

# Synthesis, Structure and Reactivity of Dimolybdenum Complexes with Multiple Metal-Metal Bonds

At the beginning of this millennium our research group became involved in the study of metal-metal bonds following the unexpected discovery of decamethylzincocene,  $Zn_2(\eta^5-C_5Me_5)_2$ , the first complex with a direct Zn-Zn bond unsupported by bridging ligands. In the following years other complexes of this type were prepared and characterized.

One year after our initial observation of the Zn-Zn bond, the group of Power made a landmark discovery with the characterization of the first complex with a quintuple bond between metal atoms. Considering the previous experience of our group on the coordination and organometallic chemistry of the Group 6 elements molybdenum and tungsten, a systematic study of new binuclear molybdenum compounds featuring a quadruple Mo-Mo bonds was undertaken. The work carried out initially provided the grounds for the PhD Theses of Dr. Mario Carrasco and Dr. Irene Mendoza. The present Thesis completes and extends the research carried out in the chemistry of dimolybdenum complexes. In these regards, two chapters are included. Chapter I contains synthetic, structural and reactivity studies on dimolybdenum complexes that exhibit quadruple or quintuple Mo-Mo bonds. Firstly, Section 1.2 concentrates on dimolybdenum complexes derived from these molecules, with formula *trans*- $[Mo_2(\mu-O_2CR)_2(\mu-N^{\wedge}N)_2]$ , where  $N^{\wedge}N$  represents a monoanionic aminopyridinate or amidinate bearing bulky ligands. The above complexes are suitable precursors for low-coordinate polymethyl and polyhydride

complexes of the Mo-Mo quadruple bond. Alkylation with an excess of LiMe of the  $[\text{Mo}_2(\mu\text{-O}_2\text{CR}_2)_2(\mu\text{-N}^{\wedge}\text{N})_2]$  aminopyridinate complex that contains two Xyl groups as substituents of both the  $\text{N}_{\text{amido}}$  donor atom and the pyridinic ring, allowed the synthesis and structural characterization of the new lithium trimethyl dimolybdenum *ate* complex  $[\text{Mo}_2(\mu\text{-Me})\{(\mu\text{-Me})_2\text{Li}(\text{OEt})\}(\mu\text{-Ap}^{\text{Xyl}_2})_2]$ . Likewise, some important features of the unsaturated Lewis base free dimethyl species were studied (with  $^{13}\text{C}$ -labelled experiments), as well as the synthesis of a new complex with the 4-dimethylaminopyridine ligand. The hydrogenation of the dimethyl complex afforded the synthesis of the bis(hydride) analogue compound, as described in a previous Thesis. We have found that this process proceeds through an intermediacy, and also kinetic studies on this reaction were carried out. To complete previous, related work from our laboratory, the unsaturated bis(hydride) complex  $[\text{Mo}_2(\text{H})_2(\mu\text{-Ad}^{\text{Dipp}_2})_2]$  was prepared for the first time and characterized by NMR spectroscopy and X-ray crystallography. Related adducts of this complex were also synthesized. Moreover, it is also described in this Section that the reaction of the paddlewheel bis(formate) complex  $[\text{Mo}_2(\mu\text{-O}_2\text{CH})_2(\mu\text{-Ad}^{\text{Dipp}_2})_2]$  with  $\text{LiAlH}_4$  proceeds in a step-wise manner forming the lithium dimolybdenum polyhydride *ate* complexes  $[\text{Mo}_2\{(\mu\text{-H})_2\text{Li}(\text{THF})\}(\mu\text{-O}_2\text{CH})(\mu\text{-Ad}^{\text{Dipp}_2})_2]$  and  $[\text{Mo}_2\{(\mu\text{-H})_2\text{Li}(\text{THF})\}_2(\mu\text{-Ad}^{\text{Dipp}_2})_2]$ , that feature unprecedented  $(\text{THF})\overline{\text{Li}(\mu\text{-H})\text{Mo}}\equiv\text{Mo}(\mu\text{-H})$  cores. Last section comprises the study of the coordination of different substituted arenes to the Mo-Mo quintuple bond, and the reaction with hydrogen, to afford the bis(hydride) complex.

On the other hand, studies related to the topological properties of the Mo-Mo bond are described in Chapter II of this Thesis. It contains experimental and theoretical charge density studies performed on the

complexes:  $[\text{Mo}_2(\mu\text{-O}_2\text{CMe})_2(\mu\text{-Ap}^{\text{Xyl}_2})_2]$  and  $[\text{Mo}_2(\mu\text{-O}_2\text{CMe})_4]$ . As far as we know, these are the first experimental charge density studies performed on multiple Mo-Mo bond complexes in the post-QTAIM age. This analysis is complementary to studies already mentioned in Chapter I and gives a fully coherent and more complete view of the bonding in complexes with quadruple Mo-Mo bond.