

Supplementary Material

Synthesis

The synthesis of the iron complexes was performed with commercially available HPLC grade solvents, which were used as supplied. Absolute ethanol was dried by refluxing over magnesium ethanolat under an argon atmosphere for 3 days. Triethylamine (NEt_3) was distilled under argon and stored over 4 Å sieves. The C, H, N, elemental analyses were carried out in triplicate for each sample on an Elementar Vario Micro elemental analyzer. The individual values did not differ by more than ± 0.3 . The mean C, H, N values are given below for each compound. The chlorine analyses were conducted by means of the sodium peroxide fusion method in a nickel microbomb followed by potentiometric titration with AgNO_3 using a Metrohm DMP-Titrino 785 device. IR spectra were recorded between 400 cm^{-1} and 4000 cm^{-1} on a Nicolet 380 FT-IR spectrometer using potassium bromide pellets made from $\sim 200\text{ mg}$ of dry KBr and $\sim 2\text{ mg}$ of the sample. KBr was predried upon heating at $110\text{ }^\circ\text{C}$ in an oven. ESI mass spectra were recorded on a Q/TOF mass spectrometer (microTOF-Q, Bruker Daltonics, Bremen) and externally calibrated with sodium formiate.

The present study required substantial amounts of compound **[1]** PF_6 in analytically pure form. Therefore, the synthesis of **[1]** PF_6 and its precursor, $[\text{FeCl}(\text{cyclam-ac})]\text{PF}_6$, were modified.^[14, 36-37] The procedures described below are simple and provide the two complexes in considerably higher yield.. The ligand 1,4,8,11-tetraazacyclotetradecane-1-acetic acid tetrahydrochloride (cyclam-AcH $\cdot$ 4HCl) was prepared following the method published in ref.^[38] The ligand was found by C, H, N and Cl analysis to contain 1.5 water molecules per formula unit.

$[\text{FeCl}(\text{cyclam-ac})]\text{PF}_6$. To a suspension of 500 mg (1.16 mmol) of cyclam-AcH $\cdot$ 4HCl $\cdot$ 1.5H $_2\text{O}$ in 15 mL of absolute ethanol, was added 0.8 mL (5.8 mmol) of triethylamine under argon atmosphere. After 5 min of stirring at room temperature (RT) a clear, colourless solution was obtained, which was then transferred under argon to a Schlenk tube containing 188 mg (1.16 mmol) of anhydrous FeCl_3 . After stirring for 5 min at RT a clear, brown/orange solution was obtained, which was heated to 50°C and kept at this temperature for 2 h . The reaction solution was then cooled to RT, and a solution of 378 mg (2.32 mmol) of NH_4PF_6 in 5 mL of absolute ethanol was added. A part of the product precipitated out as a red solid. The Schlenk tube was stored at 4°C for 12 h to complete precipitation. The red precipitate was separated from the orange mother liquor by filtration, washed with absolute ethanol ($3 \times 3\text{ mL}$), and diethyl ether ($2 \times 3\text{ mL}$) and finally dried under vacuum ($\sim 10^{-2}\text{ mbar}$) for 2 h . The product is stable in air. Yield: 500 mg (1.01 mmol , 87%). Elemental analysis calcd (%) for

$C_{12}H_{25}ClF_6FeN_4O_2P$ (493.61): C 29.20, H 5.10, N 11.35, Cl 7.18; found: C 29.06, H 4.89, N 11.65, Cl 7.67%. MS, (ESI positive, acetonitrile): m/z = 348.1 $[M - PF_6]^+$, 312.1 $[M - PF_6 - HCl]^+$. MS (ESI negative, acetonitrile): m/z = 145.0 $(PF_6)^-$. IR (KBr, cm^{-1}): ν = 3432 (m, br), 3261 (s), 3202 (m), 2981 (m), (2961 (m), 2934 (m), 2905 (m), 2879 (m), 1683 (vs, sh, $\nu(C=O)$) 1669 (vs, $\nu(C=O)$), 1466 (m), 1431 (m), 1385 (w), 1345 (m), 1323 (m), 1297 (s), 1243 (w), 1137 (w), 1103 (m, sh), 1096 (m), 1072 (sh), 1064 (m), 1040 (sh), 1031 (s), 969 (w), 937 (m), 929 (m), 911 (w), 881 (s), 841 (vs, $\nu(PF_6)$), 814 (s), 743 (w), 558 (s, PF_6), 539 (w), 522 (w), 490 (m), 428 (m), 410 (w).

$[FeN_3(cyclam-ac)]PF_6$ ([1] PF_6). A mixture of 1.046 g (2.12 mmol) of $[FeCl(cyclam-ac)]PF_6$ and 410 mg (6.31 mmol) of NaN_3 was suspended in 80 mL of MeCN and the suspension was stirred at RT for 2h. The red-brown solution was filtered, and the filtrate was evaporated to dryness *in vacuo*. The remaining solid was cooled with an ice bath, washed with methanol (3×1 mL) and diethyl ether (3×3 mL) and dried under vacuum ($\sim 10^{-2}$ mbar) for 1h to give [1] PF_6 as a brown solid. Yield: 830 mg (1.66 mmol, 78%). Elemental analysis calcd (%) for $C_{12}H_{25}F_6FeN_7O_2P$ (500.18): C 28.82, H 5.04, N 19.60; found: C 28.95, 5.00, N 19.53%. MS, (ESI positive, acetonitrile): m/z = 355.2 $[M - PF_6]^+$, 327.2 $[M - PF_6 - N_2]^+$, 312.2 $[M - PF_6 - HN_3]^+$. IR (KBr, cm^{-1}): ν = 3433 (m, br), 3262 (m), 3231 (m), 3209 (m), 2962 (m), 2932 (m), 2882 (m), 2051 (vs, $\nu(N_3)$), 1682 (vs, sh, $\nu(C=O)$) 1663 (vs, $\nu(C=O)$), 1470 (m), 1458 (m), 1435 (m), 1384 (w), 1341 (m), 1328 (m), 1299 (m,sh), 1284 (s), 1256 (m,sh), 1135 (w), 1106 (m,sh), 1095 (s), 1073 (sh), 1064 (m), 1042 (m), 1032 (s), 969 (w), 937 (m), 929 (m), 910 (w), 881 (s), 838 (vs, $\nu(PF_6)$), 812 (s), 740 (m), 559 (s, PF_6), 538 (w), 522 (w), 489 (m), 429 (m), 408 (w).

References:

- 1) W. S. Szulbinski and D. H. Busch, *Inorg. Chim. Acta*, 1995, **234**, 143–148.
- 2) M. Studer and T. A. Kaden, *Helv. Chim. Acta*, 1986, **69**, 2081–2086.