Supporting Information

belonging to

Piano-Stool Iron(II) Complexes as Probes for the Bonding of N-Heterocyclic Carbenes: Indications for π Acceptor Ability

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Crystallographic details:

Table S1. Selected bond lengths and angles for complex 3b [a)]

bond length (Å)		bond angle (deg)	
Fe1–C6	1.970(3)	C6–Fe1–C15	94.2(1)
Fe1–C15	1.774(4)	C6–Fe1–C16	94.4(2)
Fe1–C16	1.780(3)	C15–Fe1–C16	92.8(2)
Fe1–cp	1.716(2)	C6–Fe1–cp	122.2(1)
C15–O1	1.142(4)	C15–Fe1–cp	123.5(1)
C16–O2	1.135(4)	C16–Fe1–cp	121.8(1)
C7–C8	1.332(4)	N1–C6–N2	103.5(2)
C6–N1	1.357(4)	N1–C6–Fe1	128.3(2)
C6–N2	1.367(4)	N2–C6–Fe1	128.2(2)

a) estimated standard deviations in parentheses; cp denotes centroid position of cp ring.

Table S2. Selected bond lengths and angles for complex 5c [a)]

bond length (Å)		bond angle (deg)	
Fe1–C2	1.952(5)	C2–Fe1–C14	86.1(2)
Fe1–C14	1.955(5)	C2–Fe1–C31	97.7(2)
Fe1–C31	1.747(5)	C14–Fe1–C31	95.7(2)
Fe1–cp	1.732(3)	C2–Fe1–cp	123.2(2)
C31–O1	1.113(7)	C14–Fe1–cp	123.9(2)
C3–C4	1.331(7)	C31–Fe1–cp	121.8(2)
C15–C16	1.327(9)	N1–C2–N2	102.5(4)
C2–N1	1.360(6)	N3–C14–N4	103.6(4)
C2–N2	1.363(6)		
C14–N3	1.352(6)	C2–Fe1–C14–N3	37.9(4)
C14–N4	1.357(7)	C14–Fe1–C2–N1	–36.0(5)

a) estimated standard deviations in parentheses; cp denotes centroid position of cp ring.

Table S3. Selected bond lengths and angles for the pyridine-carbene complexes 8a-c [a)]

	8a (R = Me)		**8b** (R = *i*Pr)		**8c** (R = Mes)
	Molecule 1	molecule 2[b)]	molecule 1	molecule 2[b)]	
bond length (Å)					
Fe1–C7	1.935(9)	1.928(10	1.952(10)	1.942(9)	1.932(2)
Fe1–C1	1.715(11)	1.741(11	1.733(11)	1.741(12	1.741(2)
Fe1–N1	1.974(9)	1.961(8)	1.999(8)	2.000(7)	1.997(2)
Fe1–cp	1.710(5)	1.731(4)	1.715(5)	1.723(5)	1.727(1)
C1–O1	1.165(13)	1.135(12	1.144(11)	1.155(12	1.146(3)
C8–C9	1.310(14)	1.351(15	1.307(12)	1.331(13	1.343(3)
bond angle (deg)					
C1–Fe1–C7	92.9(4)	92.7(5)	92.6(4)	92.6(4)	95.15(11)
C1–Fe1–N1	94.5(5)	93.8(4)	94.1(4)	93.4(4)	94.59(9)
C7–Fe1–N1	89.7(4)	90.0(4)	88.9(9)	90.0(3)	87.81(8)
C1–Fe1–cp	121.5(4)	125.6(5)	124.0(4)	124.0(4)	122.87(9)
C7–Fe1–cp	125.3(4)	123.8(4)	125.1(4)	125.5(4)	125.23(8)
N1–Fe1–cp	123.8(3)	121.7(3)	122.7(3)	122.0(3)	122.13(7)

a) estimated standard deviations in parentheses; cp denotes centroid position of cp ring; b) labelling scheme adapted to molecule 1.

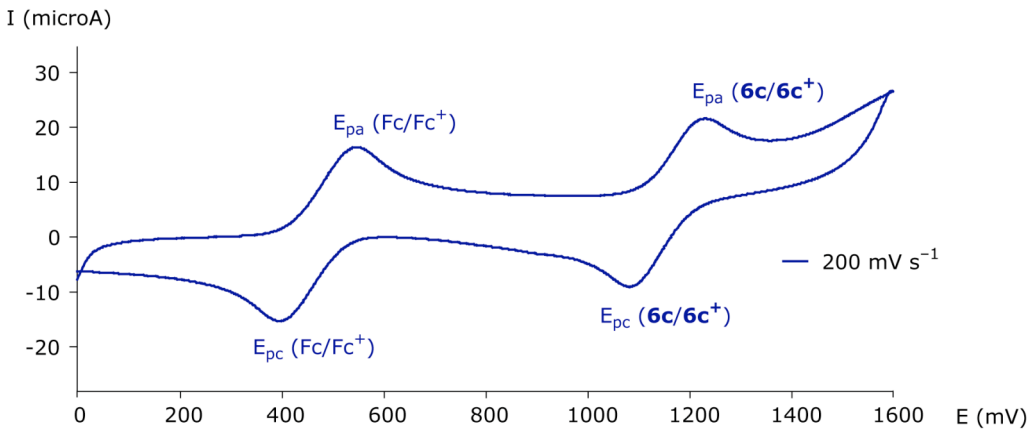
Table S4. Crystallographic Data for 3b, 5c, 8a, 8b, and 8c

	3b	5c	8a	8b	8c
color, shape	yellow plate	green plate	yellow block	orange rod	orange plate
crystal size /mm	0.50×0.30×0.10	0.30×0.25×0.15	0.45×0.40×0.35	0.45×0.20×0.20	0.50×0.27×0.15
empirical formula	$C_{16}H_{21}BF_4FeN_2O_2$	$C_{31}H_{34}Cl_3FeIN_4O$	$C_{16}H_{16}FeIN_3O$	$C_{18.375}H_{20.75}Cl_{0.75}FeIN_3O$	$C_{24}H_{24}FeIN_3O$
formula weight	416.01	767.72	449.07	508.97	553.21
T /K	173	173	173	173	173
crystal system	triclinic	monoclinic	orthorhombic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell dimensions					
a /Å	9.0722(11)	10.7751(9)	14.607(3)	6.5664(7)	7.3425(12)
b /Å	10.1558(11)	23.908(3)	17.019(5)	18.2658(19)	12.434(3)
c /Å	10.2117(10)	13.0755(11)	13.356(3)	18.5978(19)	13.988(2)
α /deg	89.614(13)	90	90	90.350(12)	67.109(16)
β /deg	79.026(13)	93.870(6)	90	96.867(12)	81. 442(13)
γ /deg	76.716(13)	90	90	92.036(12)	72.819(15)
V /Å^3	898.27(17)	3360.8(5)	3320.3(14)	2213.1(4)	1123.2(4)
Z	2	4	8	4	2
D_{calc} /g cm^{-3}	1.538	1.517	1.797	1.528	1.636
μ (Mo Kα) /mm^{-1}	0.891	1.636	2.772	2.177	2.066
rflcns total, unique	7147, 3270	24604, 6094	11108, 5268	17370, 8021	21864, 6049
R_{int}	0.0658	0.0820	0.0609	0.0696	0.0486
transmission factrs					
min., max.	---	0.729, 0.880	0.402, 0.500	0.603, 0.639	0.627, 0.831
param., restraints	239, 0	385, 0	399, 1	461, 4	274, 0
R_1,[a] wR_2 [b]	0.037, 0.079	0.050, 0.109	0.046, 0.103	0.056, 0.144	0.031, 0.065
S [c]	0.860	0.907	0.927	0.841	1.025
residual density					
min., max. /e Å^{-3}	–0.662, 0.544	–0.833, 0.774	-1.261, 0.668	–1.533, 2.364	–0.894, 0.817

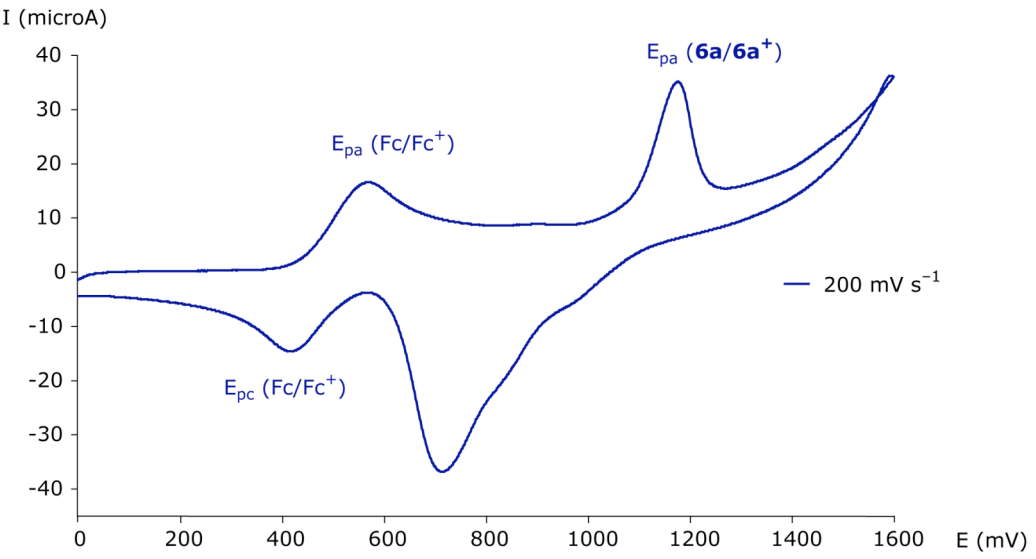
[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$ for all $I > 2\sigma(I)$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$; [c] Flack parameter 0.01(4) for **8a**.

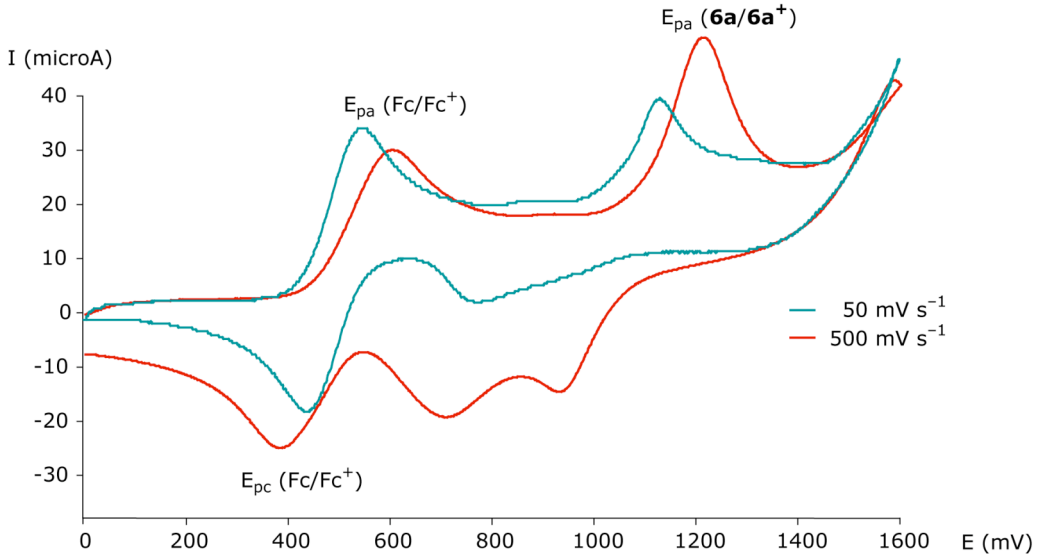
Representative cyclic voltammograms:

CV of **6c**



CV of **6a**





DFT calculations:

Table S5. Most important structural parameters of the geometry optimization.[a)]

	Fe-cp	Fe-CO	Fe-NHC	Fe-py
A	1.754	1.801	---	---
B	1.755	1.778	---	2.014
C	1.757	1.771	1.952	---
D	1.764	1.746	---	2.018
E	1.762	1.753	1.943	2.000
F	1.768	1.732	1.932	---

a) values in Å, cp denotes the centroid position of the cp ring.

Table S6. Calculated and measured IR spectroscopic data of $[Fe(cp)(CO)LL']^+$ species.[a)]

entry	structure	L, L'	ν (CO) calc	ν (CO) meas	reference
1	**A**	CO, CO	2088, 2115	2079, 2125	[1]
2	**B**	CO, pyr	2048, 2073	2025, 2070	[2]
3	**C**	CO, NHC	2033, 2058	2002, 2050	this work, **3b**
4	**D**	pyr, pyr	2018	1990	[2] (L,L' = bpy)
5	**E**	pyr, NHC	2011	1964	this work, **9a**
6	**F**	NHC, NHC	1981	1950	this work, **6a**

a) values in cm^{-1}; ν (CO) calc are scaled by a factor of 0.953.

Table S7. Calculated d-orbital energies E_d for the cations A–F (see also Fig. 6).[a)]

E_d	**A**	**B**	**C**	**D**	**E**	**F**
occ.	–12.61	–11.25	–10.06	–10.10	–8.71	–8.67
occ.	–11.76	–10.26	–9.68	–8.90	–8.51	–8.54
occ.	–11.34	–9.91	–9.58	–8.77	–8.08	–8.00
vir.	–7.75	–6.89	–6.29	–6.00	–5.76	–5.08
vir.	–6.57	–6.17	–6.25	–5.77	–5.71	–5.05

a) values in eV.

Table S8. Total bonding energies and Cartesian coordinates of structures A-F.

cation	bonding energy (a.u.)	atom	coordinates (Å)		
			x	y	z
A	-4.073832	Fe	-0.00663800	0.02726900	0.00000000
		C	-1.08374700	-0.56292400	1.31773200
		O	-1.77027800	-0.91700400	2.16672400
		C	-1.08374700	-0.56292400	-1.31773200
		O	-1.77027800	-0.91700400	-2.16672400
		C	0.99242500	-1.47131000	0.00000000
		O	1.64191600	-2.41748100	0.00000000
		H	-1.03005400	2.38203600	-1.34851900
		C	-0.22157600	2.03068500	-0.71174200
		C	1.03142300	1.48353500	-1.15967300
		H	-1.03005400	2.38203600	1.34851900
		H	1.34485300	1.35864300	-2.19289600
		C	1.80390800	1.16607600	0.00000000
		H	2.80452500	0.73957700	0.00000000
		C	1.03142300	1.48353500	1.15967300
		H	1.34485300	1.35864300	2.19289600
		C	-0.22157600	2.03068500	0.71174200
B	-6.101937	Fe	0.06652700	0.00905500	0.00000000
		C	-1.13091700	0.02065700	1.31607000
		O	-1.90756600	-0.03858500	2.16863400
		C	-1.13091700	0.02065700	-1.31607000
		O	-1.90756600	-0.03858500	-2.16863400
		H	2.99865900	0.44527200	0.00000000
		C	2.22503000	-0.31605700	0.00000000
		C	1.64152000	-0.89482400	-1.16013500
		H	1.89292100	-0.66714500	2.19231000
		H	1.89292100	-0.66714500	-2.19231000
		C	0.69071600	-1.87988000	-0.71166500
		H	0.08353200	-2.52000900	-1.34665600
		C	0.69071600	-1.87988000	0.71166500
		H	0.08353200	-2.52000900	1.34665600
		C	1.64152000	-0.89482400	1.16013500
		N	0.15404800	2.05870600	0.00000000
		C	-1.01124000	2.75965400	0.00000000
		C	1.30244900	2.77898200	0.00000000
		C	-1.06329400	4.14824600	0.00000000

cation	bonding energy (a.u.)	atom	coordinates (Å)		
			x	y	z
		H	-1.93185300	2.18028700	0.00000000
		C	1.32710600	4.17034800	0.00000000
		H	2.23240400	2.22384000	0.00000000
		C	0.12611400	4.87801900	0.00000000
		H	-2.03544000	4.64021100	0.00000000
		H	2.28969600	4.68111300	0.00000000
		H	0.11668600	5.96834600	0.00000000
C	-6.101936	Fe	-0.00224900	-0.04683900	0.00000000
		H	-0.41709300	-2.97155200	0.00000000
		C	0.32982900	-2.18072400	0.00000000
		C	0.91887100	-1.60240600	1.15912400
		H	0.68901300	-1.84713000	-2.19258700
		H	0.68901300	-1.84713000	2.19258700
		C	1.91047800	-0.65803000	0.71090000
		H	2.54957700	-0.05303000	1.34725700
		C	1.91047800	-0.65803000	-0.71090000
		H	2.54957700	-0.05303000	-1.34725700
		C	0.91887100	-1.60240600	-1.15912400
		C	-0.11103000	1.14257600	-1.30648300
		O	-0.16084800	1.91848600	-2.16259100
		C	-0.11103000	1.14257600	1.30648300
		O	-0.16084800	1.91848600	2.16259100
		C	-1.95618500	-0.24038300	0.00000000
		N	-2.73630300	-1.35601600	0.00000000
		C	-4.09504200	-1.05743600	0.00000000
		C	-4.18095300	0.29848500	0.00000000
		N	-2.87424200	0.76700300	0.00000000
		H	-2.36326800	-2.29603100	0.00000000
		H	-4.86219200	-1.82102000	0.00000000
		H	-5.03989600	0.95733200	0.00000000
		H	-2.62389800	1.75059100	0.00000000
D	-8.126085	Fe	-0.92936000	0.05993000	0.03114500
		C	-1.12567700	1.79425400	0.03853000
		O	-1.35793800	2.93803300	0.04304400
		H	-3.64282300	0.92325800	0.09759900
		C	-3.02961000	0.02602900	0.06973400

cation	bonding energy (a.u.)	atom	coordinates (Å)		
			x	y	z
		C	-2.52768100	-0.67707200	1.20930200
		H	-2.79030800	-0.34773700	-2.13766800
		H	-2.70642100	-0.42479300	2.25063900
		C	-1.80625200	-1.81774200	0.71975800
		H	-1.31247000	-2.56363400	1.33699600
		C	-1.83396900	-1.79237700	-0.69235700
		H	-1.36130800	-2.51319200	-1.35439300
		C	-2.57253100	-0.63666800	-1.11350600
		N	0.48070700	0.03791900	-1.41256600
		C	1.19247700	-1.08777500	-1.67536700
		C	0.74524500	1.12292300	-2.18604500
		C	2.15137800	-1.17107900	-2.68001700
		H	0.97504200	-1.95453900	-1.05680500
		C	1.69266600	1.11718100	-3.20458000
		H	0.17118800	2.02213200	-1.97813500
		C	2.41423100	-0.04826900	-3.46553100
		H	2.67978900	-2.11132200	-2.83564600
		H	1.85274200	2.02739800	-3.78198500
		H	3.16067500	-0.08111700	-4.25966300
		N	0.50220300	0.02446100	1.45333300
		C	1.21962700	-1.10278400	1.69265900
		C	0.77408300	1.10030800	2.23699700
		C	2.19162900	-1.19667600	2.68398100
		H	0.99684900	-1.96171400	1.06535900
		C	1.73465000	1.08375100	3.24333200
		H	0.19521700	2.00057600	2.04776100
		C	2.46196700	-0.08339600	3.48024800
		H	2.72388500	-2.13781100	2.82074000
		H	1.90021700	1.98665300	3.83056100
		H	3.21837200	-0.12464200	4.26457800
E	-7.643105	Fe	-0.10125300	-0.59452000	-0.52176000
		C	-0.42692200	-1.90487100	0.59594100
		O	-0.63880000	-2.82268500	1.28172400
		H	1.94280000	-1.02328000	-2.52703800
		C	0.87210000	-0.91197200	-2.37921600
		C	0.14986000	0.32277700	-2.44941100
		H	0.18128000	-3.02239800	-2.05199600

cation	bonding energy (a.u.)	atom	coordinates (Å)		
			x	y	z
		H	0.57225300	1.29808700	-2.67217200
		C	-1.23437500	0.01316400	-2.25924700
		H	-2.04878800	0.73342700	-2.23182500
		C	-1.37248500	-1.38432900	-2.06608300
		H	-2.30206400	-1.92257900	-1.90450200
		C	-0.05533300	-1.96514600	-2.13953300
		N	-1.02195300	0.83707900	0.52659400
		C	-2.41373300	2.90906800	1.84101000
		C	-1.96637300	0.57131900	1.46825500
		C	-0.77645400	2.14807100	0.24960500
		C	-1.44826100	3.19503800	0.87242400
		C	-2.66750300	1.56915500	2.13953600
		H	-2.15634100	-0.47840000	1.67903200
		H	-0.00835700	2.33849600	-0.49680100
		H	-1.20557200	4.22105200	0.59622100
		H	-3.40621000	1.28371400	2.88830200
		H	-2.95092700	3.70931000	2.35081700
		C	1.57509900	-0.22111300	0.38552800
		N	2.80081800	-0.79025900	0.18771100
		C	3.76285900	-0.31339400	1.07115900
		C	3.12977900	0.59333500	1.86132900
		N	1.81038100	0.62817300	1.42709400
		H	4.79211600	-0.64864000	1.05744100
		H	3.49708500	1.20616300	2.67470100
		H	1.08190300	1.20224500	1.83787100
		H	2.96120700	-1.52127000	-0.49437900
F	-7.16088	Fe	-0.28555900	0.62646400	0.00000000
		H	1.50610200	1.26887800	-2.19257400
		C	1.28999200	1.51010500	-1.15526600
		C	1.84442100	0.86420100	0.00000000
		H	-0.16779000	3.19490900	-1.36045500
		H	2.62106900	0.10298000	0.00000000
		C	1.28999200	1.51010500	1.15526600
		H	1.50610200	1.26887800	2.19257400
		C	0.40281200	2.52880700	0.71959800
		H	-0.16779000	3.19490900	1.36045500
		C	0.40281200	2.52880700	-0.71959800

cation	bonding energy (a.u.)	atom	coordinates (Å)		
			x	y	z
		C	-1.95688400	1.07954700	0.00000000
		O	-3.09293500	1.36995200	0.00000000
		C	-0.56392000	-0.70366300	1.37374200
		C	-0.20652000	-2.33156100	2.95589100
		C	-1.53476600	-2.04590800	2.96311000
		H	0.37357600	-3.02877100	3.54701200
		H	-2.34448200	-2.44686000	3.55936100
		N	0.35791300	-1.51009400	1.98420900
		H	1.34153300	-1.49647500	1.74598300
		N	-1.72380800	-1.06322300	1.99864300
		H	-2.61406300	-0.62097600	1.79597600
		H	-2.61406300	-0.62097600	-1.79597600
		H	1.34153300	-1.49647500	-1.74598300
		H	-2.34448200	-2.44686000	-3.55936100
		H	0.37357600	-3.02877100	-3.54701200
		C	-1.53476600	-2.04590800	-2.96311000
		C	-0.20652000	-2.33156100	-2.95589100
		C	-0.56392000	-0.70366300	-1.37374200
		N	-1.72380800	-1.06322300	-1.99864300
		N	0.35791300	-1.51009400	-1.98420900

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