Mendeleev Commun., 1998, 8(4), 143–145

Formation of stable σ-aryliron(III) complexes from the reaction of chloroiron(III) octaphenyltetraazaporphyrinate with aryl Grignard reagents

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Chloro(octaphenyltetraazaporphyrinato)iron(III) [(Cl)Fe^{III}OPTAP] reacts with aryl Grignard reagents (ArMgBr; Ar = phenyl or *p*-tolyl) forming stable low-spin σ-aryliron(III) complexes [(Ar)Fe^{III}OPTAP].

The inactivation of hemoproteins by arylhydrazines includes formation of aryl–iron σ-bonded complexes of heme as intermediates.[1] The structure, physico-chemical properties and reactivity of σ-aryliron(III) complexes of synthetic porphyrins [(Ar)Fe^{III}P; P = OEP (octaethylporphine) or TPP (tetraphenylporphine)] which form in the reaction of iron(III) porphyrins with aryl Grignard reagents under strictly anaerobic conditions[2,3] have been extensively investigated.[4,5] The preparation of σ-aryliron(III) phthalocyanines [(Ar)Fe^{III}Pc] has also been demonstrated,[6–8] but no full report on their synthesis and characterization has appeared since then. Thus σ-phenyliron(III) phthalocyanine (Ph)Fe^{III}Pc was prepared[7,8] by oxidation of σ-phenyliron(II) complex Li[(Ph)Fe^{II}Pc] which in turn forms in the reaction of BrFe^{III}Pc (or Py$_2$Fe^{II}Pc) with phenyllithium.[6] Grignard reagents can not be used in the synthesis of (Ar)Fe^{III}Pc because they reduce iron(III) phthalocyanines to the iron(0) complex ([Fe^{0}Pc]$^{2-}$).[6] Unlike σ-phenyliron(III) phthalocyanine, which was reported to be a stable compound,[7] σ-aryliron(III) porphyrins are easily oxidized in the presence of dioxygen forming μ-oxodiiron(III) or aryloxoiron(III) complexes [μ-O(Fe^{III}P)$_2$ or (PhO)Fe^{III}P][9] and give upon addition of acids HX acidoiron(III) complexes [(X)Fe^{III}P].[2] Thus the stability of the Ar–Fe bond depends strongly on the properties of the macrocyclic ligand. In order to throw some more light on the factors determining the stability of the C–Fe bond we have obtained the σ-phenyliron(III) complex of octaphenyltetraazaporphine, a macrocyclic ligand having an intermediate structure between common porphyrins and phthalocyanine.

σ-Phenyl(octaphenyltetraazaporphyrinato)iron(III) [(Ph)Fe^{III}OPTAP **2**] was obtained by addition of phenylmagnesium bromide (PhMgBr) to a solution of chloro(octaphenyltetraazaporphyrinato)iron(III) [(Cl)Fe^{III}OPTAP **1**][10] in dry benzene in aerobic conditions (Scheme 1). The colour of the solution changed immediately from red-brown to dark blue and then to green. Excess PhMgBr was hydrolyzed with water and the benzene layer (after drying with Na$_2$SO$_4$) was chromatographed on neutral Al$_2$O$_3$. σ-Phenyliron(III) complex **2** was obtained from the second greenish-blue fraction (yield 14%)† while the first green fraction contained mostly μ-oxodiiron(III) complex [μ-O(Fe^{III}OPTAP)$_2$]. In a similar manner using various aryl Grignard reagents other σ-aryliron(III) complexes (Ar)Fe^{III}OPTAP (Ar = *p*-MePh, *p*-MeOPh *etc.*) can be obtained. Complex **2** is air-stable in the solid for several weeks, but in a solution in neutral solvents such as benzene or toluene it converts after several days to μ-O(Fe^{III}OPTAP)$_2$. Addition of acid HX (X = Cl, CCl$_3$COO) to a solution of **2** results in slow formation of the corresponding acidoiron(III) complex (X)Fe^{III}OPTAP and dissolution of **2** in pure pyridine leads to (py)$_2$Fe^{II}OPTAP.

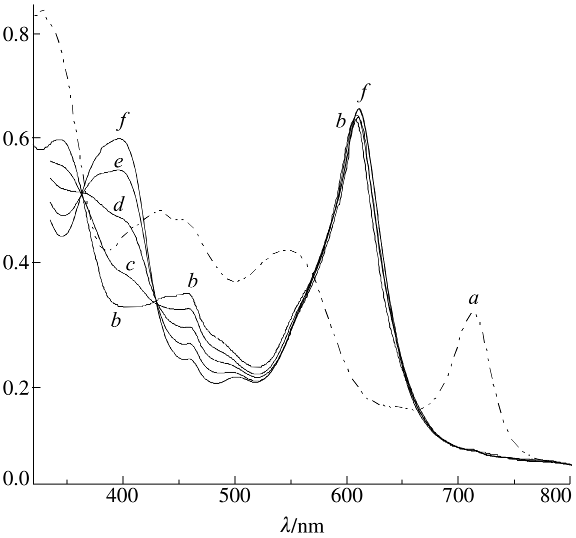

Figure 1 UV/VIS spectra of (*a*) (Cl)Fe^{III}OPTAP, (*b*) (Ph)Fe^{III}OPTAP in toluene (2.1×10^{-5} M) and (*c*)–(*f*) spectral changes observed after addition of 1-methylimidazole (2.55×10^{-4}, 8.90×10^{-4}, 3.56×10^{-3}, 2.09×10^{-2} M, respectively) to a solution of (Ph)Fe^{III}OPTAP.

The CHN elemental analysis data for **2** are in agreement with the formula (Ph)Fe^{III}OPTAP. The mass spectrum of **2** obtained by a fast atom bombardment method contains mass peaks corresponding to the molecular ion [(Ph)FeOPTAP]$^+$ and to the dephenylated fragment [FeOPTAP]$^+$. In the IR spectrum of (Ph)Fe^{III}OPTAP the vibrations of the axially coordinated phenyl (Ph$_{ax}$) coincide with that of the eight equatorial phenyls (Ph$_β$) attached to the β-pyrrole positions of the macrocyclic ligand, but some structural information can be obtained from the skeleton vibrations of the latter. Thus the band at 1296 cm^{-1} is characteristic of the five-coordinated (X)Fe^{III}OPTAP complexes[10] and the position of the oxidation-state sensitive band at 1152 cm^{-1} is typical of the iron(III) complexes.[11]

Conversion of the chloride complex **1** to the σ-phenyl complex **2** is accompanied by strong changes in the UV/VIS spectra (Figure 1). This is not unusual because the oxidation and spin states of the iron(III) ion have a large impact on the energies of the π → π* transitions of the OPTAP macrocycle and on the appearance of the charge-transfer transitions.[10,11] The spectrum of (Ph)Fe^{III}OPTAP [Figure 1(*b*)] differs greatly from the spectrum of the initial intermediate-spin (IS) Fe^{III} complex (Cl)Fe^{III}OPTAP[10] [Figure 1(*a*)] and is typical of complexes with low-spin (LS) Fe^{III}. However, all known LS Fe^{III} complexes of OPTAP^{2-} are six-coordinate {*e.g.* [(CN)$_2$Fe^{III}OPTAP]$^-$, [(N$_3$)$_2$Fe^{III}OPTAP]$^-$, [(HIm)(N$_3$)Fe^{III}OPTAP] or

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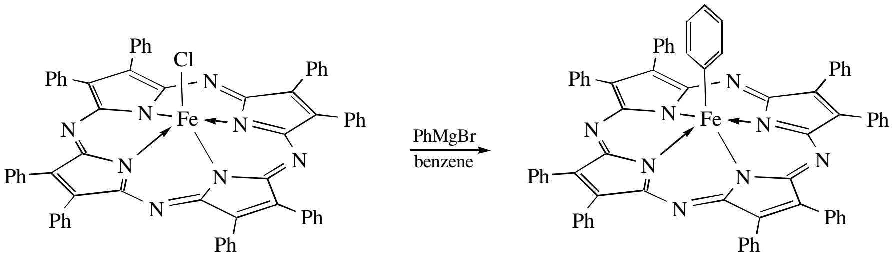
† *Analysis for* **2**: ^{1}H NMR (300 MHz, [^{2}H$_8$]toluene, 293 K) δ: 1.25 (*o*-Ph$_β$), 7.40 (*m*-Ph$_β$) and 3.53 (*p*-Ph$_β$) (OPTAP); 84.34, 8.00 and −30.85 (*o*-Ph$_{ax}$, *m*-Ph$_{ax}$ and *p*-Ph$_{ax}$). UV/VIS [benzene, λ_{max}/nm (log ε)]: 344 (4.45), 440sh, 458 (4.17), 489sh, 555sh, 607 (4.45). IR (KBr, ν/cm^{-1}): 536m, 608m, 640w, 696vs, 744s, 776m, 832s, 888w, 916w, 992vs, 1064w, 1152s, 1204w, 1296w, 1372s, 1440m, 1460m, 1484s. Found (%): C, 79.5; H, 4.4; N, 10.4. Calc. for C$_{70}$H$_{45}$N$_8$Fe (%): C, 79.77; H, 4.30; N, 10.63. FAB-MS *m/z*: (Ph)FeOPTAP$^+$ (1053, 14%; 1052, 28%; 1051, 35%; 1050, 44%; 1049, 39%; 1048, 29%); FeOPTAP$^+$ (976, 46%; 975, 57%; 974, 100%; 973, 86%; 972, 71%; 971, 38%; 970, 28%).



1
(Cl)FeOPTAP

2
(Ph)FeOPTAP

Scheme 1

$[(HIm)_2Fe^{III}OPTAP]^+\}$.[11,12] Five-coordinate complexes even with axial ligands possessing a stronger field than the halogenide [*e.g.* $(N_3)Fe^{III}OPTAP$ or even $(CN)Fe^{III}OPTAP$] usually have UV/VIS spectra typical of IS Fe^{III} complexes. Evidently the -Ar carbanion forming the strong -bond with the iron atom raises the energy of the d_{z^2} orbital and makes favourable the LS state of Fe^{III} even in the five-coordinate complex. -Aryliron(III) porphyrins and phthalocyanine are also LS complexes.[2,7] Addition of small amounts of N-bases L (L = pyridine, imidazole) to a solution of **2** in neutral solvents results in spectral changes that are indicative of coordination of L in the *trans*-position to the -phenyl anion with formation of $(L)(Ph)Fe^{III}OPTAP$ **3** and under certain conditions an equilibrium between five- and six-coordinate complexes **2** and **3** can be observed [Figure 1, spectra (*b*)–(*f*)]. Formation of the six-coordinate complex **3** from **2** is accompanied by a strong bathochromic shift of the B-band [$a_{2u}( ) \rightarrow e_g(*)$ transition] from 344 to 397 nm, whereas the position of the Q-band [$a_{1u}( ) \rightarrow e_g(*)$ transition] at 607 nm remains practically unchanged. This is well explained by the different symmetry properties of the two highest occupied molecular orbitals. The $a_{2u}( )$ orbital destabilizes upon coordination of the -donor ligand in the sixth position, in contrast to the $a_{1u}( )$ orbital which, having nodes on the coordinating pyrrole N-atoms of the OPTAP macrocycle, is much less sensitive to the changes in the coordination state of the Fe atom.

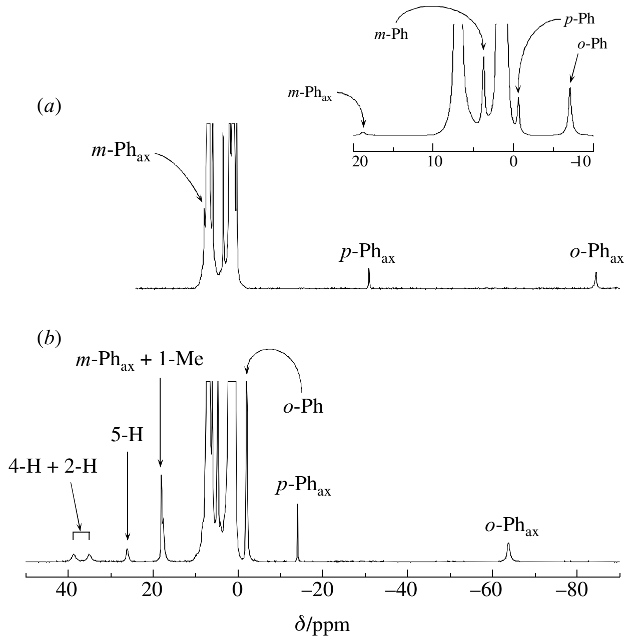


Figure 2 300 MHz ^1H NMR spectra of (*a*) $(Ph)Fe^{III}OPTAP$ (293 K) and (*b*) $(1MeIm)(Ph)Fe^{III}OPTAP$ (253 K) in $[^2H_8]$toluene. Inset in trace (*a*) presents details of the –10 to +20 ppm region (spectrum recorded at 180 K). Resonance assignments: *o*-Ph, *m*-Ph and *p*-Ph, resonances of *ortho*, *meta* and *para* phenyl protons (axial and -phenyl signals are marked by subscripts Ph_{ax} or Ph , respectively); 2-H, 4-H, 1-Me, 5-H resonances of coordinated 1-MeIm.

In the ^1H NMR spectra of $(Ph)Fe^{III}OPTAP$ [Figure 2(*a*)] the paramagnetically-shifted phenyl protons of the macrocycle are observed at 1.25 (*o*-Ph), 7.40 (*m*-Ph) and 3.53 ppm (*p*-Ph) ($[^2H_8]$toluene, 293 K). The pattern of three singlets suggests fast rotation of the -phenyl rings with respect to the $C -C_{phenyl}$ bond. The signals of the axial phenyl protons are located at –84.34, 8.00 and –30.85 ppm for *o*-Ph_{ax}, *m*-Ph_{ax} and *p*-Ph_{ax}, respectively. An identical ^1H NMR spectrum has been obtained in the course of titration of $(Cl)Fe^{III}OPTAP$ with PhMgBr in $[^2H_8]$toluene. The strong isotropic shift of the axial phenyl proton resonances is dominated by the contact contribution. The analysis indicates the large -spin density at the axial ligand as the contact shift decreases in the characteristic order *ortho* > *para* > *meta* and can be accounted for by the spin delocalization from the d orbitals to the -type orbitals of the axially-coordinated phenyl ligand (although some contribution of the -contact mechanism should be considered as well).[14,15] In the relevant case of -phenyliron(III) porphyrins the resonances of the axial phenyl protons were observed in the same region [for $(Ph)Fe^{III}TPP$ at 294 K by –81, 13.6 and –27 ppm for *o*-Ph_{ax}, *m*-Ph_{ax} and *p*-Ph_{ax}, respectively].[3] Coordination of a strong -donor ligand such as 1-methylimidazole (1MeIm) in the *trans*-position to phenyl [(1MeIm)-$(Ph)Fe^{III}OPTAP$] decreases the range of paramagnetic shifts found for the Ph_{ax} protons (–57.46, 14.30 and –14.42 ppm for *o*-Ph_{ax}, *m*-Ph_{ax} and *p*-Ph_{ax}, respectively) [Figure 2(*b*)]. The effect is comparable with that demonstrated for (1MeIm)(Ph)-$Fe^{III}TMP$ (TMP = *meso*-tetramesitylporphyrin dianion).[13] The ^1H NMR data suggest that $(Ph)Fe^{III}OPTAP$ and (1MeIm)-$(Ph)Fe^{III}OPTAP$ present the $(d_{xy})^2(d\ )^3(d_{z^2})^0(d_{x^2-y^2})^0$ ground electronic state, as previously shown for the corresponding iron(III) porphyrin species.[13,15] Tetraazasubstitution in the *meso*-positions of the porphyrin ligand endows the macrocyclic ligand with stronger -acceptor and -donor properties. These factors determine the strengthening of the Fe ← Ph_{ax} -bonding and Fe ← OPTAP -bonding which can explain the higher oxidation stability observed for the -aryliron(III) complexes of tetraazaporphyrins (and phthalocyanine as well).

Further study of -aryliron(III) octaphenyltetraazaporphyrin complexes using Mössbauer, NMR and EPR spectroscopy which are now in progress will reveal the details of their formation mechanism.

We thank Professor B. Floris (Università di Roma 'Tor Vergata', Italy) for help in obtaining the mass spectra.

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Received: Moscow, 28th April 1998
Cambridge, 18th June 1998; Com. 8/03519I