

4. Conclusions and Outlook

Molecules of the type F_5M-OR ($M = Mo$ or W , $R = -CH_2CF_3$ or $-C_6F_5$) and $F_5W-OC(CF_3)_3$ were successfully synthesized and characterized. At elevated temperatures the non equivalent metal bonded fluorine atoms of these complexes undergo an intramolecular exchange.

The intramolecular exchange is confirmed mainly by the following statements:

1. Tungsten satellites were observed for $F_5W(OC_6F_5)$ in the ^{19}F NMR spectra even at 185 °C, therefore at high temperatures all fluorine atoms remained bonded to the metal.
2. There is no scrambling of the $-OR$ groups during the heating process, as it is evidenced by the ^{19}F NMR spectra, therefore the ligands remain attached the whole time to the central atom.
3. Different concentrations of $F_5Mo(OC_6F_5)$ in two different solvents provided the same energy value for the rearrangement.

NMR simulations of the ^{19}F spectra using either the Bailar twist (3:3) or the 2:4 exchange mechanisms are indistinguishable. The preferred mechanism is the Bailar twist, as it is depicted from the theoretical calculations, and furthermore, the rate constant (k) between the two mechanisms is related according to $k_{2:4} = 2k_{3:3}$. This equation indeed says that the 2:4 exchange mechanism goes twice as fast as the Bailar twist. This factor of two is explained in terms of the number of operators (permutations) needed for both mechanisms, i.e. the 3:3 Bailar twist has twice the amount of operators than the 2:4 mechanism.

A series of temperature-dependant rate constants using the Bailar twist mechanism can be obtained successfully for all complexes studied. ΔH^\ddagger which corresponds to the octahedral-trigonal prismatic rearrangement is obtained from the Eyring plot of the two variables. The following values are obtained: $F_5Mo(OCH_2CF_3)$ 12.6, $F_5Mo(OC_6F_5)$ 12.3, $F_5Mo(OC_6F_5)$ (in CD_2Cl_2) 12.4, $F_5W(OCH_2CF_3)$ 13.0, $F_5W(OC_6F_5)$ 13.4, and $F_5W(OC(CF_3)_3)$ 15.9 kcal mol⁻¹.

Experimental and theoretical values are in full agreement with each other. The errors of the experimentally determined activation energies can only be guessed. Slight variation of some of the parameters produces changes in the energy values of about ± 0.5 kcal mol⁻¹.

The molybdenum derivatives have a lower energy barrier for the octahedral-trigonal prismatic rearrangement than the corresponding tungsten ones, as it was also predicted by the theoretical calculations performed. Furthermore, because of these low energy barrier for such an interconversion, MoF₆, WF₆, and their derivatives are highly fluxional above room temperature and they are at the edge of structural stability.

The derivatives of these two hexafluorides studied here and the activation energies obtained are the first examples of an experimental proof for an *O_h-D_{3h}* rearrangement for six coordinated complexes.

DFT calculations for F₅M(C₆F₅) complexes, where M = Mo or W, predicted a trigonal prismatic geometry as the structure with the minimum energy. Attempts to synthesize such complexes using reagents like (C₆F₅)BF₂, (C₆F₅)SiF₃, and (C₆F₅)Sn(CH₃)₃ proved to be unsuccessful. For the first two reagents no reaction occurs with the metal hexafluoride. In the reaction mixture of (C₆F₅)Sn(CH₃)₃ and WF₆ the ¹⁹F NMR (CH₂Cl₂) spectroscopy gave signals with a very low intensity corresponding to a doublet at 118.4 ppm (64 Hz), a quintet at 88.5 ppm (64 Hz), and to the aromatic region (-140.1, -155.6, -163.8 ppm). A substitution on the central atom takes place on a very small scale. Attempts to crystallize this material out of the solution were futile. No conclusive statement about the geometry of the expected species was given because only traces of this material are detected.

Unlike the -C₆F₅ derivatives and for reasons that are still unclear, DFT calculations for -C₆H₅ molybdenum and tungsten derivatives predicted a very distorted trigonal prism as the most stable structure for the former, whereas for the later an octahedron is the most favorable structure predicted. Attempts to synthesize such complexes using reagents like Zn(C₆H₅)₂, LiC₆H₅, (C₆H₅)SiCl₃, and (C₆H₅)SiF₃ were also unsuccessful. If the starting

materials such as $\text{Zn}(\text{C}_6\text{H}_5)_2$ and LiC_6H_5 are purified by sublimation and freshly distilled solvents are used no reaction between the educts is observed.

A SHAPE^[23c] analysis of the theoretical complexes reveals the following aspects:

1. For molecules of the type $\text{F}_5\text{M}(\text{CX}_3)$ ($\text{M} = \text{Mo}$ or W , $\text{X} = \text{H}$ or F) the tungsten derivatives are less distorted from a D_{3h} structure than the corresponding molybdenum ones, and the main type of distortion they present is C_{3v} , which agrees with experimental results.^[15,16]
2. However, for molecules of the type $\text{F}_{6-n}\text{M}(\text{C}_6\text{X}_5)_n$ for $1 \leq n \leq 4$ ($\text{M} = \text{Mo}$ or W , $\text{X} = \text{H}$ or F) the molybdenum complexes have a smaller distortion towards an ideal trigonal prism than the corresponding tungsten ones. This distortion is mainly of the Bailar type and not of the C_{3v} type.
3. For ligands bigger than $-\text{CX}_3$ the Bailar distortion provides more space for the ligands than a C_{3v} distortion type, therefore complexes with ligands like $-\text{C}_6\text{X}_5$ will adopt a Bailar distortion rather than a C_{3v} type.
4. The trigonal twist angle can be used to compare the degree of distortion from a D_{3h} structure of six coordinated molecules only if the distortion is mainly of the Bailar type. In any other case of trigonal prismatic distortion, like C_{3v} for example, it is meaningless to use this angle as a comparison parameter.

DFT calculations on molecules of the type $\text{F}_5\text{M}(\text{SCX}_3)$ ($\text{X} = \text{H}$ or F) predicted an even lower energy barrier ($< 2 \text{ kcal mol}^{-1}$ for $\text{M} = \text{Mo}$, and $< 5 \text{ kcal mol}^{-1}$ for $\text{M} = \text{W}$) for an octahedral-trigonal prismatic rearrangement than the alkoxy and phenoxy derivatives. Attempts to synthesize $\text{F}_5\text{M}(\text{SCF}_3)$ complexes were futile. Both hexafluorides were reacted with $\text{Hg}(\text{SCF}_3)_2$, in the case of tungsten hexafluoride no reaction between the two species is detected in the ^{19}F NMR spectroscopy. In the case of molybdenum hexafluoride the only byproduct observed by ^{19}F NMR spectroscopy is $\text{F}_3\text{CS}-\text{SCF}_3$.

From the SHAPE^[23c] analysis on the theoretical complexes $F_5M(SCX_3)$ the following correlation can be made: The lower the energy barrier for the octahedral-trigonal prismatic rearrangement, the more Bailar distorted the octahedral ground state is and the less C_{3v} distorted the trigonal prismatic transition will be.

The molybdenum complexes presented a more Bailar distorted octahedral structure as a ground state than the corresponding tungsten ones, but in the transition state the former present a less C_{3v} distorted trigonal prismatic geometry. Indeed, the molybdenum complexes have a lower energy barrier for such a rearrangement than the analogous tungsten ones.

From the energy values obtained it can be predicted that if $F_5Mo(SCH_3)$ (which has the lowest O_h-D_{3h} energy barrier compared to the other derivatives) would be isolated, if the structure is octahedral, then it will be very distorted and lie somewhere in between the octahedron-trigonal prism path. But if it is trigonal prismatic, then it will possess almost no distortion. Only experimental evidence will give definitive proof for such assumptions.