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Francois Mathey

Transition Metal Organometallic Chemistry

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Francois Mathey
Chemistry and Biological Chemistry
Nanyang Technological University
Singapore
Singapore

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Preface

Today, chemistry textbooks tend to become bigger and bigger, following the development of the field. This trend has two consequences: these books become more and more useful for researchers and, at the same time, more and more frightening for students. After having taught transition metal chemistry for more than 20 years in France, California, and Singapore, I am convinced that there is room for a concise textbook focusing on the main products, reactions, and key concepts of the field. This philosophy means that this book necessarily will not be comprehensive and will treat only the core of the subject. In practice, the text is based on the course given to the students of NTU. Brevity does not mean superficiality. The level of this book is not elementary. Whenever possible, it blends theoretical explanations and experimental description. The student using this book should know basic organic chemistry and molecular orbital theory. In spite of its conciseness, it is hoped that this book will help students to quickly grasp the essence of the current developments in the field. Finally, I would like to acknowledge the help of Dr. Matthew P. Duffy who read the initial manuscript and suggested some improvements and all those who worked on the proofs. I dedicate this book to my wife Dominique who faithfully supported me during a long and sometimes difficult career.

Singapore, August 2012

Francois Mathey

Contents

1	General Topics	1
1.1	Some Historical Facts.	1
1.2	Basic Data.	3
1.3	Electronic Structures	5
1.4	Molecular Orbitals of Some Representative Complexes	9
1.5	Main Reaction Types	14
1.5.1	Ligand Substitution	14
1.5.2	Oxidative Addition	16
1.5.3	Reductive Elimination	18
1.5.4	Oxidative Coupling and Reductive Decoupling.	19
1.5.5	Migratory Insertion, Elimination	19
1.5.6	Nucleophilic Attack on Coordinated Ligand	21
1.5.7	Electrophilic Attack on Coordinated Ligand	22
1.6	Problems	23
	References.	25
2	Main Types of Organometallic Derivatives	27
2.1	Metal Hydrides.	27
2.2	Metal Carbonyls	30
2.3	Metal Alkyls and Aryls.	32
2.4	The Zirconium–Carbon Bond in Organic Synthesis	34
2.5	Metal Carbenes.	36
2.6	Metal Carbynes.	45
2.7	Some Representative π Complexes	47
2.7.1	η^4 -Diene-Irontricarbonyls.	47
2.7.2	Ferrocene	49
2.7.3	η^6 -Arene-Chromiumtricarbonyls	50
2.8	Problems	52
	References.	56

3 Homogeneous Catalysis	57
3.1 Catalytic Hydrogenation.	57
3.2 Asymmetric Hydrogenation	60
3.3 Hydrosilylation, Hydrocyanation	62
3.4 Alkene Hydroformylation	65
3.5 Alkene Polymerization.	67
3.6 Alkene Metathesis	70
3.7 Palladium in Homogeneous Catalysis	72
3.8 Gold in Homogeneous Catalysis	77
3.9 Problems	79
References	83
Solutions to the Problems	85
Index	97

Abbreviations

acac	Acetylacetonate	$[\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3]^-$
bipy	2,2'-bipyridine	
Bu	<i>n</i> -butyl	
cod	1,5-cyclooctadiene	
Cp	Cyclopentadienyl	C_5H_5
Cp*	Pentamethyl-Cp	C_5Me_5
Cy	Cyclohexyl	
δ	Chemical shift (NMR)	
diphos		$\text{Ph}_2\text{P}-\text{CH}_2\text{CH}_2\text{PPh}_2$
DMF	Dimethylformamide	Me_2CHO
DMSO	Dimethylsulfoxide	Me_2SO
Et	Ethyl	C_2H_5
HMPT	Hexamethylphosphoro-triamide	$(\text{Me}_2\text{N})_3\text{P}=\text{O}$
HOMO	Highest occupied molecular orbital	
L	Neutral 2-electron ligand	
LUMO	Lowest unoccupied molecular orbital	
Me	Methyl	CH_3
MO	Molecular orbital	
NHC	<i>N</i> -heterocyclic carbene	
ν	Frequency (IR)	
OAc	Acetate	$\text{CH}_3\text{C}(\text{O})\text{O}-$
OS	Oxidation state	
Ph	Phenyl	C_6H_5
py	Pyridine	$\text{C}_5\text{H}_5\text{N}$
TBP	Trigonal bipyramid	
THF	Tetrahydrofuran	$\text{C}_4\text{H}_8\text{O}$
TMEDA	Tetramethylethylenediamine	$\text{Me}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NMe}_2$
TMS	Tetramethylsilane	Me_4Si
T.O.F.	Turnover frequency (catalysis)	
T.O.N.	Turnover number (catalysis)	
X	Anionic 1-electron ligand	

Chapter 1

General Topics

Abstract This introductory chapter starts by a brief history of the subject from the discovery by Zeise of a platinum-ethylene complex in 1827 to the last Nobel prizes awarded to Heck, Negishi, and Suzuki in 2010 for their work on palladium-catalyzed carbon–carbon coupling reactions. Then, the electronic characteristics of the transition metals are presented (number of *d* electrons, electronegativities), together with the shapes of the atomic *d* orbitals. The various types of ligands are introduced with their coordination modes, terminal, bridging, mono- and poly-hapto. The special cases of CO, NO are discussed. The molecular orbitals of ML_6 , ML_5 , ML_4 , ML_3 , and ML_2 complexes are qualitatively studied. In each case, the structure of the *d* block is deduced from that of ML_6 using simple geometrical arguments. The main types of reactions of transition metal complexes are defined, including substitution, oxidative addition, reductive elimination, oxidative coupling, reductive decoupling, 1, 1 and 1, 2 migratory insertions, nucleophilic and electrophilic attacks on coordinated ligands. For each type, the main mechanisms are discussed with their consequences for the electronic structures of the complexes. All this introductory material can serve to decipher the modern literature on transition metal chemistry together with its applications in catalysis and synthetic organic chemistry.

Keywords Transition metals • *d* orbitals • 18-electron rule • Ligand field theory • Reaction mechanisms

1.1 Some Historical Facts

It is not an exaggeration to consider 1828 as the birthday of modern chemistry. It was in this year that Wöhler, a German chemist, accidentally discovered that heating ammonium carbonate, a common inorganic substance, transformed it into urea, a typical organic compound. He thus, established the first unambiguous link between inorganic and organic chemistry and killed the vital force theory that was supposed to control organic chemistry. This founding event was followed by a fast and continuous development of organic chemistry.

Almost at the same time, Zeise, a Danish chemist working at the university of Copenhagen, discovered the so-called Zeise's salt $K[PtCl_3(C_2H_4)]$, which can be obtained by bubbling ethylene into a water solution of K_2PtCl_4 . This compound contained the first three-center η^2 bond between ethylene and platinum but this structure was not definitively established before 1969 by X-ray crystal structure analysis. At the time of its discovery, this compound remained a curiosity and did not induce any significant development of transition metal chemistry.

Much later in 1890, Mond, a German chemist working in England, discovered the reaction of carbon monoxide with nickel which leads to nickel tetracarbonyl $[Ni(CO)_4]$ and patented the process for the purification of nickel based on the conversion of crude nickel into pure $[Ni(CO)_4]$. This became a widely used industrial process, but it did not induce a notable interest from the academic chemists because $[Ni(CO)_4]$ is a low-boiling and highly toxic liquid.

In 1893, Werner, working at the University of Zurich, proposed the correct ionic structure for the adduct between ammonia and cobalt trichloride $[Co(NH_3)_6]Cl_3$ with a hexacoordinate central metal and laid the foundations of modern coordination chemistry. He was awarded the Nobel prize in 1913 for this work.

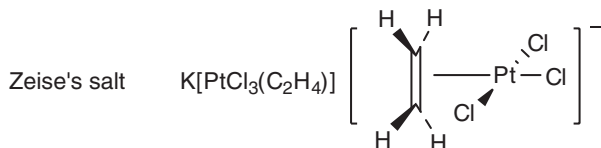
In 1925, the Fischer–Tropsch process converting a mixture of $CO + H_2$ into hydrocarbons was introduced. It uses heterogeneous cobalt or iron catalysts and can provide a gasoline substitute made from coal. It could become a major process when oil resources are exhausted.

In 1938, Roelen in Germany discovered the cobalt-catalyzed hydroformylation of olefins (or “oxo” process) which converts alkenes into aldehydes by formal addition of $H...CHO$ onto the $C=C$ double bond. This remains today one of the major processes of the chemical industry. More than 6 million tons of “oxo” products are synthesized each year.

In 1951, Pauson and Kealy accidentally discovered ferrocene $[Fe(C_5H_5)_2]$ as a stable orange solid but were unable to establish its correct structure. Its genuine structure in which iron is sandwiched between the two cyclopentadienyls with ten identical $Fe-C$ bonds was independently established one year later by Wilkinson and Fischer who were awarded the Nobel prize in 1973 for their work on sandwich compounds.

The titanium-catalyzed polymerization of olefins (mainly ethylene and propene) was introduced in 1955 by Ziegler and Natta and has revolutionized our everyday lives. Around 100 million tons of these polymers are produced each year. Ziegler and Natta were awarded the Nobel prize in 1963.

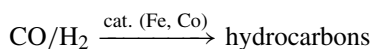
Then, an almost continuous flow of discovery took place. Among them, the first carbene complexes by Fischer in 1964, the metathesis of olefins around 1964, the so-called Wilkinson catalyst for the hydrogenation of olefins in 1965, and so on. This extraordinary dynamism of transition metal organometallic chemistry was rewarded by several Nobel prizes: in 2001, Knowles, Noyori and Sharpless for asymmetric catalysis, in 2005, Chauvin, Grubbs and Schrock for the metathesis of olefins and in 2010, Heck, Negishi and Suzuki for the palladium-catalyzed cross-coupling reactions in organic synthesis.



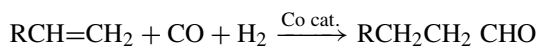
Mond process



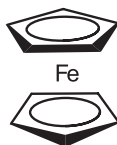
Fischer–Tropsch process



Oxo process



Ferrocene



Ziegler-Natta process



Olefin metathesis



1.2 Basic Data

A main group element such as carbon, nitrogen, etc., reacts through the electrons of its outside shell (n) and has typically the electronic configuration $ns^2 np^x$ ($0 \leq x \leq 6$). Through its reactions, it tends to complete the np subshell at six electrons to reach the highly stable configuration of the next noble gas $ns^2 np^6$. For