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Supporting Information

Figure S1. The β electron orbital for each of the five complexes [Fe(PN-iPr)Cl₂ (5a), [Fe(SN-iPr)Cl₂ (8a), [Fe(SeN-iPr)Cl₂ (9), [Fe(ON-iPr)₂Cl]Cl (7a), and [Fe(ON-iPr)₂Br]Br (7b)
**Figure S2.** Difference absorbance UV-Vis spectrum of [Fe(PN-iPr)Br$_2$] (5b) in CO-saturated CH$_2$Cl$_2$ at -50 °C ($\lambda_{\text{max}}$ = 584 nm).

**Figure S3.** Structural diagram of [Fe(PN-iPr)Br$_2$] (5b) showing 50% displacement ellipsoids. Selected distances and angles (Å, °): Fe1–N1 2.0995(14), Fe1–P1 2.4277(6), Fe1–Br1 2.3643(4), Fe1–Br2 2.3974(4), P1–N2 1.702(2), N2–C1 1.379(2), N1–Fe1–P1 80.74(4), N1–Fe1–Br1 110.86(4), N1–Fe1–Br2 105.71(4), P1–Fe1–Br1 121.97(2), P1–Fe1–Br2 110.86(2), Br1–Fe1–Br2 118.80(2), Fe1–P1–N2 96.22(5), P1–P1–C1 122.9(1), N1–C1–N2–P1 8.8(2), C1–N2–P1–Fe1 4.0(2); hydrogen bond N2···Br2 3.429(2) not shown. [Fe(PN-iPr)Br$_2$] (5b) is not isostructural with the chloride homologue [Fe(PN-iPr)Cl$_2$] (5a).
**Figure S4.** Structural diagram of [Fe(PN-tBu)Cl₂] (6a) showing 50% displacement ellipsoids. Selected distances and angles (Å, °): Fe1–N1 2.0978(12), Fe1–P1 2.4249(4), Fe1–Cl1 2.2624(4), Fe1–Cl2 2.2336(4), P1–N2 1.7032(13), N2–C1 1.3848(17), N1–Fe1–P1 80.39(4), N1–Fe1–Cl1 111.17(4), N1–Fe1–Cl2 108.57(4), P1–Fe1–Cl1 112.53(2), P1–Fe1–Cl2 122.79(2), Cl1–Fe1–Cl2 115.37(2), Fe1–P1–N2 97.71(4), P1–N2–C1 121.74(10), N1–C1–N2–P1 7.14(18), C1–N2–P1–Fe1 -7.49(12); hydrogen bond N2···Cl1 3.314(1) not shown.

**Figure S5.** Structural diagram of [Fe(SN-iPr)Br₂] (8b) showing 50% displacement ellipsoids. Selected distances and angles (Å, °): Fe1–N1 2.121(2), Fe1–S 1.9934(7), Fe1–Br1 2.4264(4), Fe1–Br2 2.3887(4), P1–S1 1.9934(7), P1–N2 1.682(2), N2–C1 1.398(2), N1–Fe1–S1 104.19(5), N1–Fe1–Br1 100.91(5), N1–Fe1–Br2 106.32(5), S1–Fe1–Br1 113.11(2), S1–Fe1–Br2 112.78(29), Br1–Fe1–Br2 117.57(2), Fe1–S1–P1 99.88(2), S1–P1–N2 114.36(7), N1–C1–N2–P1 40.9(3), C1–N2–P1–S1 67.1(2), N2–P1–S1–Fe1 34.25(7); hydrogen bond N2···Br1 3.444(2) not shown, the hydrogen atom bonded to N2 is hidden behind N2. Compounds [Fe(SN-iPr)Cl₂] (8a), [Fe(SN-iPr)Br₂] (8b), and [Fe(SeN-iPr)Cl₂] (9) form an isostructural series.
**Figure S6.** Packing diagram of [Fe(PN-iPr)$_2$(CO)Cl]Cl.solv (10a), which crystallizes in the tetragonal space group $I ar{4}$ (no. 82) and features hydrogen bonded cyclic tetramers (dashed lines) of [Fe(PN-iPr)$_2$(CO)Cl]$^+$ cations and chloride anions (green dots). Disordered solvent is located in channels parallel to $z$ at $x,y = 0,0; 1/2,0; $ etc.