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Review

Synthesis, characterization and dynamic behavior of some iridium carbonyl cluster complexes derived from $Ir_4(CO)_{12}$ with N-, P- and C-donor ligands: A survey

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ABSTRACT

The synthesis of iridium dodecacarbonyl cluster derivatives $Ir_4(CO)_{12}$ with donor ligand such as amine, phosphites, hydrido and cyclic mono and dioxycarbene, NMR and X-ray characterization and fluxional behavior study in solution at variable temperature is briefly reviewed.

Augusto Tassan *initiated its research activity in the Chemistry Department of the Venice University. He then moved to the University of Padova, Industrial Chemistry Institute, under the supervision of Prof. R. Ros and R.A. Michelin, and collaborating with the Prof. R. Roulet of EPFL in Lausanne. His research focuses on the synthesis of new organometallic platinum and iridium clusters, with particular interest on NMRcharacterization*

Mirto Mozzon *took a degree of Industrial Chemistry at the University of Padova with full marks. He became then CNR researcher in the group headed by Prof. U. Belluco, and finally researcher at the University of Padova, under the supervision of Prof. R. A. Michelin. He is now Associate Professor. He maintained a research cooperation whit Prof. A.J.L. Pombeiro at Instituto Superior Tecnico in Lisbon. He coauthored about 80 papers published on peerreviewed international journals in Inorganic and Organometallic Chemistry. He also filled 4 International Patents and written 2 student's book.*

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Alessandro Dolmella *entered the Department of Pharmaceutical and Pharmacological Sciences in 1990 to work in the research group headed by Prof. M. Nicolini, studying radiopharmacy and computational chemistry. He is presently interested in bioinorganic and coordination chemistry, with a special emphasis on transition metals complexes.*

Serena Detti *graduated in chemistry at the University of Pisa in 1996, under the supervision of Prof. F. Calderazzo and G. Pampaloni. She received her PhD in Chemistry at the Swiss Federal Institute of Technology of Lausanne in 2002, working in the group of Prof. R. Roulet in the field of metals carbonyl clusters. She worked at the Italian forensic science service and later she devoted to research on nanotechnology, studying potential interactions of metal nanostructures and the environment.*

Contents

1. Introduction

The chemistry of iridium carbonyls, notably, the chemistry of clusters derived from $Ir_4(CO)_{12}$, were developed along various research lines. Among the investigated topics, we can mention the stereochemistry of the ligands [1], the fluxional processes occurring in solution [2], the studies on the kinetics of carbonyl substitution reactions [3], the modellisation of metal surfaces for absorption reactions of unsaturated substrates [4], the use of such materials as catalysts or precursors in the hydrogenation processes of hydroformylation of unsaturated organic molecules [5].

Along with these perspectives, Garlaschelli and co-workers [6] prepared the starting complex $Ir_4(CO)_{12}$ from $IrCl_3{\cdot}nH_2O$ in ethylene glycol monomethylether medium under a CO gas flow with more than 80% yield.

The IR spectrum of the obtained mixture shows the typical bands of terminal carbonyls in the range 2114–2000 cm^{-1}.

A few years later Pruchnik et al. [7] reported an even more efficient method (*ca.* 95% yield) to obtain $Ir_4(CO)_{12}$ by reacting $IrCl_3{\cdot}3H_2O$ with formic acid in autoclave at 100 °C for 12 h.

Tri- and tetra-substituted derivatives of $Ir_4(CO)_{12}$ can be obtained in good yield by means of the direct reaction of the tetrairidium complex with different ligands (L). Further studies of substitution reactions have identified as a process made of three consecutive steps:

$$Ir_4(CO)_{12} + L \xrightarrow{-CO} Ir_4(CO)_{11}L + L \xrightarrow{-CO} Ir_4(CO)_{10}L + L \xrightarrow{-CO} Ir_4(CO)_9L$$