Supplementary Information

Ammonium and Phosphonium Salts Containing Monoanionic Iron(II) Half-Sandwich Complexes [Fe(η5-Cp\*)X2]− (X = Cl – I)

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**Table S1.** X-ray crystallographic details.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | sv1190  N*n*Pr4[Fe(η5-Cp\*)Cl2] | i3202  N*n*Pr4[Fe(η5-Cp\*)BrCl] | sv1445  N*n*Pr4[Fe(η5-Cp\*)Br2] | sv1442  PPh4[Fe(η5-Cp\*)Cl2] | i3435  PPh4[Fe(η5-Cp\*)Br2] | i3446  PPh4[Fe(η5-Cp\*)I2] | i3467  [Fe(η5-Cp\*)Cl(CO)2] |
| Empirical formula | C22H43Cl2FeN | C22H43BrClFeN | C22H43Br2FeN | C34H35Cl2FeP | C34H35Br2FeP | C34H35FeI2P | C12H15ClFeO2 |
| 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*21 | *Pna*21 | *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/Å3 | 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/mm3 | 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) |
| 2*θ* 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*>2*σ* (*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 | *R*1 = 0.0665  *wR*2 = 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 | *R*1 = 0.0947  *wR*2 = 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*Pr4[Fe(η5-Cp\*)Br2] in the crystal (ORTEP with 50% probability ellipsoids). The asymmetric unit contains four anions and four cations. Only one each is shown.



**Figure S2.** 1H NMR spectrum (400 MHz, THF-*d*8) of N*n*Pr4[Fe(η5-Cp\*)Cl2].



**Figure S3.** 1H NMR spectrum (400 MHz, THF-*d*8) of N*n*Pr4[Fe(η5-Cp\*)BrCl]. Signals marked belong to small amounts of decamethylferrocene (#) and silicone grease (§).



**Figure S4.** 1H NMR spectrum (400 MHz, THF-*d*8) of N*n*Pr4[Fe(η5-Cp\*)Br2]. Signals marked belong to residual *n*-hexane (§).



**Figure S5.** 1H NMR spectrum (500 MHz, THF-*d*8) of PPh4[Fe(η5-Cp\*)Cl2].



**Figure S6.** 1H NMR spectrum (500 MHz, THF-*d*8) of PPh4[Fe(η5-Cp\*)Br2].



**Figure S7.** 1H NMR spectrum (500 MHz, THF-*d*8) of PPh4[Fe(η5-Cp\*)I2]. Signals marked belong to residual n-hexane (§), decamethylferrocene (#) and an unknown impurity ($).



**Figure S8.** 1H NMR spectrum (400 MHz, C6D6) of [Fe(η5-Cp\*)Cl(CO)2].



**Figure S9.** 13C NMR spectrum (101 MHz, C6D6) of [Fe(η5-Cp\*)Cl(CO)2].