Chapter 1

Introduction

The present work has been carried out within the project "Computation of Cluster Properties" supported by the Deutsche Forschungsgemeinschaft (Center for Functional Nanostructures). It attempts to gain chemical insight into the properties of systems containing transition metal atoms by means of theoretical chemistry. The tools employed are based on Density Functional Theory (DFT), through the efficient implementation offered by the program package TURBOMOLE [1–3].

The theoretical treatment of transition metal particles raises some difficulties. Their geometries are often very flexible with a few structures very close in energy and they usually possess complicated electronic schemes. As a consequence little or no reliable theoretical (or experimental) data are available to assess the accuracy of the present computational methods. Nevertheless, Density Functional Theory based methods are claimed to be reliable in the treatment of metallic species and they surely allow one to get significant chemical information. Indeed Density Functional Theory is of great help in the validation of structures determined from X-ray diffraction analysis.

The results reported in this document deal mainly with clusters of palladium. This investigation was inspired by two experimental works published by Dahl and coworkers [4, 5], where they report synthesis and characterization of some unusual ligand-stabilized structures of palladium. The occurrence of such systems motivated two studies: in the first, ligand-free clusters of palladium have been treated to rationalize structural trends in relation to the system size; in the second, the effect of ligands has been investigated to determine their role in

stabilizing the known clusters.

In addition to the theoretical treatment of the palladium clusters, calculations on a compound containing silver and indium are reported. The structure of this system could not be confirmed solely on the basis of the X-ray analysis and quantum chemical calculations played a fundamental role in the identification of the final structure.

The present work is organized as follows. In Chapter 2 the theoretical foundations of the method employed are reviewed. Chapter 3 presents computational details of relevance to the treatment of metallic systems within DFT approaches. The discussion of ligand-free and ligand-stabilized palladium clusters is reported in Chapters 4 and 5; Chapter 6 deals with the theoretical investigation on the silver-indium compound. Finally, Chapter 7 summarizes the results of the entire work.