

## 5. Summary

DFT calculations performed on  $\text{MoF}_6$  and  $\text{WF}_6$  revealed that the octahedral–trigonal prismatic–octahedral rearrangement ( $O_h$ – $D_{3h}$ – $O_h$ ) has a relatively low energy barrier (6–10 kcal mol<sup>-1</sup>). Experimental evidence using dynamic <sup>19</sup>F NMR spectroscopy on complexes of the type  $\text{F}_5\text{M–OR}$  where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{R} = -\text{CH}_2\text{CF}_3$ ,  $-\text{C}_6\text{F}_5$ , and  $-\text{C}(\text{CF}_3)_3$  confirmed these predictions. At room temperature or below these complexes present in the <sup>19</sup>F NMR spectroscopy an  $\text{AB}_4$ -type spectrum typically for octahedral structures. At higher temperatures the non-equivalent metal-bonded fluorine atoms undergo exchange. Experimental evidence supports the intramolecular exchange for such species. The <sup>19</sup>F NMR spectra at different temperatures for all studied complexes were simulated successfully using the program gNMR. Two intramolecular exchange mechanisms can be used for the simulations, namely a 3:3 process (Bailar twist) and the 2:4 mechanism. Both mechanisms are experimentally undistinguishable, from theoretical calculations the preferred mechanism is the Bailar twist.

Theoretical calculations on species of the type  $\text{F}_5\text{M–C}_6\text{X}_5$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ,  $\text{X} = \text{H}$  or  $\text{F}$ ) predicted in most of the cases a trigonal prismatic geometry as the ground state. Attempts to synthesize such complexes, as well as species of the type  $\text{F}_5\text{M–SCF}_3$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) were undertaken. From theoretical calculations on the latter even a lower energy barrier for the  $O_h$ – $D_{3h}$ – $O_h$  rearrangement than for the corresponding alkoxy and phenoxy derivatives is predicted. Attempts to synthesize such complexes were unsuccessful.