Influence of the R Group in $[Mo_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2Cp_2]$, R=H, CH_3, Ph, Bz

Luciano Marchiò[a], Miguel A. Ruiz[b], Alberto Ramos[b], M. Esther Garcia[b], Roberto Cammi[a], Maurizio Lanfranchi[a], Antonio Tiripicchio[a], [a]*Dipartimento di Chimica GIAF, Università di Parma. 43100, Parma, Italy.* [b]*Departamento de Quimica Organica e Inorganica, Universidad de Oviedo, E-33071, Oviedo, Spain.* E-mail: marchio@unipr.it

The experimental geometry obtained from single-crystal X-ray diffraction for the dimolydbenum complexes $[Mo_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2Cp_2]$ (R=H, CH_3, Ph, Bz) are compared with the results of DFT calculations with the B3LYP, B3PW91 density functionals and the Lanl2dz basis set [1]. The crystal structure of the methyl derivative presents a symmetric bridging group whereas the calculations are in accordance with an asymmetric Mo-CH_3-Mo moiety that exhibits an agostic interaction on one of the two molybdenum centers. The agostic interaction is clearly evident in the crystal structure of the benzyl derivative, in agreement with the geometry obtained from the calculations. The geometry of the phenyl derivative was obtained by optimisation of a partial solution from a poor data set of X-ray data where the connectivity of all the non-hydrogen atoms was unambiguously determined. The phenyl ring is symmetrically bound, and it presents a π interaction with the two molybdenum atoms. The nature and the strength of the agostic and π interactions were analyzed by means of the AIM (atoms in molecules) [2] and the NBO (natural bond orbitals) [3] theories.

[1] Gaussian Inc., Pittsburgh PA, 2001, *Gaussian 01*. [2] Bader R.F.W., *Atoms in Molecules*, Oxford University Press, Oxford, 1990. [3] Reed A. E., Curtiss L.A., Weinhold F., *Chem. Rev*., 1988, **88**, 899.

Keywords: molybdenum, crystal structure, ab-initio calculations