

## 1. Introduction

Interest in six coordinated homoleptic complexes with ligands having  $\sigma$ -bonding character, and little or no  $\pi$ -bonding character began to grow in the late 80's and early 90's, because theoretical calculations<sup>[1]</sup> and crystallographic evidence<sup>[2]</sup> showed that they should be trigonal prismatic instead of octahedral which is the preferred geometry adopted for an hexa-coordinated central atom according to the VSEPR theory.<sup>[3]</sup>

A complex which was first thought to be octahedral, hexamethyl tungsten<sup>[4]</sup>, was in fact proven from a gas phase electron diffraction study 18 years later to be trigonal prismatic.<sup>[5]</sup> Furthermore, its crystal structure<sup>[6]</sup> published in 1996 indeed revealed the trigonal prismatic geometry of this compound.

Theoretical calculations<sup>[7-14]</sup> and the discovery of many other complexes of this type<sup>[15-18]</sup> have provided relevant information about the necessary conditions that need to be fulfilled by the central atom and ligands in order for the trigonal prismatic geometry to prevail over the octahedral one.

Based on experimental evidence on bis- or tris-chelate hexa-coordinated complexes<sup>[19]</sup> and mathematical analysis,<sup>[20-23]</sup> many mechanisms for a possible octahedral-trigonal prismatic rearrangement have been proposed. Still, there is no report in the literature of any kind of experimental proof for a possible  $O_h$ - $D_{3h}$  interconversion and some questions have not been answered:

Which mechanism is responsible for such an interconversion in monodentate six coordinated molecules?

How high or low is this energy barrier?

Is it possible to give experimental proof for this rearrangement?

If so, is it intramolecular or intermolecular?

To answer these questions, complexes of the type  $F_{6-n}M(OR)_n$  ( $M = Mo$  or  $W$ ) were studied. In contrary to complexes of the type  $F_{6-n}M(R)_n$  they have a strong  $\pi$ -bonding character<sup>[24]</sup> and therefore an octahedral structure is expected in all of them,<sup>[24]</sup> as it has been proven experimentally to be the case.<sup>[25-38]</sup> In order to approach this problem, such derivatives were chosen under the assumption that increasing the temperature of them would produce a rearrangement so that at elevated temperatures they would present a trigonal prismatic structure. Since the complexes have one axial fluorine atom and four equatorial ones, which in the  $^{19}F$  NMR spectroscopy will produce an  $AB_4$  type spectrum, if any changes in the geometry of the molecules take place at high temperatures, then they could be observed also in the  $^{19}F$  NMR spectroscopy.

The auxiliary ligands  $-OCH_2CF_3$ ,  $-OC_6F_5$ , and  $-OC(CF_3)_3$  were chosen because they are fairly easy to introduce and the resulting compounds are at least in part stable enough for subsequent high temperature NMR investigations.<sup>[28,31,33,38]</sup> DFT calculations on such species could also be relatively easily performed in order to compare experimental and theoretical results.

Two possible mechanisms for the octahedral-trigonal prismatic rearrangement were postulated, namely the Bailar twist<sup>[19]</sup> (also called 3:3) and the 2:4 mechanism.<sup>[14,20]</sup> Theoretically as well as experimentally answers to the proposed questions as well as for the mechanism responsible for such an interconversion were obtained.

From theoretical calculations<sup>[7-14]</sup> and experimental evidence<sup>[15-18]</sup> on hexa-coordinated organometallic complexes it is known that they possess a trigonal prismatic structure. Based on that, molybdenum and tungsten derivatives with phenyl or perfluoro-phenyl ligands should be most probably trigonal prismatic. Since there is no experimental evidence of molecules of the type  $X_{6-n}M(C_6H_5)_n$  or  $X_{6-n}M(C_6F_5)_n$  for  $n \geq 1$  and  $M = W$  for  $X = F$  or  $Cl$ , or  $M = Mo$  for  $X = F$ , attempts to synthesize such complexes by reacting the metal hexafluoride or hexachloride (in the case of tungsten) with  $-C_6F_5$  or  $-C_6H_5$  group donors, as well as DFT calculations were performed in order to confirm those assumptions.

Furthermore,  $-SR$  ligands ( $R = -CF_3, -CH_3$ ) which have a weaker  $\pi$ -bonding character<sup>[24]</sup> than  $-OR$  ones, might produce hexa-coordinated molybdenum or tungsten complexes which present an intermediate structure between an octahedron and a trigonal prism, or even a trigonal prismatic one, and they might be even more fluxional than the corresponding alkoxy derivatives. DFT calculations as well as experiments were carried out to corroborate these assumptions.

For comparison means and with the aid of the program SHAPE,<sup>[23a-c]</sup> the degree of distortion from an ideal  $D_{3h}$  or  $O_h$  structure and the type of distortion presented by all studied molecules were quantified successfully.