New Theoretical Insights Concerning the Molecular Structures of $M_2(CO)_9$ and $M_3(CO)_{12}$ (M=Fe,Ru,Os)

A. Barthel[a], J. Reinhold[a], E. Hunstock[a,c], C. Mealli[b], M. J. Calhorda[c,d]

[a] *Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig*

[b] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Firenze*

[c] *Instituto de Tecnologia Química e Biológica, UNL, Oeiras*

[d] *Department of Chemistry and Biochemistry, University of Lisboa*

A different number of bridging carbonyls is found in bi- or tri-nuclear clusters having the title formulas. Comparative calculations at the SCF, MP2 and DFT levels show that only the latter is able to describe properly the energetics of various isomers of the whole triad. For Fe, DFT gives excellent agreement with the experimental structures, whereas the MP2 approach fails completely. Conversely for Ru and Os, the best agreement with the experiment is obtained by the MP2 optimizations. The quantitative computational results, associated to a qualitative MO analysis, allow to conclude that the structural preferences are determined by a critical balance of metal-bridge bonding, metal-metal bonding as well as intermetallic repulsion.