Supplementary Information

Ammonium and Phosphonium Salts Containing Monoanionic Iron(II) Half-Sandwich Complexes $[Fe(\eta^5\text{-}Cp^*)X_2]^-$ (X = Cl – I)

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Table S1. X-ray crystallographic details.

	N*n*Pr$_4$[Fe(η^5-Cp*)Cl$_2$]	N*n*Pr$_4$[Fe(η^5-Cp*)BrCl]	N*n*Pr$_4$[Fe(η^5-Cp*)Br$_2$]	PPh$_4$[Fe(η^5-Cp*)Cl$_2$]	PPh$_4$[Fe(η^5-Cp*)Br$_2$]	PPh$_4$[Fe(η^5-Cp*)I$_2$]	[Fe(η^5-Cp*)Cl(CO)$_2$]
Empirical formula	$C_{22}H_{43}Cl_2FeN$	$C_{22}H_{43}BrClFeN$	$C_{22}H_{43}Br_2FeN$	$C_{34}H_{35}Cl_2FeP$	$C_{34}H_{35}Br_2FeP$	$C_{34}H_{35}FeI_2P$	$C_{12}H_{15}ClFeO_2$
Formula weight	448.32	492.78	537.24	601.34	690.26	784.24	282.54
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	triclinic
Space group	*P*-1	*P*-1	*Pca*2$_1$	*Pna*2$_1$	*Pnma*	*Pnma*	*P*-1
a/Å	8.5399(4)	8.526(2)	34.9997(10)	29.237(7)	29.7108(15)	30.170(2)	7.4528(16)
b/Å	12.3334(5)	12.334(2)	12.6237(4)	7.5015(9)	14.0744(7)	14.3281(14)	7.6886(16)
c/Å	14.2796(6)	14.310(3)	23.2128(7)	14.075(4)	7.4002(3)	7.4587(5)	11.905(4)
α/°	69.433(3)	69.577(13)	90	90	90	90	79.38(2)
β/°	79.375(3)	79.840(17)	90	90	90	90	78.75(2)
γ/°	86.175(3)	85.489(18)	90	90	90	90	69.59 0(16)
Volume/Å^3	1384.00(11)	1388.0(5)	10256.0(5)	3087.0(13)	3094.5(3)	3224.3(4)	622.0(3)
Z	2	2	16	4	4	4	2
ρ_{calcd}/g cm^{-3}	1.076	1.179	1.392	1.294	1.482	1.616	1.509
μ/mm^{-1}	6.165	2.085	8.390	6.147	3.143	2.453	1.408
F(000)	484.0	520.0	4448.0	1256.0	1400.0	1544.0	292.0
Crystal size/mm^3	0.12 × 0.09 × 0.02	0.18 × 0.13 × 0.05	0.15 × 0.07 × 0.02	0.23 × 0.14× 0.04	0.45 × 0.21 × 0.07	0.22 × 0.11 × 0.04	0.15 × 0.08 × 0.03
Radiation used	Cu Kα (λ = 1.54186)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54186)	Cu Kα (λ = 1.54186)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.712 to 143.33	3.076 to 51.752	5.05 to 143.418	6.046 to 140.404	3.986 to 51.134	3.92 to 51.61	3.516 to 51.478
Index ranges	−5 ≤ *h* ≤ 10 −14 ≤ *k* ≤ 15 −16 ≤ *l* ≤ 17	−10 ≤ *h* ≤ 10 −13 ≤ *k* ≤ 15 −17 ≤ *l* ≤ 17	−22 ≤ *h* ≤ 41 −11 ≤ *k* ≤ 15 −28 ≤ *l* ≤ 27	−31 ≤ *h* ≤ 35 −9 ≤ *k* ≤ 4 −16 ≤ *l* ≤ 16	−30 ≤ *h* ≤ 35 −17 ≤ *k* ≤ 14 −8 ≤ *l* ≤ 7	−36 ≤ *h* ≤ 32 −15 ≤ *k* ≤ 17 −7 ≤ *l* ≤ 9	−7 ≤ *h* ≤ 8 −9 ≤ *k* ≤ 9 −14 ≤ *l* ≤ 14
Refl. collected	11462	9633	60397	14812	6839	8493	4139
Independent refl.	5213 [R_{int} = 0.0403]	5258 [R_{int} = 0.0561]	19487 [R_{int} = 0.0534]	5553 [R_{int} = 0.0412]	2951 [R_{int} = 0.0354]	3182 [R_{int} = 0.0261]	2312 [R_{int} = 0.0653]
Data/restr./param.	5213/0/244	5258/2/251	19487/135/936	5553/1/348	2951/2/197	3182/2/199	2312/0/150
Goodness-of-fit on F^2	1.045	1.020	1.566	1.052	1.144	1.078	1.028
Final *R* indexes [*I*>2σ (*I*)]	R_1 = 0.0488 wR_2 = 0.1261	R_1 = 0.0626 wR_2 = 0.1278	R_1 = 0.1434 wR_2 = 0.3794	R_1 = 0.0453 wR_2 = 0.1047	R_1 = 0.0518 wR_2 = 0.1344	R_1 = 0.0348 wR_2 = 0.0949	$R1$ = 0.0665 $wR2$ = 0.1597
Final *R* indexes [all data]	R_1 = 0.0618 wR_2 = 0.1355	R_1 = 0.1001 wR_2 = 0.1459	R_1 = 0.1974 wR_2 = 0.4676	R_1 = 0.0584 wR_2 = 0.1132	R_1 = 0.0626 wR_2 = 0.1425	R_1 = 0.0417 wR_2 = 0.0980	$R1$ = 0.0947 $wR2$ = 0.1815
Largest diff. peak/hole / e Å^{-3}	0.34/−0.52	0.50/−0.51	2.65/−0.99	0.40/−0.36	1.14/−0.58	1.35/−1.03	0.52/−1.31
Flack parameter			0.29(3)	−0.003(8)			
CCDC No.	2300615	2300616	2300617	2300618	2300619	2300620	2300621

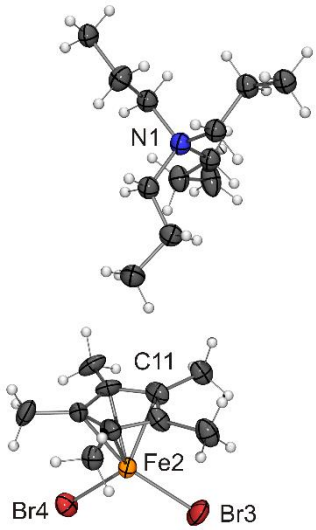

Figure S1. Molecular structure of N*n*Pr$_4$[Fe(η^5-Cp*)Br$_2$] in the crystal (ORTEP with 50% probability ellipsoids). The asymmetric unit contains four anions and four cations. Only one each is shown.

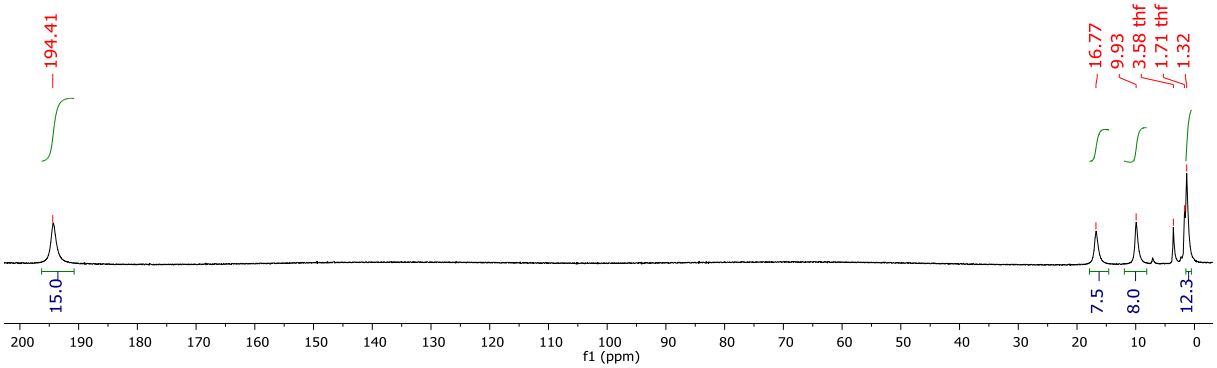

Figure S2. ^{1}H NMR spectrum (400 MHz, THF-d_8) of N*n*Pr$_4$[Fe(η^5-Cp*)Cl$_2$].

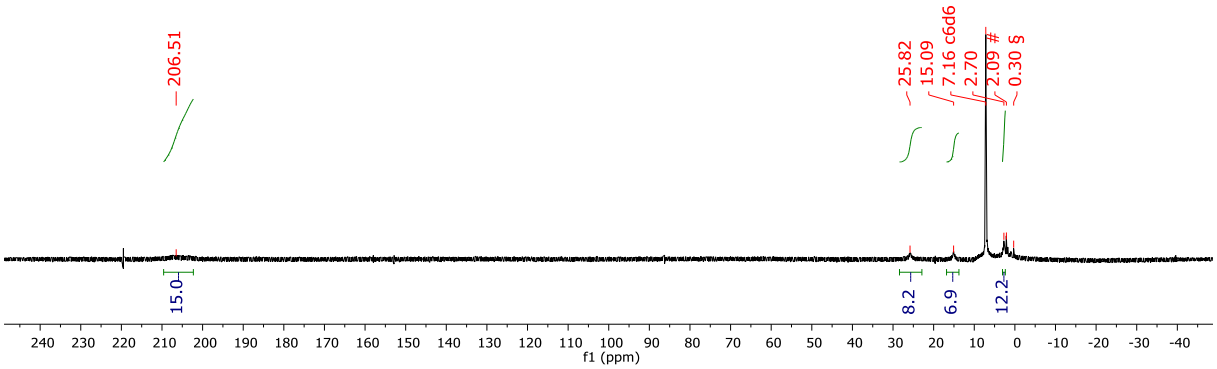

Figure S3. ^{1}H NMR spectrum (400 MHz, THF-d_8) of N*n*Pr$_4$[Fe(η^5-Cp*)BrCl]. Signals marked belong to small amounts of decamethylferrocene (#) and silicone grease (§).

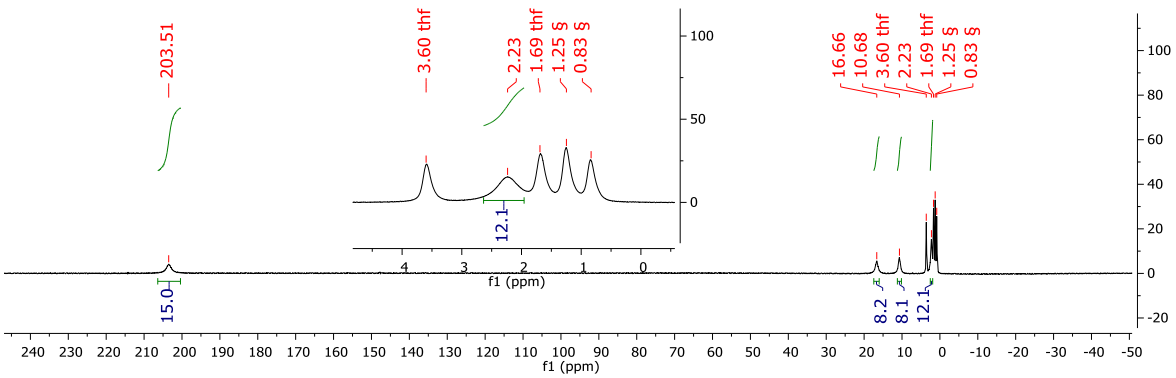

Figure S4. ^{1}H NMR spectrum (400 MHz, THF-d_8) of N*n*Pr$_4$[Fe(η^5-Cp*)Br$_2$]. Signals marked belong to residual *n*-hexane (§).

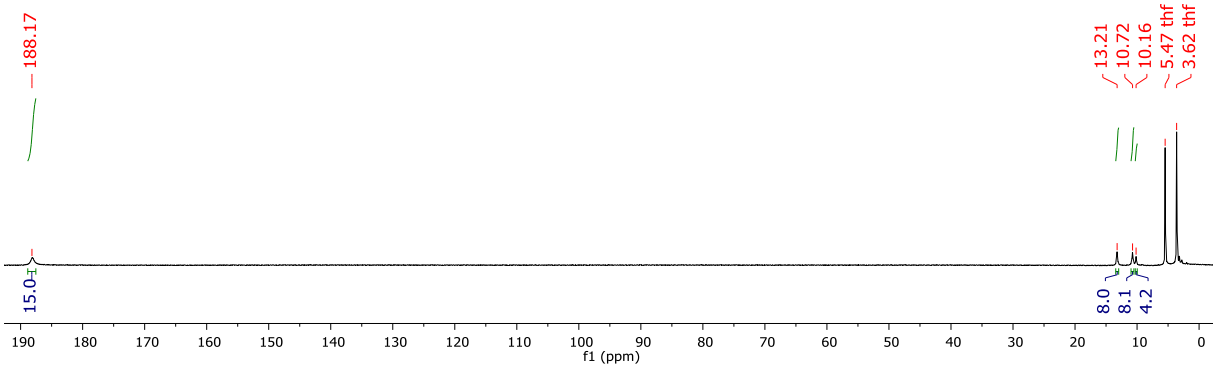

Figure S5. ^{1}H NMR spectrum (500 MHz, THF-d_8) of $PPh_4[Fe(\eta^5\text{-}Cp^*)Cl_2]$.

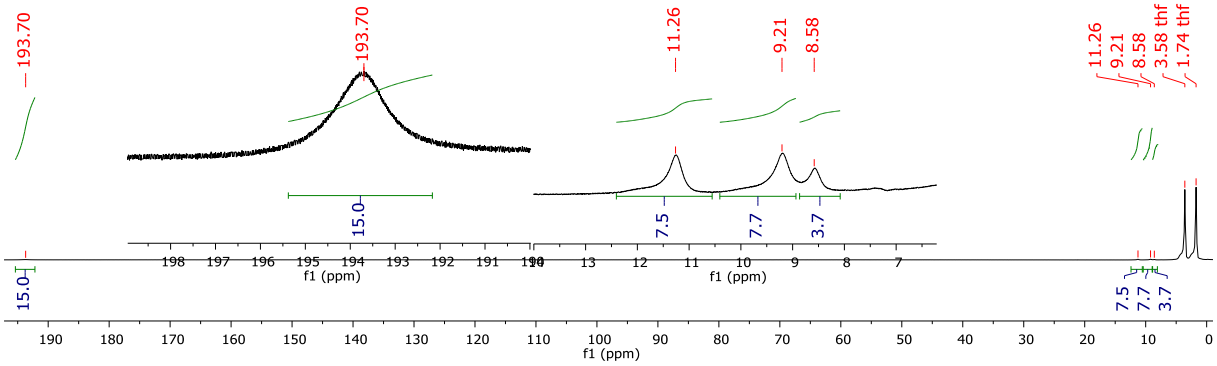

Figure S6. ^{1}H NMR spectrum (500 MHz, THF-d_8) of $PPh_4[Fe(\eta^5\text{-}Cp^*)Br_2]$.

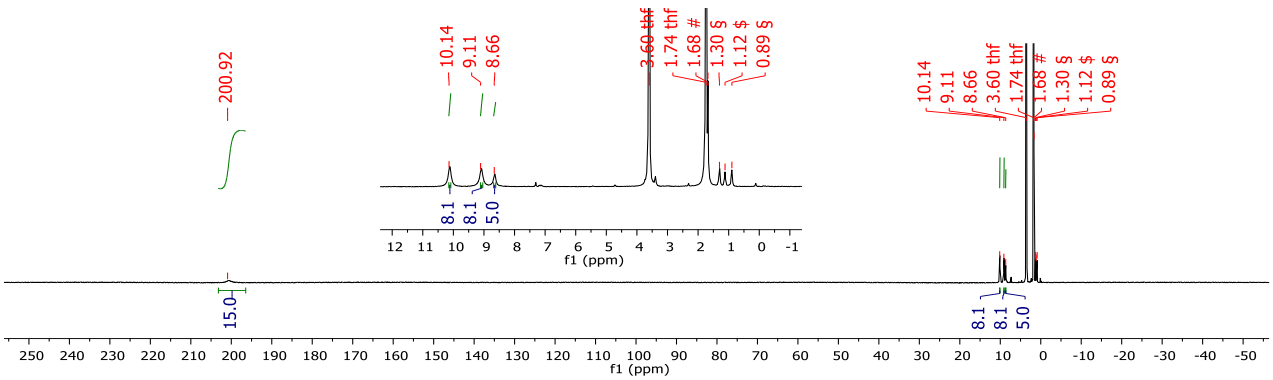

Figure S7. ^{1}H NMR spectrum (500 MHz, THF-d_8) of $PPh_4[Fe(\eta^5\text{-}Cp^*)I_2]$. Signals marked belong to residual n-hexane (§), decamethylferrocene (#) and an unknown impurity ($).

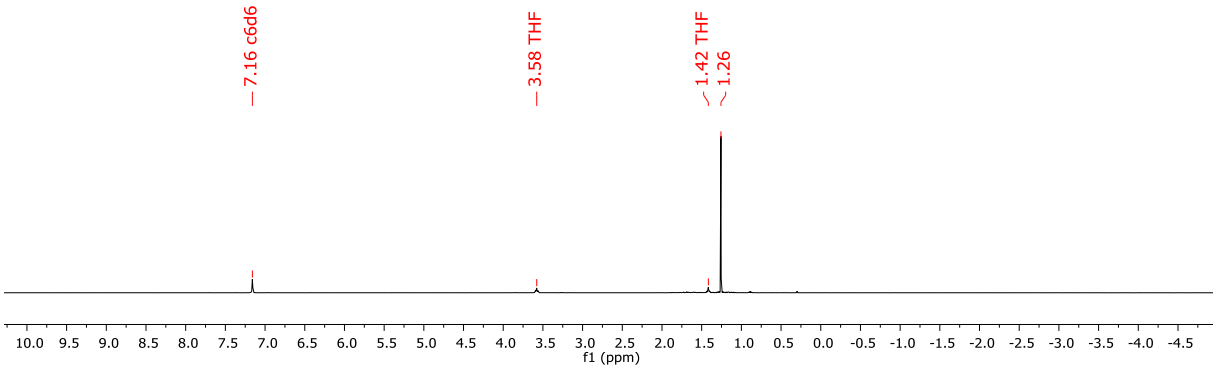

Figure S8. ^{1}H NMR spectrum (400 MHz, C_6D_6) of [Fe(η^5-Cp*)Cl(CO)$_2$].

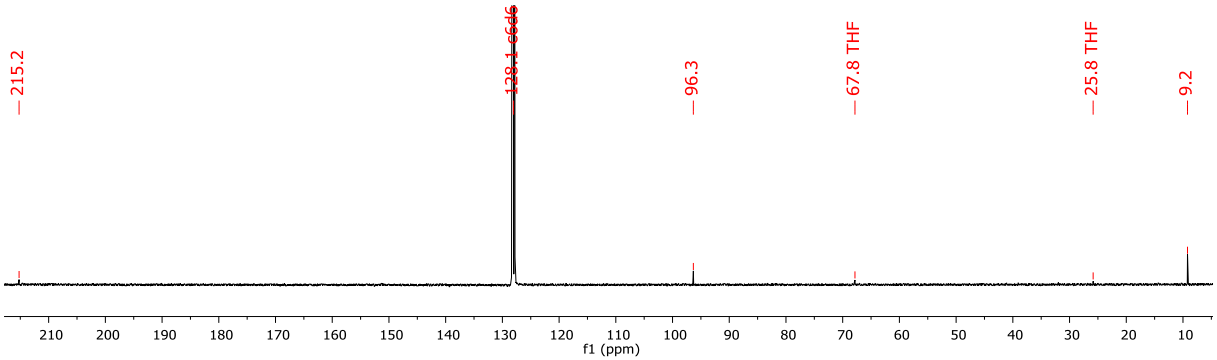

Figure S9. ^{13}C NMR spectrum (101 MHz, C_6D_6) of [Fe(η^5-Cp*)Cl(CO)$_2$].