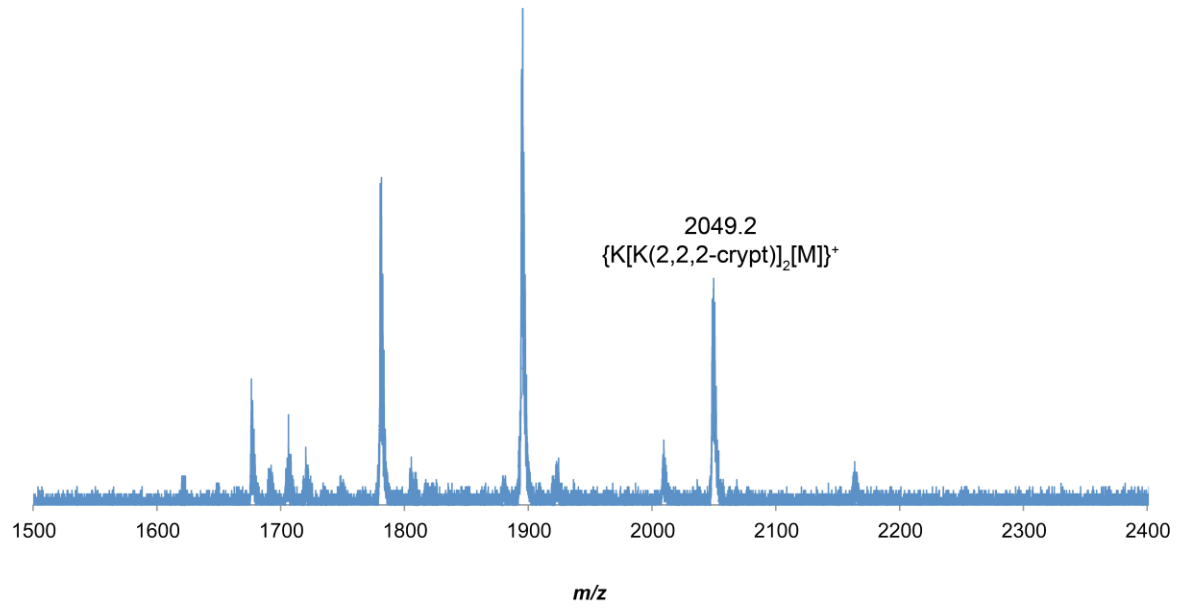

Figure S16. Positive ion mode mass spectrum of a THF solution of [K(2,2,2-crypt)][**6**].

6. References

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