Fluorocarbon Coordination

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Fluorocarbons Modulate the Coordination Sphere of f-Element Complexes

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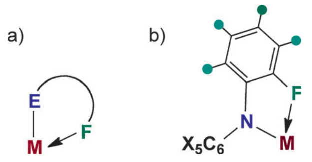
Fluorocarbons, R–F, are characterized by their thermal stability and marked chemical inertness. The compactness of the fluorine valence shell and its involvement in the robust C–F bond leave the R–F functionality with little residual nucleophilicity.[1] Fluorocarbons show, in fact, the least coordinating ability of all halocarbons, which are a family of poorly coordinating ligands on their own.[2] Consistently, $[B(C_6F_5)_4]^-$ is one of the least coordinating anions.[3] Nevertheless, coordination of fluorocarbons to metal centers, R–F→M, is a highly desirable goal since it might result in weakening of the strong C–F bond and thus favor its activation[4]

Fluorocarbon coordination is favored for highly electrophilic metal centers, especially if the R–F unit is anchored to the metal through another donor end (Scheme 1 a).[5] Ligands of diverse complexity containing fluorinated aryl groups are particularly suited for that purpose. Examples of fluorocarbon coordination are known for metals in every block (s, p, d, f) of the periodic system.[4] The R–F→M interaction is, in general, weak,[6] but may exert a distinct stabilizing or protective effect,[7] often influencing the activity of some metal-based catalytic systems.[7b] Interestingly, Schelter and co-workers have recently found that R–F→M interactions (Scheme 1 b; X = H, F) can also forge the coordination sphere of f elements, thereby enabling quite unusual geometries.[8]



Scheme 1. a) Generic and b) specific intramolecular R–F→M interactions.

In the homoleptic compound $[U\{N(C_6F_5)_2\}_4]$,[8a] the uranium atom has an unprecedented square-planar coordination, which is most likely stabilized by four short contacts with *ortho*-F atoms at around 2.6 Å. In the analogous compound with the partially fluorinated amide ligand $PhNC_6F_5$, however, the uranium atom forms a distorted UN_4 tetrahedron, again with four *ortho*-F atoms establishing short contacts at approximately 2.7 Å. Those distances are not significantly longer than some U–F bonds,[9] and are indeed well below the onset of the van der Waals region at 3.58 Å.[10] Moreover, the involved C_6F_5 rings are tilted to favor a closer F···U contact (Scheme 1 b).

Schelter et al. showed that such R–F→M bonds or secondary interactions affect the electronic absorption spectra and are also important to saturate the uranium coordination sphere, thus stabilizing the low oxidation states U^{III} and U^{IV}. The analysis of the variable-temperature ^1H NMR spectra of $[U(PhNC_6F_5)_4]$ sets an upper limit of about 9 kcal mol^{-1} for the F→U donation, thus pointing to a lability which can lead to facile substitution at the uranium atom.

If one considers these two uranium complexes as eight-coordinate, the stereochemistries of the UN_4F_4 cores appear to be highly interesting. A shape analysis[11] of that group in $[U(PhNC_6F_5)_4]$ tells us that the closest eight-vertex ideal polyhedron is the triangular dodecahedron (Figure 1), although its shape measure (2.18) reveals a significant distortion. An appraisal of distortion paths places that core precisely along the D_{2d} interconversion path between a UN_4 tetrahedron and a UN_4F_4 dodecahedron, which has been shown to represent the stereochemistry of the W site in

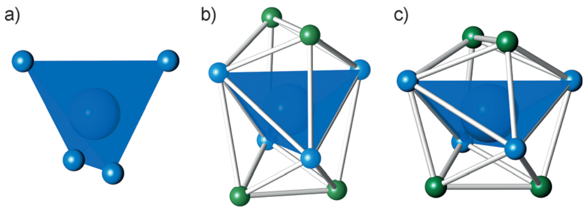


Figure 1. a) Ideal tetrahedron. b) Coordination sphere of uranium in $[U(PhNC_6F_5)_4]$. c) Ideal eight-vertex triangular dodecahedron. Green F, light blue N. The N-M-N bond angles are 109.5, 123.5, and 138.9°, respectively.

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compounds with the $La_2(WO_4)_3$ structure.[12] In the present case, the UN_4 core is almost midway between the four-coordinate tetrahedron and the eight-coordinate dodecahedron, as illustrated in Figure 1, where the experimental coordination sphere is seen to be in-between the two ideal polyhedra.

In contrast, $[U\{N(C_6F_5)_2\}_4]$ shows an unprecedented eight-coordinate stereochemistry (Figure 2), which is practically midway along the distortion path from the hexagonal bipyramid to the gyrobifastigium with the axis of the distorted hexagonal bipyramid defined by U and two N atoms. No structures had been previously detected along this particular path.[13] A search for similar structures led us to complexes of the $[M(18\text{-crown-}6)L_2]$ type with geometries close to that of a hexagonal bipyramid.[13] In most compounds of that family, though, the hexagonal bipyramid is distorted rather toward the triangular dodecahedron and only the Yb atom in $[Yb(18\text{-crown-}6)(NPh_2)_2]$ presents a 23% distortion toward the gyrobifastigium, thus underlining the uniqueness of this uranium structure.

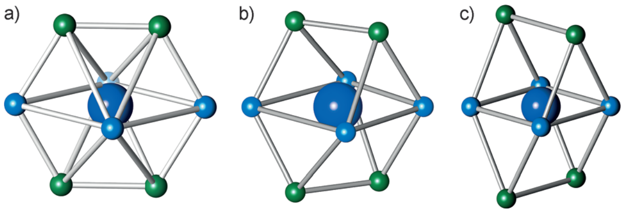

Figure 2. a) Ideal hexagonal bipyramid. b) Coordination sphere of uranium in $[U\{N(C_6F_5)_2\}_4]$. c) Ideal gyrobifastigium. Color code as defined in Figure 1. The N atoms form a square in all three polyhedra.

The complex $[La\{N(C_6F_5)_2\}_3]$, prepared by the same group,[8b] offers an interesting example of the versatility of the R−F→M interaction. In this compound, each perfluorinated amide provides two intramolecular F→La contacts. Additional intermolecular F→La interactions build a dimer in which the ten-vertex La-coordination polyhedron is a staggered dodecahedron (Figure 3), a chiral Johnson polyhedron. It has been shown by NMR spectroscopy that the intramolecular F→Ln interactions persist in solution for both the La and the analogous Ce species, which are mononuclear in C_6D_6. The latter derivative undergoes reversible displacement of the weak R−F→Ln interactions by ligands such as ethers or arenes.

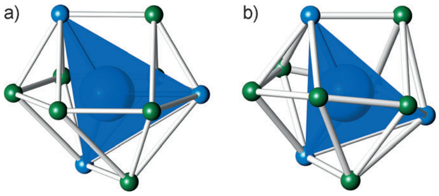

Figure 3. a) Ideal staggered dodecahedron. b) Coordination sphere of La in $[La(N\{C_6F_5\}_2)_3]$ showing the trigonal LaN_3 core. Color code as defined in Figure 1.

The R−F→M interactions, although weak in general, can drive the molecular geometry of the central atom. This interaction, however, must necessarily be strengthened at some later stage wherever C−F activation should occur.[4] The search for stronger R−F→M interactions is still in progress but, along the way, great advances and interesting findings are being made.

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