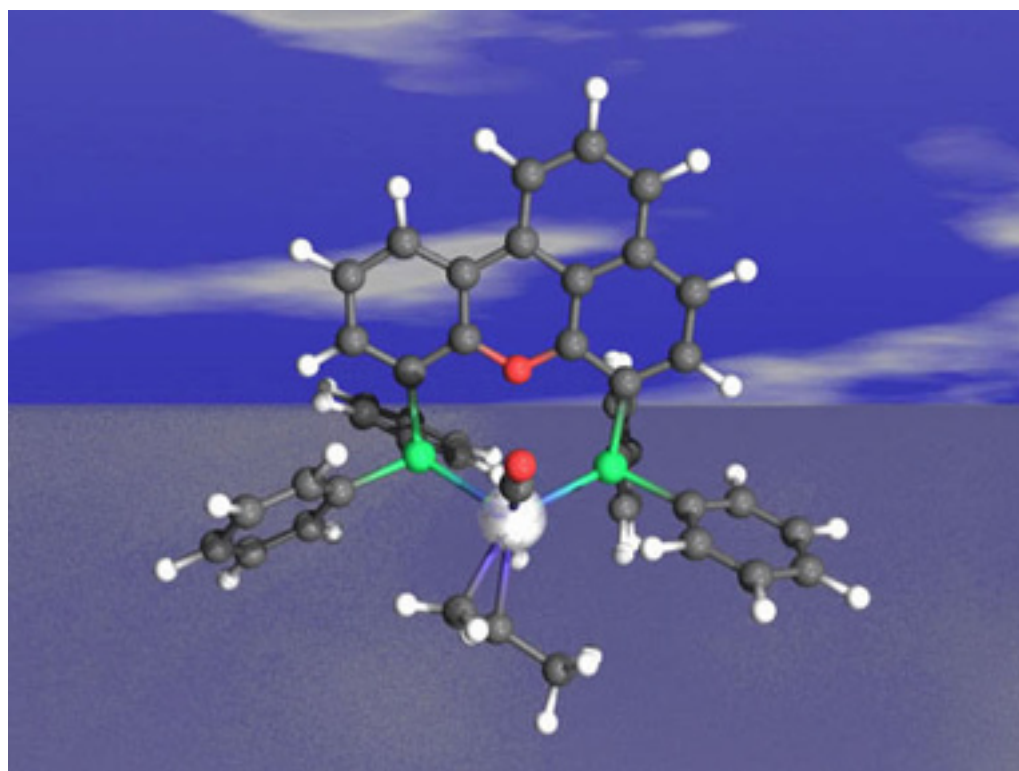


**THEORETICAL INSIGHTS INTO THE  
CHEMISTRY OF ORGANOMETALLIC  
COMPOUNDS WITH C<sub>2</sub> π-LIGANDS: ALKENES  
AND ALKYNES**



Ph. D. THESIS

Jorge Juan Carbó Martín

2002

**Theoretical Insights into the Chemistry  
of Organometallic Compounds with C<sub>2</sub>  
π-Ligands: Alkenes and Alkynes**

by

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A thesis submitted in partial fulfilment of  
the requirements for the degree of Doctor  
of Philosophy

April 2002

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CERTIFIQUEM:

que el treball que porta per títol “*Theoretical Insights into the Chemistry of Organometallic Compounds with C<sub>2</sub> π-Ligands: Alkenes and Alkynes*” ha estat realitzat sota la nostra direcció per **Jorge Juan Carbó Martín**, Llicenciat en Ciències Químiques, i es presenta en aquesta memòria per tal d'optar al grau de Doctor en Ciències Químiques.

I perquè així consti, signem la present certificació a Bellaterra, a 15 d'abril de 2002

Agustí Lledós Falcó

Carles Bo Jane

A la memoria de mi padre

## LIST OF PUBLICATIONS

**The work presented in this thesis has given rise to the following publications.**

Carbó, J. J.; Bo, C.; Moretó, J. M.; Poblet, J. M.

“Carbonylative Cycloaddition of Allyl Halides and Acetylenes Promoted by Ni(CO)<sub>4</sub>. A DFT Study on the Reaction Mechanism”

*Organometallics*, **2000**, *19*, 3516-3526.

García-Yebra, C.; López Mardomingo, C.; Fajardo, M.; Antiñolo, A.; Otero, A.; Rodríguez, A.; Vallat, A.; Lucas, D.; Mugnier, Y.; Carbó, J. J.; Lledós, A.; Bo, C.

“Facile Synthesis of Alkynyl- and Vinylidene-Niobocene Complexes. Unexpected <sup>1</sup>-Vinylidene-<sup>2</sup>-Alkyne Isomerization”

*Organometallics*, **2000**, *19*, 1749-1765.

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“Two- and Four-Electron Alkyne Ligands in Osmium-Cyclopentadienyl Chemistry: Consequences of the  $\pi$ -M Interaction”

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“Rhodium Diphosphine Hydroformylation”

in “Computational Modeling of Homogeneous Catalysis” Lledós, A.; Maseras, F., Eds.; Kluwer Academic Publishers, (accepted).

### **Other scientific publications achieved during the Ph. D.**

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“Synthesis, molecular structure and computational study of a ruthenium bis(thietane) complex”

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“The Reaction of the unsaturated rhenium fragment  $\{\text{Re}(\text{}^5\text{-C}_5\text{Me}_5)(\text{CO})_2\}$  with 1,4-difluorobenzene. Thermal intramolecular conversion of a rhenium (difluorophenyl)(hydride) to  $\text{Re}(\text{}^2\text{-C}_6\text{H}_4\text{F}_2)$  and a [1,4]-metallotropic shift”

*J. Chem. Soc., Dalton Trans.* **2001**, 1452-1461.

**CONTENTS**

<b>Contents</b> .....	i
<b>List of Abbreviations</b> .....	v
<b>1 Introduction and Scope</b> .....	1
1.1 Complexes of $\pi$ -Bound Ligands.....	3
1.1.1 Alkene Complexes.....	4
1.1.1.1 Bonding and Structure.....	4
1.1.1.2 Reactivity of Alkene Complexes.....	5
1.1.1.2.1 Alkene Insertion into the M-R Bond.....	6
1.1.1.3 Industrial Applications. Homogeneous Catalysis .....	7
1.1.1.3.1 Alkene Hydroformylation .....	8
1.1.2 Alkyne Complexes .....	12
1.1.2.1 Bonding and Structure.....	12
1.1.2.2 Reactivity of Alkyne Complexes .....	15
1.1.2.2.1 Alkyne-Vinylidene Isomerization.....	16
1.1.2.3 Synthetic Applications .....	18
1.1.2.3.1 The Pauson-Khand Reaction and Related [2 + 2 + 1] Cycloadditions.....	19
1.2 Objectives of the Thesis.....	21
References .....	24
<b>2 Theoretical Treatment of Organometallic Compounds</b> .....	31
2.1 Qualitative Molecular Orbital Theory .....	33
2.2 Nonempirical Methods .....	33
2.2.1 Standard Ab Initio Methods .....	35
2.2.2 Density Functional Theory Methods .....	36
2.3 Hybrid QM/MM Methods .....	38
2.3.1 The IMOMM Method.....	40
2.4 Analysis of the Electronic Structure.....	40
2.4.1 Bader Analysis: Information from the Electron Density.....	41
2.4.2 Natural Bond Orbital Method.....	42
References .....	43
<b>3 Two- and Four-Electron-Alkyne Ligands: Consequences of the <math>\pi_{\perp} \rightarrow M</math> Interaction</b> .....	47
3.1 Introduction .....	49
3.2 Results and Discussion .....	50
3.2.1 Experimental Data on the Studied Chemical Systems .....	50

3.2.1.1	Synthesis, X-Ray, and Spectroscopic Characterization of Os( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cl( $\eta^2$ -alkyne)(P <sup>t</sup> Pr <sub>3</sub> ) and [Os( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^2$ -alkyne)(P <sup>t</sup> Pr <sub>3</sub> )] <sup>+</sup> .....	50
3.2.2	Computational Studies on the Alkyne Complexes .....	53
3.2.2.1	Bonding Scheme .....	53
3.2.2.2	Geometries and Bond Energies .....	55
3.2.2.3	Rotational Barriers .....	58
3.2.2.4	NMR Properties .....	61
3.2.2.5	Bader Analysis .....	63
3.3	Concluding Remarks .....	65
3.4	Computational Details .....	66
	References .....	68
<b>4</b>	<b>Unexpected <math>\eta^1</math>-Vinylidene-<math>\eta^2</math>-Alkyne Isomerization in the Coordination Sphere of Niobocene Complexes .....</b>	<b>73</b>
4.1	Introduction .....	75
4.2	Results and Discussion .....	76
4.2.1	Experimental Data on the Studied Chemical Systems .....	76
4.2.1.1	Preparation and Characterization of Alkynyl-Niobocene Complexes ..	76
4.2.1.2	Oxidation Processes of Alkynyl-containing Niobocene Complexes ....	77
4.2.1.3	Electrochemical Studies .....	80
4.2.1.4	Isomerization of $\eta^1$ -Vinylidene to $\eta^2$ -Alkyne Niobocene Complexes .	84
4.2.2	Theoretical Study .....	86
4.2.2.1	Relative Stability of the Vinylidene and Acetylene Isomers .....	86
4.2.2.2	Mechanism of the $\eta^1$ -Vinylidene- $\eta^2$ -Alkyne Isomerization.....	88
4.2.2.2.1	Reaction Intermediates.....	89
4.2.2.2.2	Reaction Path for the $\eta^1$ -Vinylidene $\eta^2$ -Alkyne Isomerization.	91
4.2.2.3	<i>exo</i> <i>endo</i> Interconversion.....	96
4.3	Concluding Remarks .....	97
4.4	Computational Details .....	98
	References .....	100
<b>5</b>	<b>Carbonylative Cycloaddition of Allyl Halides and Acetylenes Promoted by Ni(CO)<sub>4</sub>. A Study on the Reaction Mechanism .....</b>	<b>105</b>
5.1	Introduction .....	107
5.2	Computational Details and Test Calculations .....	108
5.3	The Reaction Mechanism.....	109
5.3.1	Formation of the Active Ni(II) Complex .....	109
5.3.2	C <sub>acetylene</sub> -C <sub>allyl</sub> Bond Making .....	112
5.3.3	Carbonyl Insertion.....	116
5.3.4	Closing the ring .....	117
5.3.4.1	Cyclopentenone Formation.....	117



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5.3.4.2	Cyclohexenone Formation .....	120
5.3.5	Mechanism Energy Profile .....	121
5.4	Influence of Acetylene Substitution .....	123
5.5	Influence of Allyl Substitution .....	125
5.6	Concluding Remarks .....	126
	References .....	127
<b>6</b>	<b>Unraveling the Origin of Regioselectivity in Rhodium Diphosphine Catalyzed Hydroformylation</b> .....	<b>131</b>
6.1	Introduction .....	133
6.2	Computational Details .....	136
6.3	Mechanistic Considerations and Assumptions .....	137
6.4	Results and Discussion .....	141
6.4.1	Ethene Insertion.....	141
6.4.2	Propene Insertion.....	142
6.4.3	Analysis of Substrate-Ligand Interactions .....	147
6.5	Concluding Remarks .....	150
	References .....	151
<b>7</b>	<b>Final Conclusions</b> .....	<b>155</b>
	<b>Acknowledgment/Agraiments</b> .....	<b>157</b>

**LIST OF ABBREVIATIONS**

AIM	Atoms In Molecules
B3LYP	Becke-exchange-3-parameter-Lee-Yang-Parr-correlation
BLYP	Becke-exchange-Lee-Yang-Parr-correlation
bcp	bond critical point
CASSCF	Complete Active Space Self-Consistent Field
CC	Coupled Cluster
CCW	CounterClockWise
CI	Configuration Interaction
COD	CycloOctaDiene
cp	critical point
CSD	Cambridge Structural Database
CV	Cyclic Voltammogram
CW	ClockWise
DFT	Density Functional Theory
ECP	Effective Core Potential
EH	Extended Hückel
ESR	Electron Spin Resonance
FMO	Fragment Molecular Orbital
GGA	Generalized Gradient Approximation
GIAO	Gauge-Including Atomic Orbitals
HF	Hartree-Fock
HK	Hohenberg-Kohn
HOMO	Highest Occupied Molecular Orbital
IMOMM	Integrated Molecular Orbital Molecular Mechanics
IMOMO	Integrated Molecular Orbital Molecular Orbital
IRC	Intrinsic Reaction Coordinate
KS	Kohn-Sham
LDA	Local Density Approximation
LCAO	Linear Combination of Atomic Orbitals
LUMO	Lowest Unoccupied Molecular Orbital
MCSCF	Multi-Configurational Self-Consistent Field
MM	Molecular Mechanics
MO	Molecular Orbital
MP	Møller-Plesset
MRCI	Multi-Reference Configuration Interaction

NBO	Natural Bond Orbital
NMR	Nuclear Magnetic Resonance
NPA	Natural Population Analysis
PES	Potential Energy Surface
PM3(tm)	Parametric Method Number 3 (transition metals)
PK	Pauson-Khand
QM	Quantum Mechanics
QM/MM	Quantum Mechanics / Molecular Mechanics
rcp	ring critical point
SCF	Self-Consistent Field
THF	TetraHydroFuran
TS	Transition State
VSEPR	Valance Shell Electron Pair Repulsion
VWN	Vosko-Wilk-Nusair-correlation
ZPE	Zero Point Energy

# Chapter 1

## Introduction and Scope

*Transition metal compounds present a vast array of structures, along with a full diversity of properties and chemistry. This diversity offers rich opportunities for their application in organic synthesis and in selective catalytic processes. However, the huge variety of organometallic chemistry results in an increasing complexity of its study. These features of transition metal compounds have long been an attractive subject for theoretical chemists.*

*The importance of computational chemistry in the field of transition metal compounds was comparatively low until the end of the 1980s. The development of computers and computational methods has dramatically changed this scene. The use of density functional theory (DFT), and the use of relativistic effective core potentials (ECPs) have allowed calculation of geometries, bond energies, vibrational spectra, NMR chemical shifts, activation energies of chemical reactions, and other important properties of transition metal compounds with high accuracy. Very recently, the development of hybrid quantum mechanics/ molecular mechanics methods (QM/MM) has made possible to treat more realistic systems. Moreover, the combined experimental and theoretical work is generating a fruitful synergism, which is helping to understand and predict structural and reactivity trends in organometallic chemistry. Also, theory and experiment give information that can hardly be obtained from only one of the two sides.*

*Among transition metal compounds, this work deals with organotransition metal complexes of two-carbon ( $C_2$ )  $\pi$ -ligands, i. e., alkene and alkyne complexes. The aim of this work is to study some representative examples of the chemistry of alkene and alkyne complexes and show how computational chemistry methods can be applied to solve real problems for which the theoretical chemist can significantly contribute to find an answer. Coverage is extensive, but not exhaustive due to the huge variety of topics in this field, including bonding, reactivity, and synthetic and industrial applications.*

*This first introductory chapter is divided in two sections. The first section presents a plain introduction to the chemistry of alkene and alkyne complexes, giving a general*

presentation of the topics studied in this work. The second section describes the main objectives of this Thesis. The second chapter exposes a general overview of the theoretical methods of the most widespread acceptance for the study of transition metal chemistry. Afterwards, the results obtained in this Thesis are presented and discussed. The discussion includes four different topics, which are organized in chapters (from third chapter to sixth chapter). In each chapter, the reader will find a brief introduction of the particular subject, trying to place it into a general chemical perspective. At the end of each chapter a summary with the most relevant results is also included.

The third chapter presents a study of the nature of the bonding of alkyne as a two- or four-electron donor ligand. In the fourth chapter, an important aspect of alkyne reactivity, the alkyne-vinylidene isomerization, has been investigated on the coordination sphere of niobocene. The two following chapters examine a homogeneous metal-assisted and a homogeneous metal-catalyzed reaction that have an outstanding interest synthetically and industrially, respectively. The former is a [2 + 2 + 1] cycloaddition of alkynes with allyl halides and carbon monoxide by nickel tetracarbonyl leading to cyclopentenones, while the latter is the hydroformylation of alkenes catalyzed by rhodium diphosphine. Finally, the main conclusions of this Thesis are enumerated in the last chapter.

Note that each chapter includes its own references in order to make easy the reading of this work. Thus, redundant references could appear along the chapters.

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## 1.1 Complexes of $\pi$ -Bound Ligands

### 1.1.1 Alkene Complexes

#### 1.1.1.1 Bonding and Structure

#### 1.1.1.2 Reactivity of Alkene Complexes

##### 1.1.1.2.1 Alkene Insertion into the M-R Bond

#### 1.1.1.3 Industrial Applications. Homogeneous Catalysis

##### 1.1.1.3.1 Alkene Hydroformylation

### 1.1.2 Alkyne Complexes

#### 1.1.2.1 Bonding and Structure

#### 1.1.2.2 Reactivity of Alkyne Complexes

##### 1.1.2.2.1 Alkyne-Vinylidene Isomerization

#### 1.1.2.3 Synthetic Applications

##### 1.1.2.3.1 The Pauson-Khand Reaction and Related [2 + 2 + 1] Cycloadditions

## 1.2 Objectives of the Thesis

## References

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## 1.1 COMPLEXES OF $\pi$ -BOUND LIGANDS

Transition metals can coordinate almost any organic functional group, and when this happens, the organic fragments usually change their electronic properties and reactivity in a dramatic way. This phenomenon has important implications in the application of transition metals as reagents in organic synthesis and catalysis.

Traditionally, organotransition metal compounds have been roughly classified in two types of complexes, those containing metal-ligand  $\sigma$  bonds by using a lone pair of a specific atom ligand, and those with unsaturated ligands interacting with the metal via their  $\pi$  electrons.<sup>1-4</sup> Nowadays, a new type of complexes have to be considered, the  $\pi$ -complexes, in which a  $\pi$  bonding electron pair binds the ligand to the metal.<sup>5-6</sup> In  $\pi$ -complexes, the  $\pi$  electrons of unsaturated organic fragments are donated to the metal to help form the metal-ligand bond. This form of metal-ligand interaction is characteristic to transition metals, whose energetically accessible d-orbitals allow efficient overlap with the  $\pi$  orbitals of C-C and C-X multiple bonds.<sup>1-5</sup> The chemistry of the organotransition-metal compounds is dominated by the nature of the ligand. In general, the ability of  $\pi$  ligands attached to metals to undergo reactions is quite different from that of the free ligands. These  $\pi$ -complexes have stimulated the modern development of organometallic chemistry and homogeneous catalysis.

Among  $\pi$ -complexes, those containing two-carbon ( $C_2$ ) ligands (alkene and alkyne) represent the simplest example of bonding interaction between a metal and an unsaturated hydrocarbon. Furthermore, they play an important role as cheap raw materials in several industrial processes, as well as starting materials for organic synthesis.<sup>1,7</sup> The first  $\pi$ -complex, the Zeise's salt, was obtained as early as 1837 by the Danish chemist W. O. Zeise. However, only in 1950s the compound was correctly described as a complex containing a coordinated alkene,  $K[PtCl_3C_2H_4]$ .<sup>8</sup> Since then, the chemistry of  $\pi$ -complexes (and alkene and alkyne complexes) has experienced an enormous development. Despite nowadays the basis of the chemistry of d-block transition metals with alkene and alkyne ligands is well documented,<sup>9</sup> this is an active field that continues growing and yielding novel discoveries.

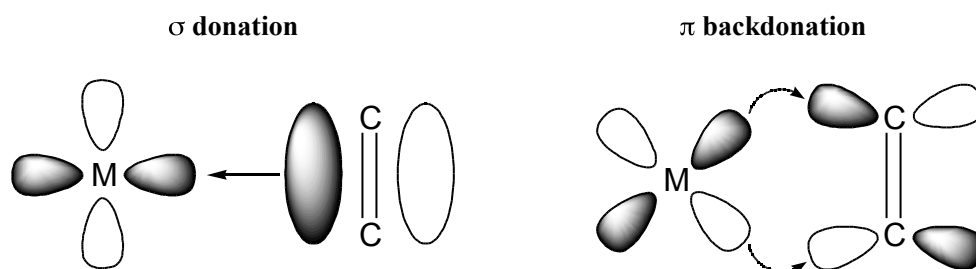
In this first part of the introduction, we will be concerned with the chemistry of alkene and alkyne complexes. Their chemistry covers a wide range of facets including preparation, structure, nature of the bonding, stoichiometric and catalytic reactions, and their respective synthetic applications. This account does not pretend to be an exhaustive description of the chemistry of alkene and alkyne complexes, but a general overview about its main aspects, taking special emphasis on those aspects more closely related to this work. Thus, the general trends of the chemistry of alkene and alkyne complexes will be briefly commented. The particular topics dealt in this work will be described in more detail and placed them into the alkene and alkyne chemical

perspective, from both, experimental and theoretical point of view. The discussion of the chemistry of alkene and alkyne complexes will be done separately. Each topic will be separated in three parts: bonding and structure, reactivity, and industrial and synthetic applications. Afterwards, in next chapter, we will briefly discuss the theoretical methods that are currently most widely used for the study of organometallic compounds and their reactions.

## 1.1.1 Alkene Complexes

### 1.1.1.1 Bonding and Structure

Interaction of a transition metal complex with alkene ligands presents a dichotomy of the bonding models. The bonding can be described in terms of donor-acceptor interactions (Dewar-Chatt-Duncanson model) or shared-electron bonding. In fact, alkene complexes were the first example for which Dewar, and Chatt and Duncanson suggested the donor-acceptor model.<sup>8</sup> This model involves  $\sigma$ -donation of the C=C electrons to an empty d orbital on the metal, accompanied by  $\pi$ -backdonation from a filled metal d orbital into the empty C=C  $\pi^*$  orbital (Figure 1.1). Thus, in this synergic bonding situation, the greater the  $\sigma$ -donation to the metal is, the greater is the  $\pi$ -backbonding. The  $\sigma$ -donation depopulates the C=C  $\sigma$ -bonding orbital of the alkene, and  $\pi$ -backdonation populates the antibonding orbital ( $\pi^*$ ). As a consequence of the combination of effects, the C=C bond of the coordinated alkene lengthens, and its substituents bent away from the metal. This indicates that there is a partial change in hybridization of ethylenic carbon atoms, from  $sp^2$  to  $sp^3$ . In the extreme case, the transition metal-alkene bond may be regarded as a metallacyclopropane, possessing two distinct metal-carbon bonds (Figure 1.2).

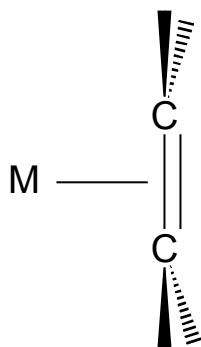


**Figure 1.1:** Schematic representation of donor-acceptor interactions of the Dewar-Chatt-Duncanson model.

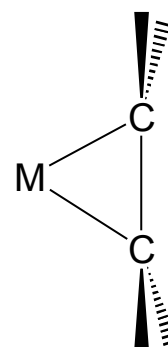
In the metallacyclopropane case, the bonding is described as an electron-sharing interaction, in which two  $\sigma$  bonds between the metal and the two ethylenic carbons are formed (Figure 1.2). This bonding model represents the extreme situation of maximal backdonation. The presence of electron-withdrawing substituents at the alkene (such as F and CN) and  $\pi$ -basic metals enhance backdonation and approach metal-alkene system to metallacyclopropane model.<sup>5</sup> For example, the  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2(\text{CN})_4)$  complex has a C=C distance of 1.49 Å,<sup>10</sup> greatly lengthened compared with that of a typical donor-acceptor model alkene complex (C=C: 1.375 Å),<sup>11</sup> the Zeise's salt.

The two bonding models are complementary to each other, being the real situation somewhere between these two borderline cases.<sup>3,12</sup> These models are very helpful for understanding the chemical behavior of alkene transition metal complexes, and other compounds whose ligands present this dichotomy. Thus, the electronic structure and the reaction chemistry of the molecules can be rationalized with the contribution of each component.

### Dewar-Chatt-Duncanson



### Metallacyclopropane



**Figure 1.2:** Schematic representation of the bonding models for transition-metal alkene complexes.

#### 1.1.1.2 Reactivity of Alkene Complexes

Reactivity of alkene complexes is quite broad and could form a textbook in itself. Perhaps one of the most important reactions of alkene complexes is the insertion to give alkyls.<sup>5</sup> These reactions are fundamental elementary steps in a variety of industrial catalytic reactions such as polymerization, copolymerization, hydrogenation, isomerization, and hydroformylation.<sup>1-5, 13, 14</sup> The alkene insertion will be discussed in detail in the next subsection.



Coordination of an alkene to the transition metal leads to its activation. Thus, the alkene may react with electrophilic or nucleophilic reagents, depending on the nature and charge of the metal center. Electron rich metal centers in low oxidation states (strong  $\pi$ -backbonding) tend to react like metallacycles and are attacked by electrophiles such as proton. Likewise, high formal charge on the metal center (weak  $\pi$ -complexes) favors the nucleophilic attack. Whereas free alkenes are remarkably unreactive to nucleophilic attacks, coordinated alkenes can react with a number of nucleophiles. This has especially interesting applications because it allows the synthesis of a variety of compounds. For example, in the Wacker process, the alkene is oxidized by an external nucleophilic reagent to give acetaldehyde, which is a valuable intermediate mainly for synthesis of acetic acid. The key step of the process is the intermolecular attack of water or  $\text{OH}^-$  on the coordinated alkene.<sup>15</sup>

Another characteristic reaction of alkene complexes is ligand substitution, which provides an important method for the synthesis of metal complexes.<sup>3</sup> Alkenes are often weak Lewis bases, and therefore they can be easily displaced by other ligands such as phosphines, CO, or alkynes. Other outstanding examples of reactions of alkene complexes are the alkene exchange reactions, the photochemical reactions, the alkene metathesis, or the C-H activation to form allyl or vinyl complexes.

#### 1.1.1.2.1 Alkene Insertion into the M-R Bond

As the name suggests, alkene insertion reaction involves the formal insertion of one alkene ligand into another metal-ligand bond on the same complex. The characteristic alkene insertions take place into a metal-hydride, metal-alkyl, or metal-acyl bond.<sup>1</sup> The generic reaction is shown in Scheme 1.1. The net result is a decrease in the coordination number by one, along with the formation of a new C-R bond. Experimental and theoretical evidences point to a mechanism in which the alkene carbons and the M-R bond must have a nearly coplanar arrangement to react.<sup>1-5</sup> Once the metal alkene complex has achieved such geometry, insertion can occur. The reaction proceeds through a four-center transition state. It involves simultaneous breaking of the M-R and C=C bonds as well as formation of an M-C bond and a C-R bond at the two carbon positions of the alkene. The usual stereochemistry of the insertion is syn with retention of configuration at alkene carbons.

It was stated above that insertion reactions are one of the most important reactions of alkene complexes since their implication in variety catalytic cycles. Numerous experimental<sup>16</sup> and theoretical<sup>17</sup> studies have been concerned with the kinetic and thermodynamic behavior of these transformations in order to discover the basic principles and to search for more selective catalysts. In fact, in the particular catalytic process studied in this work, hydroformylation, alkene insertion into metal-hydride

bond has revealed to be the key step governing the regioselectivity of the process. Insertion into M-H bond and its microscopic reverse  $\beta$ -elimination are also involved in other catalytic processes such as hydrogenation and isomerization. Likewise, insertion into metal-alkyl bond is a fundamental step of catalytic polymerization. According to the generally accepted Cossee mechanism,<sup>18</sup> the propagation step in the polymerization of alkenes occurs via a prior  $\pi$ -coordination, followed by alkene insertion into the metal-alkyl bond. Finally, the alkene insertion into the metal-acyl bond has interesting application in homogeneously catalyzed copolymerization of alkene and CO.



**Scheme 1.1**

The understanding of elementary reactions provides valuable information for the improvement and design of new chemical processes of industrial and synthetic interest. A large amount of effort has been devoted to it. In this concern, the joint experimental and theoretical work has proved to be very helpful to enhance the knowledge of organometallic reactivity.

### 1.1.1.3 Industrial Applications. Homogeneous Catalysis

Industrial application of homogeneous catalysis has an enormous importance in chemical industry. Its applications involve the manufacturing of a range of products, including both, bulk and fine chemicals. The impact of homogeneous catalysis on industrial processes has grown to the same extent that organometallic chemistry has developed as a science. New knowledge regarding structure and reactivity of organometallic compounds has improved catalytic condition or has created new catalytic systems. Outstanding examples are Ziegler-Natta catalysts<sup>19</sup> for ethylene polymerization, and Wilkinson catalysts<sup>20</sup> for alkene hydrogenation. Further developments in industrial chemistry clearly depend on improved catalysts. Molecularly defined, tailor-made structures are the safest prerequisites for chemical selectivity. Thus, organometallic compounds with their overwhelming variety of compositions and structures offer a promising approach.

Despite homogeneous catalysis field is rapidly evolving, quite often the progress is guided by trial and error approaches, rather than by rational design. There are still unresolved questions that demand further work, and depend primarily on mechanistic insight. Unfortunately, mechanistic studies based on either new experimental techniques or theoretical approaches are still lacking due to the intrinsic difficulty of the problem as compared to other areas of organometallic chemistry. In many cases, the detection of short-lived highly reactive intermediates playing a decisive role, require extreme conditions or instrumentation. This area should therefore receive greater emphasis, and theoretical approaches should be better integrated in mechanistic studies. The understanding of the factors governing activity and selectivity would provide new criteria for the design of catalytic systems.

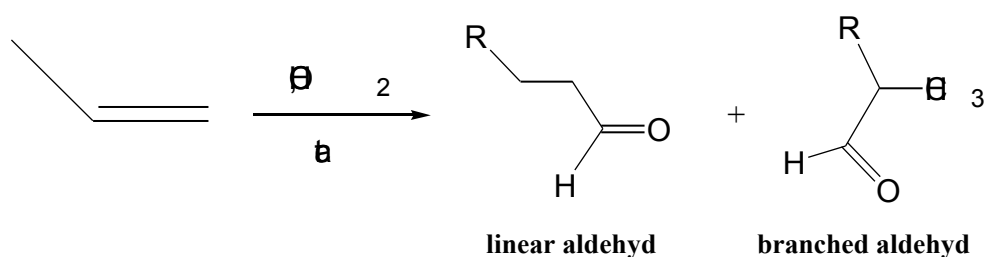
Many transition metal-catalyzed reactions proceed via an alkene  $\pi$ -complex intermediate. Mechanisms involving alkene  $\pi$ -complex intermediates have been postulated for a number of catalytic systems. Thus, several industrial processes have provided practical application to the achievements in alkene complex chemistry. Moreover, alkenes play an important part as cheap raw materials in several industrial processes in which transition metal-containing catalysts are used. Commercially, the most significant of them include polymerization, hydrogenation, or hydroformylation.

#### 1.1.1.3.1 Alkene Hydroformylation

Hydroformylation or oxo process<sup>21</sup> is the oldest and largest homogenous catalytic reaction of alkenes,<sup>14</sup> which are converted into aldehydes by addition of CO and H<sub>2</sub> (synthesis gas).<sup>1-5, 14</sup> Scheme 1.2 shows that hydroformylation produces a mixture of linear and branched aldehyde. Usually, the linear aldehyde is more desirable than the branched one. Since its discovery in 1938 by Otto Roelen,<sup>22</sup> hydroformylation has become one of the largest industrial processes catalyzed by a homogeneous transition metal complex.<sup>14, 23, 24</sup> The amount of products obtained via this method worldwide in 1993 were over 6 million tons per year.<sup>23</sup> One of the most prominent examples is manufacture of butanal, which can be hydrogenated to give 1-butanol (a useful solvent), or self-condensed to form 2-ethylhexanol (used to make a diester of phthalic acid, which serves as plasticizer).<sup>14</sup> Also, hydroformylation allows the functionalization of C=C bonds, and consequently it can be seen as an efficient synthetic route for the preparation of fine chemicals.

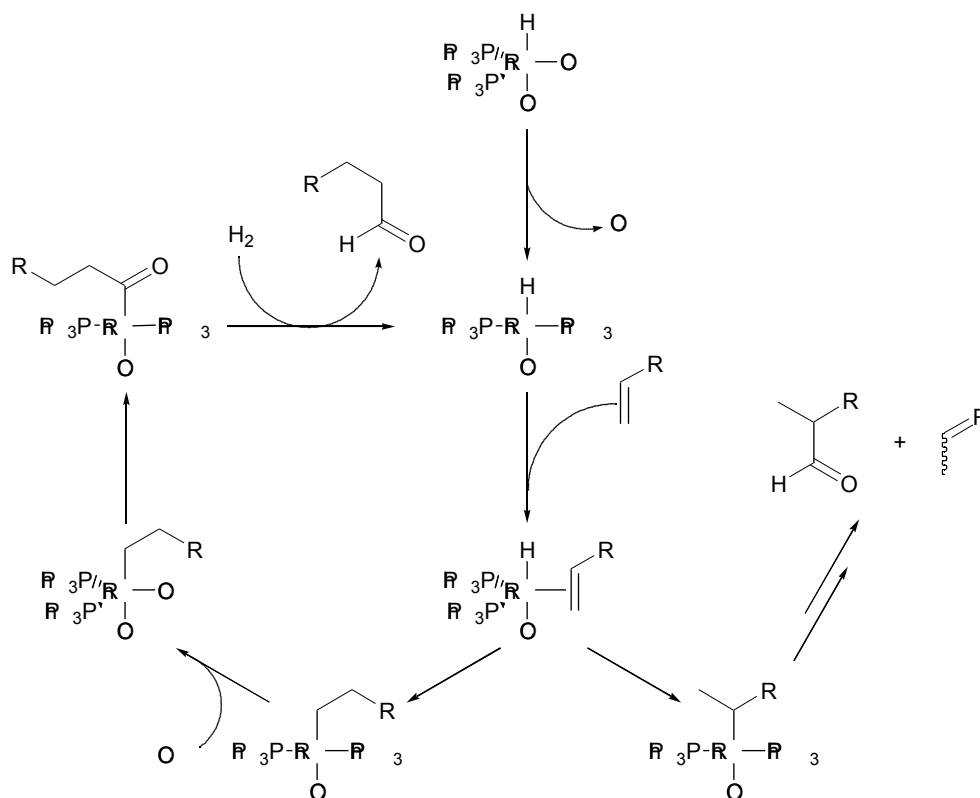
The most popular hydroformylation catalysts used in industry are the low-valent cobalt and rhodium catalysts. However, other metals such platinum, ruthenium, iridium, and palladium have also been employed, especially in the field of asymmetric hydroformylation.<sup>25</sup> The original hydroformylation catalyst discovered by Roelen<sup>22</sup> was the Co<sub>2</sub>(CO)<sub>8</sub>, which hydrogenates to yield the precatalyst species HCo(CO)<sub>4</sub>. The

dissociation of one of the carbonyl ligands generates the  $\text{HCo}(\text{CO})_3$  active catalyst and initiates hydroformylation. The analogue hydrido-rhodium complex  $\text{HRh}(\text{CO})_4$ , formed from Rh-carbonyl clusters, also catalyzes hydroformylation, showing a high activity. However, this rhodium catalyst tends to actively catalyze the competing alkene hydrogenation and isomerization, and exhibits lower selectivity toward the desirable linear product than the respective cobalt system. Slauch and Mullineaux (Shell Oil Company) observed that the use of phosphine-modified cobalt catalysts, with phosphines such as  $\text{PBu}_3$ , result in higher linear:branched aldehyde product ratios.<sup>26</sup> The increased steric bulk of the phosphines is believed to favor the formation of the less hindered linear alkyl complexes. The phosphine-modified rhodium systems are very active catalysts that exhibit a high degree of selectivity for the desired linear aldehyde product. The most famous rhodium catalyst precursor for hydroformylation is undoubtedly  $\text{HRh}(\text{PPh}_3)_3\text{CO}$ .<sup>27</sup> It was first reported by Vaska in 1963,<sup>28</sup> but its activity for hydroformylation was discovered by Wilkinson and co-workers few years later.<sup>29</sup> Since then, many ligand-modified rhodium catalysts have been developed such as diphosphine and diphosphite chelate ligands, which have exhibited high selectivities in the hydroformylation of terminal alkenes.<sup>30</sup>



**Scheme 1.2**

In most catalytic systems, the stereoelectronic properties of the ligands have a pronounced influence on the course of the hydroformylation. Thus, the activity, regio- and stereoselectivity of the process can strongly depend on the electronic and steric properties of the ligands. Electronic properties refer to the ligand basicity and acceptor/donor capabilities, whereas steric ones are those related with ligand bulkiness. A great effort has been devoted to fine-tuning of the catalytic performance by ligand modification. However, and despite the development of a wide variety of ligands, systematic studies of the influence of ligand structure on catalytic performance in the hydroformylation are rare.



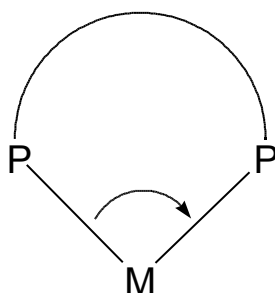
Scheme 1.3

For the  $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$  catalytic system the generally accepted mechanism is that proposed by Wilkinson et al.<sup>29b</sup> Scheme 1.3 shows the seven fundamental steps involved in the catalytic cycle: (i) ligand dissociation to generate the catalyst, (ii) alkene coordination, (iii) alkene insertion, (iv) CO addition, (v) CO insertion to give acyl complex, (vi)  $\text{H}_2$  oxidative addition, and (vii) aldehyde reductive elimination. Likewise Heck and Breslow<sup>31</sup> proposed a similar mechanism for  $\text{HCo}(\text{CO})_4$  system. In literature there is a big controversy about the rate-determining step, whether this is the insertion (or complexation) of the alkene or the oxidative addition of dihydrogen. Most of the textbooks state that the rate-determining step is the oxidative addition,<sup>1, 14</sup> while other authors such as van Leeuwen, Casey and Whiteker propose that for phosphine-modified rhodium catalysts under industrial conditions the rate-determining step is at the early stages of the catalytic cycle, i. e., insertion (or complexation) of the alkene.<sup>27</sup> Alkene insertion step can lead either to linear or to branched Rh-alkyl complexes, which, in subsequent catalytic steps, will generate linear and branched aldehydes, respectively. Thus, the selectivity for linear or branched product is determined in the alkene insertion step, provided that this is irreversible.

Hydroformylation have received a lot of attention from the theoretical point of view. Investigations on some of the steps or on the overall catalytic cycle have been recently review by Torrent et al.<sup>32</sup> Most of calculations have been carried out on simple model systems, using ethene as substrate and  $\text{PH}_3$  as phosphines. Despite their significance for understanding catalytic processes, there are still unresolved questions that demand further work. For example, it has not yet been undertaken an accurate theoretical description of solvation effects on hydroformylation catalysis. Furthermore, more elaborate computational models, mimicking as much as possible the structure of the catalyst, would be required to understand all steric and electronic factors that influence the regio- and stereoselectivity, as well as to clarify which is the rate-determining step. Rocha and Almeida<sup>33</sup> studied the regioselectivity in  $\text{HRh}(\text{CO})(\text{PH}_3)_2$  model catalyst, using propene instead of ethene. Herrmann and co-workers<sup>34</sup> made a first contribution to the theoretical description of systems tested experimentally using a quantum mechanics/molecular mechanics (QM/MM) approach, with frozen QM reaction centers. They investigated the regio- and stereoselectivity on rhodium-catalyzed hydroformylation. Also some lower level computational methods, like molecular mechanics, have been employed to investigate ligand-substrate interactions in intermediates of hydroformylation process and their influence on regioselectivity.<sup>35</sup> In this work we make a first contribution to the study of regioselectivity in rhodium-diphosphine catalyzed hydroformylation, using a first principles method such as IMOMM (Integrated Molecular Orbital Molecular Mechanics),<sup>36</sup> whose main features will be described below. More lately in a series of papers,<sup>37</sup> Decker and Cundari have reported their investigations on different aspects of rhodium-catalyzed hydroformylation. The authors characterized the whole catalytic cycle of the ethene hydroformylation in  $\text{HRh}(\text{CO})(\text{PH}_3)_2$  system by means of accurate ab initio calculations. Also, they performed hybrid QM/MM studies in order to assess the origin of regioselectivity in monophosphine-modified ( $\text{PPh}_3$ ) catalyst, and to analyze the steric influence of different monophosphine ligands on the ethene insertion into the Rh-H bond. Finally, Alagona and co-workers<sup>38</sup> have analyzed the influence on regioselectivity of different alkene substrates in unmodified rhodium catalyst,  $\text{HRh}(\text{CO})_4$ .

As a result of the extensive use of phosphines in catalysis, several empirical ligand parameters have been suggested to predict catalyst performance. Tolman introduced the concept of cone angle and the electronic parameter as measures of respectively the steric bulk and the electronic properties of phosphorus ligands.<sup>39</sup> While Tolman's cone angle concept is widely accepted for monodentate phosphine ligands, the extension to bidentate phosphines appears to be less straightforward. A characteristic parameter of chelate ligands is the bite angle, the angle formed by ligand-metal-ligand<sup>40</sup> (Scheme 1.4). The bite angle can be evaluated either theoretically or from

systematic crystal structure analysis. Due to its strong dependence on the metal nature, its evaluation has to be standardized with respect to the M-P bond lengths in order to obtain a meaningful comparison between the different ligands. Casey and Whiteker<sup>40a</sup> introduced the concepts of the *natural bite angle* and the *flexibility range* of bidentate ligands. The *natural bite angle* is defined as the preferred chelation angle determined only by the ligand backbone. The *flexibility range* is defined as the bite angles that can be reached within an energy barrier slightly above that of the minimized structure. These parameters are determined by means of molecular mechanics calculations, using a dummy metal atom and fixed M-P distances. The influence of the natural bite angle of diphosphine ligands has been shown for several catalytic reactions.<sup>40-43</sup>



**Scheme 1.4**

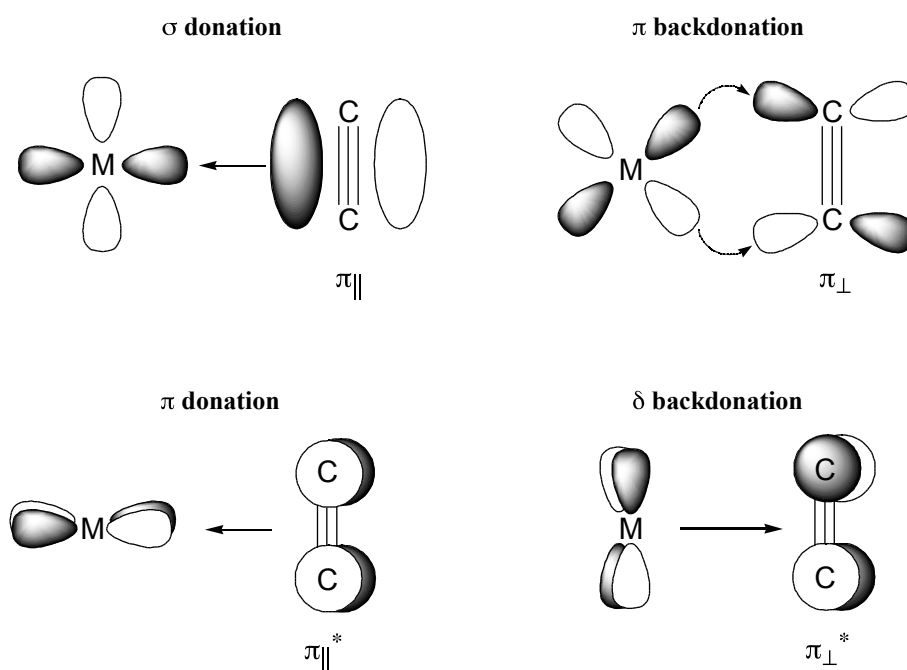
Recently, van Leeuwen and co-workers have developed a new family of diphosphine ligands based on xanthene-type backbones, the xantphos ligands.<sup>42</sup> In the hydroformylation of 1-octene and styrene an increase in selectivity for linear aldehyde formation was observed with increasing natural bite angle.<sup>43</sup> These findings have been analyzed in the present work by means of IMOMM methodology,<sup>36</sup> aiming to clarify and quantify the role of bite angle on regioselectivity.

## 1.1.2 Alkyne Complexes

### 1.1.2.1 Bonding and Structure

The chemical bonding in transition-metal alkyne complexes can be discussed in a similar way as for the transition-metal alkene complexes. The bonding may be described either to arise from donor-acceptor interactions between the alkyne ligand and the transition metal or as a metallacyclic compound. Thus, when the alkyne is sufficiently good acceptor the metal-alkyne bond can be regarded as a metallacyclopropene. The major difference in bonding between alkenes and alkynes is

that the alkyne ligand has a second occupied  $\pi$  orbital perpendicular to the equatorial plane ( $\pi_{\perp}$ ), which may engage in transition-metal alkyne bonding (Figure 1.3). When this happens the alkyne acts as a four-electron donor ligand by means of its  $\sigma$  and  $\pi_{\parallel}$  orbitals. On the other hand, the perpendicular acceptor orbital ( $\pi_{\perp}^*$ ) can only form a  $\delta$ -type bond with the metal d orbitals, and therefore it does not significantly contribute to the bonding. The degree of overlap is quite small because the two orbitals meet side-to-side rather than engaging in direct overlap. Thus, alkyne presents a dichotomy of the bonding as a two- or four-electron donor ligand. In the latter, the extreme bond formulation is to regard the metal-alkyne bond as a bis-carbene complex.



**Figure 1.3:** Schematic representation of donor-acceptor interactions for alkyne complexes. Interactions of the metal with the in-plane  $\pi_{\parallel}$  and  $\pi_{\parallel}^*$  orbitals and the out-of-plane  $\pi_{\perp}$  and  $\pi_{\perp}^*$  orbitals.

In general, alkynes tend to be stronger  $\pi$ -acceptor ligands and to bind more tightly to transition metals than alkenes.<sup>1, 5</sup> An enhancement of  $\pi$ -backdonation folds back, away from the metal, the alkyne substituents. The R-C-C angle tends to be significantly deviated from its value in free alkyne. An interesting consequence of the distorted coordination geometry is that the strained cyclic alkynes are stabilized by coordination to a metal. For example, benzyne, which is unstable as free molecule, can be trapped by a transition metal and displays its correspondingly rich reaction



chemistry.<sup>44</sup> Alkynes can also bridge two metals providing two electrons to each metal. In these cases, it may be appropriate to describe the complex as a metal-carbon cluster. The hydrocarbon is very tightly bonded, which reduces the reactivity of the alkyne to the extent that the metal fragment can be used as a protecting group.<sup>1</sup>

The transition-metal alkyne bonding has attracted the interest of numerous theoretical chemists. Their works have been recently reviewed by Frenking and Frölich.<sup>45</sup> Three major topics arise in the analysis of alkyne complexes: (i) the differences between alkene and alkyne complexes, (ii) the nature of the bonding as a donor-acceptor interaction or as a metallacycle compound, and (iii) the participation of the  $\pi$  orbital in the binding interaction. Concerning the latter topic, initial qualitative calculations have shown that both  $\pi$  and  $\sigma$  alkyne orbitals may be involved in the transition metal-ligand bonding depending on the symmetry of the complex.<sup>46</sup> Several more quantitative theoretical studies have been carried out in order to clarify the role of the alkyne  $\pi$  orbital in the chemical bonding of transition metal-alkyne complex. An important contribution has been made by Decker and Koubelousky in their study of  $M(\text{CO})_4(\text{C}_2\text{H}_2)$  ( $M = \text{Fe}, \text{Ru}, \text{and Os}$ ) system.<sup>47</sup> The authors explained the observed CO labilizing effect of the alkyne ligand from the stabilization dissociation product, in which alkyne is acting as a four-electron donor ligand. Also, Walther and coworkers have shown the participation of the two  $\pi$ -acetylenic systems in the stabilization of the formally unsaturated  $\text{Ni}(\text{C}_2\text{H}_2)_2$  and  $(\text{PH}_3)_2\text{Ni}(\text{C}_2\text{H}_2)$  complexes.<sup>48</sup> Despite of the efforts made on the understanding of metal-alkyne bonding, quantitative-theoretical studies on the two- four-electron donor dichotomy of alkyne ligands are still lacking. This thesis also includes a contribution to the understanding of such an important topic.

The participation of the alkyne perpendicular  $\pi$  orbital besides the in-plane  $\pi$  orbital in the bonding was first suggested by King.<sup>49</sup> The effect of the additional  $\pi$ -donation has implications on structure and reactivity of the alkyne complexes as well as on their spectroscopic properties. For example, nucleophilic addition to alkyne complexes is known to produce vinyl metal species.<sup>3</sup> Nevertheless, when addition takes place on four-electron-donor alkyne ligand, it usually gives the  $^2$ -vinyl complex instead of the  $^1$ -vinyl one.<sup>50</sup> Furthermore, the alkyne may function as an active spectator in promoting reactivity at other ligands through variable electron donation (two- and four-electron donation).<sup>51</sup> Additionally, Templeton and Ward have shown that  $^{13}\text{C}$  NMR can be used to gauge the number of electrons formally donated by the alkyne to the metal.<sup>52</sup> On four-electron donor alkyne ligands, the chemical shifts of the acetylenic carbon atoms are substantially shifted towards lower field than on the two-electron donor ones.

The chemical bonding and reactivity of four-electron donor alkyne complexes has been mainly centered at early-transition-metals.<sup>53</sup> Up till now, osmium-

cyclopentadienyl complexes containing four-electron-alkyne ligands were unknown. Recently, Professor Esteruelas and co-workers have discovered that the  $d^6$   $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\eta^2\text{-alkyne})(\text{P}^i\text{Pr}_3)$  complex,<sup>54</sup> in which the alkyne acts as a two-electron-donor ligand, can be converted into the  $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-alkyne})(\text{P}^i\text{Pr}_3)]^+$  species. Upon chloride dissociation, it is observed a significant shortening of Os-alkyne distances, accompanied by a substantial increase of the  $^{13}\text{C}$  chemical shift values of the acetylenic carbon atoms. Both, structural and spectroscopic changes indicate that in the former the alkyne ligand acts as a two-electron-donor ligand, whereas in the latter it acts as a four-electron-donor ligand. Such parent complexes provide an excellent prototype for studying how the differences in bonding nature, between two- and four-electron-donor alkyne ligands, are reflected in geometrical, electronic, and energetic properties. Thus, in collaboration with Professor Esteruelas, we carried out theoretical calculations on those systems in order to gain knowledge about that topic.

### 1.1.2.2 Reactivity of Alkyne Complexes

Alkyne complexes, like alkenes, exhibit a very varied reactivity. They also undergo numerous insertion reactions into metal-ligand bonds, which constitutes an important elementary reaction involved in catalytic hydrogenation, oligomerization, or polymerization,<sup>2</sup> as well as in stoichiometric organic synthesis.<sup>7</sup> Another important reaction of alkyne complexes is the terminal alkyne to vinylidene rearrangement, which has been subject of study in this thesis and will be discussed in detail in next subsection. This phenomenon has proved to be a useful entry to vinylidene complexes,<sup>55</sup> and several catalytic cycles have been established to involve alkyne and vinylidene isomerization.<sup>56</sup> For example, such isomerization process constitutes an important step in polymerization of alkynes,<sup>56a</sup> dimerization of terminal alkynes into enynes,<sup>56b-e</sup> coupling of alkynes with allylic alcohols to afford unsaturated ketones,<sup>56g</sup> and cyclization of enediynes containing a terminal triple bond into aromatic derivatives.<sup>56h</sup>

It was introduced in previous section that alkyne complexes could suffer nucleophilic attacks to form vinyl species. However, this reaction is relatively rare compared with metal-alkene complexes.<sup>7</sup> Moreover, coordination of alkynes permits the trapping of strained cyclic alkynes that would not ordinarily be stable. It is worth of mention the zircono-benzyne complexes, which have found widespread synthetic applications. These reactive benzyne complexes undergo a range of insertion reactions, which ultimately result in functionalization of the arene rings.<sup>44</sup>

Many transition-metals form very stable alkyne complexes, especially those in which alkyne acts as a bridging ligand. This complexation effectively reduces the reactivity of the triple bond to the extent that the acetylenic substituents can be

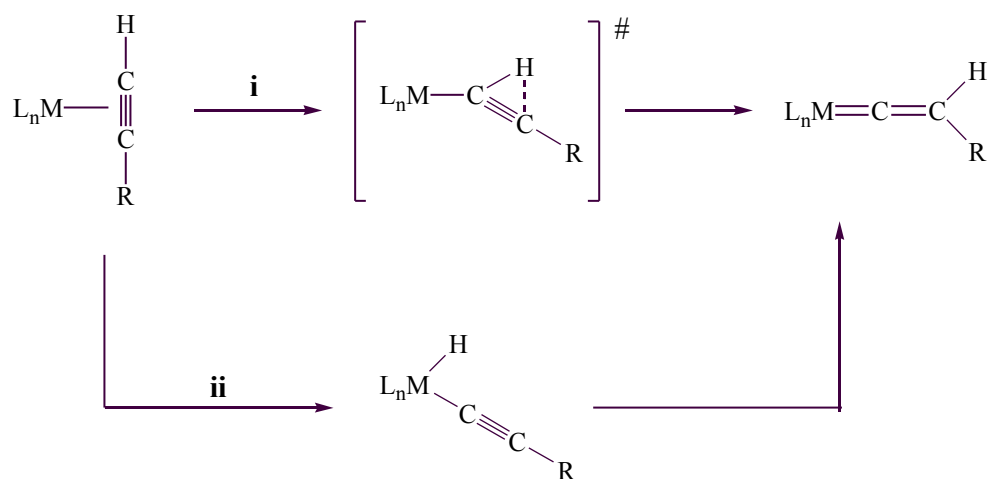
selectively reduced or hydroborated.<sup>57</sup> Complexation can also stabilize positive charge in propargylic position, allowing the reaction of stabilized propargyl cations with a variety of nucleophiles (the Nicholas reaction).<sup>58</sup> In contrast, many alkyne complexes are quite reactive toward an additional alkyne. The oxidative coupling of alkynes to form the metallacycles is a very typical reaction of alkyne and is frequently observed for a variety of metals. The metallacycle product can go on with excess of alkyne, leading to cyclooligomerization, which constitutes one of the most relevant applications of alkyne complex chemistry to synthesis. Thus, alkyne ligands can coordinate to the metal in their dimerized and trimerized forms, and incorporate carbonyl or other functional groups during the cyclooligomerization process, producing a great variety of organic products.<sup>1-5, 7</sup>

#### 1.1.2.2.1 Alkyne-Vinylidene Isomerization

The rearrangement of free acetylene ( $\text{HC}\equiv\text{CH}$ ) to its vinylidene isomer ( $:\text{C}=\text{CH}_2$ ) is a thermodynamically disfavored process. Theoretical<sup>59</sup> and physicochemical<sup>60, 61</sup> studies have established that vinylidene is 44-47  $\text{kcal}\cdot\text{mol}^{-1}$  less stable than acetylene, and there is only a small barrier ( $< 1 \text{ kcal}\cdot\text{mol}^{-1}$ ) for the vinylidene to acetylene rearrangement. It follows that free vinylidene is observed only under special conditions.<sup>60, 61</sup> However, numerous examples of the same isomerization, occurring in the coordination sphere of transition metals have been reported; in such cases, vinylidene is apparently stabilized.<sup>55</sup>

Several possible mechanisms have been proposed for this  $^2$ -alkyne to  $^1$ -vinylidene conversion on the coordination sphere of transition metals. Two intramolecular reaction mechanisms have been suggested earlier, which are schematically shown in Scheme 1.5. Initially, the photochemical studies of manganese and rhenium complexes led Anatova and co-workers<sup>62</sup> to conclude that the rearrangement takes place via an (alkynyl)hydridometal intermediate (path ii, Scheme 1.5). In this mechanism, the oxidative addition of the alkyne is followed by a 1,3-hydrogen shift of the hydride from the metal to the  $\beta$ -carbon atom of the alkynyl ligand. However, extended Hückel calculations of Silvestre and Hoffmann<sup>63</sup> made on  $[\text{CpMn}(\eta^2\text{-HC}\equiv\text{CH})(\text{CO})_2]$  have shown that the direct 1,2-hydrogen shift from the  $\beta$ - to  $\alpha$ -carbon of the  $^2$ -coordinated terminal alkyne seems more plausible (path i, Scheme 1.5). Quantitative *ab initio* calculations also support the 1,2-hydrogen shift mechanism for  $[\text{RuX}_2(\text{PR}_3)_2(\eta^2\text{-HC}\equiv\text{CR}')] \text{d}^6$  ruthenium-systems.<sup>64</sup> On the other hand, in a series of Co, Rh, and Ir  $\text{d}^8$  complexes there are experimental evidences that suggest the involvement of (alkynyl)hydridometal species in the isomerization process.<sup>65</sup> Furthermore, a recent theoretical study have proved that  $^2$ -alkyne to  $^1$ -vinylidene rearrangement in Rh(I)  $\text{d}^8$  complex takes place via an hydrido intermediate,

and the 1,3-hydrogen shift occurs intermolecularly rather than intramolecularly.<sup>66</sup> It appears that the mechanism involving oxidative addition is difficult if the metal changes from  $d^6$  to  $d^4$ , but this process may take place when the metal change from  $d^8$  to  $d^6$ . Thus the isomerization mechanism depends on the electronic configuration of the metal.



**Scheme 1.5**

Other alternative mechanisms have been proposed for  $^2$ -alkyne to  $^1$ -vinylidene isomerization under specific conditions. Puerta and co-workers<sup>67</sup> suggested that the initially formed hydrido intermediate  $[Cp^*(dippe^*RuH-(CCR))]^+$  yields the vinylidene complex via a deprotonation/reprotonation route. Eisenstein and co-workers<sup>68</sup> have theoretically studied the hydride-ruthenium and osmium complexes, proving that the hydride ligand is involved in tautomerization process via formation of  $^1$ -vinyl intermediate.

Although numerous examples of  $^2$ -alkyne to  $^1$ -vinylidene rearrangement have been reported,<sup>55</sup> the reverse process, i. e., the transformation of the vinylidene complex into the corresponding  $^2$ -alkyne, has been described in a relatively few cases.<sup>69</sup> It is also interesting to note that both isomers have been found to be in equilibrium at room temperature in complexes containing ruthenium(II) fragments,<sup>70</sup> showing that this conversion depends on the electronic properties of the metallic fragment.

Recently, the group of Professors Otero and Antiñolo, during their studies on synthetic methods for the preparation of alkynyl- and vinylidene-containing niobocene complexes, observed a surprising behavior for some vinylidene  $d^2$  niobocene compounds, which isomerize to give the corresponding alkyne complexes. In collaboration with Otero's group, a theoretical study on the unexpected  $^1$ -vinylidene

to <sup>2</sup>-alkyne isomerization on the coordination sphere of niobocene complexes was performed. Additionally, Vallat, Lucas, and Mugnier carried out electrochemical studies on these niobocene complexes. Finally, it is worth to mention that other combined experimental-theoretical studies on <sup>1</sup>-vinylidene to <sup>2</sup>-alkyne rearrangement have been almost simultaneously published.<sup>71</sup> Gimeno and coworkers, in their studies on indenyl-ruthenium(II) complexes, conclude that the process proceeds through a 1,2-hydrogen shift mechanism,<sup>71a</sup> and that the tautomerization equilibrium is dependent not only on the electronic properties of the metal fragment, but also on the steric requirements of ruthenium fragment.<sup>71b</sup> Also, Esteruelas and coworkers have performed calculations to support their investigations on the formation of cationic half-sandwich osmium-vinylidene complexes from terminal alkynes.<sup>71c</sup>

### 1.1.2.3 Synthetic Applications

Alkynes have been replaced by alkenes as the major chemical feedstock during the second half of last century.<sup>14</sup> The large amount of energy stored in the triple bond function has become a disadvantage economically. Thus, development of technology for alkene-based processes made alkyne industrially obsolete. However, and despite of the strong economic incentive to replace alkyne-based processes, some industrial applications based on alkynes are still in use, for example, the addition to aldehydes and ketones to produce butanediol and tetrahydrofuran. Furthermore, alkynes remain as a useful reagent for the synthesis of more complex organic molecules.

It was stated above that alkynes could form very stable complexes with certain transition metals. This precludes the possibility of using alkynes in synthesis, due to the lack of reactivity of the coordinated triple bond. In the other hand, many alkyne complexes are quite reactive toward additional alkyne, and react further to produce more elaborate complexes or organic products. Thus, the successful development of transition-metal-alkyne complex chemistry for use in organic synthesis has involved procedures for the management of these extremes in reactivity.<sup>1</sup>

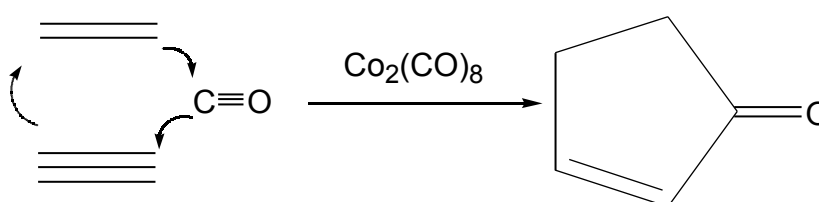
One of the most important aspects pertaining to organometallic chemistry of alkyne concerns the cyclooligomerization of alkyne, and the amazing variety of products found in the reaction between alkynes and metal-carbonyls.<sup>1-5, 7</sup> In the absence of carbon monoxide, metal complexes catalyze some remarkable di-, tri- or tetracyclomerizations of alkynes. The cyclotrimerization of alkynes can be used to synthesize substituted benzenes. Initially, the process was of little synthetic interest due to the lack of regioselectivity, and it was restricted to symmetrical internal alkynes. A solution to this problem was to use a dialkyne and an alkyne with bulky acetylenic substituents. The bulk of the substituents prevents self-trimerization,

whereas the dialkyne ensures the formation of the metallacyclopentadiene.<sup>72</sup> Also, alkynes can undergo cycloadditions [2 + 2 + 2] with other functional groups such as nitriles, alkenes, or isocyanates. These co-cyclooligomerizations result in the production of cyclic organic compounds such as pyridines, cyclodienes, pyridones, or pyrimidines. Alkynes react with many transition metals in presence of carbon monoxide to produce compounds containing both carbon monoxide and alkyne-derived fragments. Usually, reactions of this type are quite complex, and few have been controlled sufficiently to be of use in the synthesis of organic compounds. Among them, quinones had long been known to be one of the products of the reaction of alkyne with carbon monoxide.<sup>73</sup>

Other carbonylative cycloadditions involving alkyne have also proved to be excellent mediators for multicomponent synthetic reactions. In particular, the Pauson-Khand (PK) cycloaddition and related reactions, which are able to produce a variety of cyclopentenone systems in a single operation, have attracted the interest of many synthetic chemists.<sup>74</sup>

#### 1.1.2.3.1 The Pauson-Khand Reaction and Related [2 + 2 + 1] Cycloadditions

The Pauson-Khand (PK) reaction is a cocyclization of alkynes with alkenes and carbon monoxide by dicobalt octacarbonyl leading to cyclopentenones, formally a [2 + 2 + 1] cycloaddition (Scheme 1.6). It was initially discovered in the early seventies.<sup>75</sup> Since then, it has become one of the most useful methods for the synthesis of cyclopentenone ring systems, and more recently it has been applied to the synthesis of natural products and cyclopentadienyl complexes.<sup>74</sup> Transition metal complexes are excellent mediators for these multicomponent synthetic reactions. The efficiency of the metal in such systems stems from both the ability to coordinate either simultaneously or sequentially the different components of the reaction around the metal and their activation toward the required insertion reactions.



**Scheme 1.6**

Initially, the Pauson-Khand reactions were stoichiometric and slow, and their use in synthesis was compromised by the necessity of the severe conditions and the

resulting low yields. However, the addition of promoters, such as tertiary amine oxide,<sup>76</sup> accelerated the reaction, resulting in a significant improvement of reaction efficiency. In addition, intramolecular, catalytic, and asymmetric versions of the Pauson-Khand reaction have appeared.<sup>74</sup> Furthermore, a number of variations with other cobalt complexes<sup>77</sup> and with different metals including titanium,<sup>78</sup> zirconium,<sup>79</sup> molybdenum,<sup>80</sup> tungsten,<sup>81</sup> iron,<sup>82</sup> palladium,<sup>83</sup> ruthenium,<sup>84</sup> rhodium,<sup>85</sup> and nickel<sup>86-88</sup> have proven to be very effective. All these developments have enhanced the synthetic utility and the overall scope of the PK reaction tremendously.

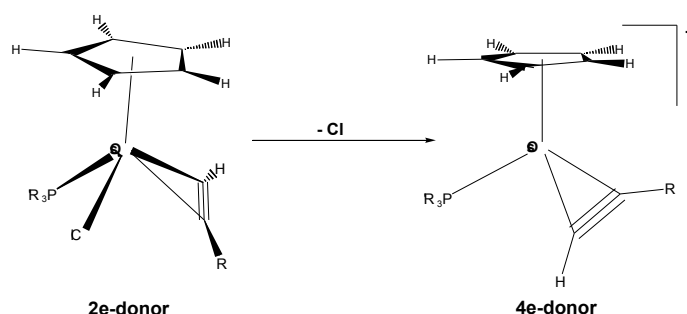
Despite the great utility of the Pauson-Khand reaction and beyond the fact that alkyne complex is involved, little is actually known about its mechanism. The currently accepted mechanistic pathway was originally proposed by Magnus.<sup>89</sup> The Magnus mechanism involves ligand exchange of a CO and an alkene on the alkyne complex, followed by a carbon-carbon bond formation to form a metallacycle. And finally, a CO insertion and reductive elimination afford the cyclopentenone complex. Although the pathway suggested by Magnus has been successfully employed to rationalize experimental results, it has not been subject of detailed studies. Very recently, several theoretical studies on the reaction mechanism of the related PK reaction have appeared,<sup>90</sup> providing a set of information on the structures and energetics of intermediates and transition states. Also, Pericàs and coworkers have used theoretical calculations to explain the diastereoselectivities in asymmetric PK reaction.<sup>91</sup>

Another formally related process is the Ni-mediated cocyclization of alkynes with allyl halides and carbon monoxide, in which a double bond of an allylic halide serves as an alkene component of a formal [2 + 2 + 1] cycloaddition. The reaction, first reported by Chiusoli in the sixties,<sup>86</sup> has been recently investigated by Moretó<sup>87</sup> and others<sup>88</sup>. Thus, in collaboration with Professor Moretó, we have performed a theoretical study on the reaction mechanism of the Chiusoli reaction, aiming to provide insight into reaction intermediates and transition states, as well as into the regio- and chemo-selectivity of the process. This reaction has found much less interest despite displaying a higher degree of regio- and stereo-selectivity than the Pauson-Khand reaction.<sup>86-88</sup> The involvement of the hazardous Ni(CO)<sub>4</sub> has much to do with its lack of popularity among the chemists' community. However, very recently, Moretó and co-workers have shown that cyclopentenones can be efficiently and selectively obtained without handling of nickel carbonyl. The Ni(CO)<sub>4</sub> can be replaced by Ni(COD)<sub>2</sub> in the preparation of the required  $\eta^3$ -allyl Ni complexes.<sup>92</sup>

## 1.2 OBJECTIVES OF THE THESIS

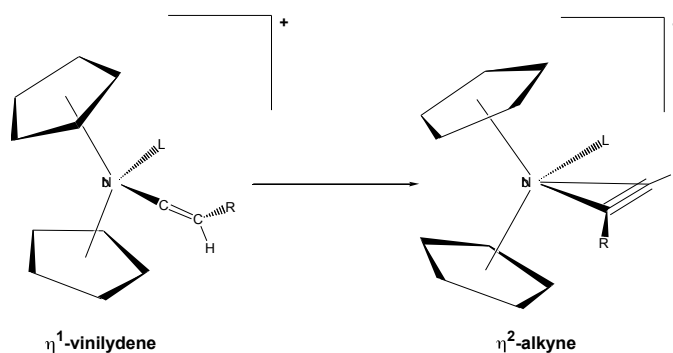
As it was introduced above, the general objective of this thesis is to study some representative examples of the chemistry of alkene and alkyne complexes by using a set of computational tools. The intention is to gain insight into both, the chemistry of these complexes and the theoretical strategies to assess organometallic problems. Also, we try to show how theoretical calculations in combination with experimental work can yield further chemical understanding and provide criteria to plan new experiments. The work covers different chemical aspects, including bonding, reactivity, synthetic and industrial applications. Thus, the aim of this thesis can be divided in several topics, each of which is discussed in a separate chapter.

### *Bonding. Dichotomy of the Alkyne as a Two- and Four-Electron Donor Ligand.*



- Study the differences in bonding nature between two parent alkyne complexes, one with the alkyne formally acting as a two-electron donor ligand and the other as a four-electron donor one.
- Analyze how the bonding differences are reflected in the structural and electronic properties of these complexes.

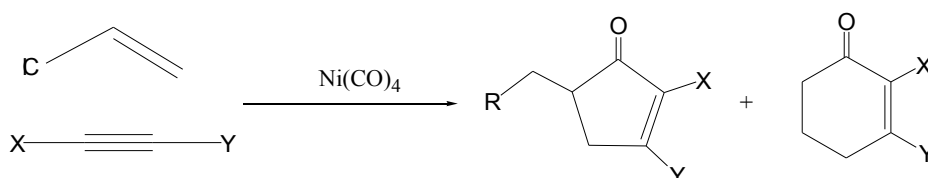
### *Reactivity. $\eta^2$ -Alkyne- $\eta^1$ -Vinylidene Isomerization.*





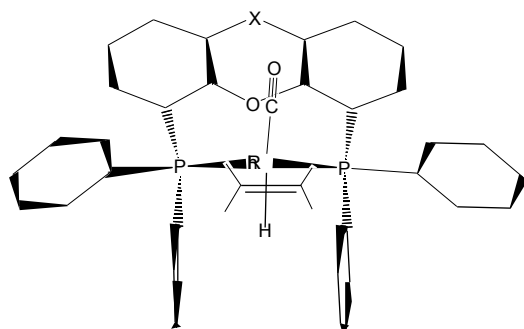
- Determine the relative stability of the <sup>1</sup>-vinilydene and <sup>2</sup>-alkyne isomers in cationic niobocene complexes. Compare the thermodynamic behavior upon ligand substitution, and with other transition metal systems.
- Determine the reaction mechanism of the unusual <sup>1</sup>-vinilydene to <sup>2</sup>-alkyne isomerization by computing the energetic profile. Consider different possibilities for the reaction mechanism.
- Explain the different experimental behavior observed for niobocene-carbonyl and niobocene-phosphine complexes, in which isomerization takes place or does not, respectively.
- Study the interconversion between the two possible geometrical isomers, *exo* and *endo*.

*Synthetic Application. [2 + 2 + 1] Cycloaddition to Yield Cyclopentenone Compounds.*



- Propose a mechanism for the carbonylative cycloaddition of allyl halides and alkynes promoted by Ni(CO)<sub>4</sub> ( a [2 + 2 + 1] cycloaddition). Give insights into this reaction type by computing structures and energies of the intermediates and the most relevant transition states.
- Analyze the influence of alkyne and allyl substitution on the regioselectivity and chemoselectivity of the formation of cyclopentenones.

*Homogeneous Catalysis. Alkene Hydroformylation Catalyzed by Rhodium-Diphosphine.*



- 
- Provide a strategy to theoretically evaluate the regioselectivity in catalyzed hydroformylation.
  - Determine the origin of regioselectivity in rhodium-diphosphine systems. Analyze the role played by the bite angle using the experimentally characterized xantphos systems.
  - Identify, separate and evaluate the different contributions of the bite angle to regioselectivity; *nonbonding* and *orbital* effects.

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