Synthetic Coordination Chemistry

Principles and Practice

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Principles and Practice

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SYNTHETIC COORDINATION CHEMISTRY: PRINCIPLES AND PRACTICE

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DEDICATION

To those who taught us and to those whom we teach

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PREFACE

Synthesis in the western philosophical tradition is often defined as the combination of separate elements to form a coherent whole or the combination of thesis and antithesis that produces a new and higher form of being.¹ Synthesis in chemistry, however, is a concrete, tangible process in which compounds are formed from atoms, ions, radicals, and molecules. These descriptions of synthesis appear to be very different, but are they?

Coordination compounds are frequently synthesized from metal salts and ligands or through transformations of other coordination compounds. Products are formed by various processes including substitution, inner-sphere transformations of ligands, and oxidation or reduction of the central metal atoms. In a sense, a "new and higher form of being" is achieved when coordination compounds are prepared in these ways. The knowledge and preparative skills of individual chemists are applied to the synthesis of new coordination compounds. Descriptions of the compounds become part of the literature and tradition of the discipline and, based on this knowledge, new coordination compounds are synthesized. A continuing cycle of chemical thesis, antithesis, and synthesis occurs each day all over the world wherever chemists are working.

This volume is a case in point. Coordination chemistry practiced behind the old Iron Curtain had a rich, full history but much of the knowledge was not transferred easily across political barriers to the United States and other countries. The same was true in the other direction. Today, however, the barriers have fallen. We have collaborated freely on this text, often over great distances and occasionally within the same room. We have written, revised, updated, and expanded this manuscript without regard to our individual locations around the globe.

The first coordination compound synthesized in the laboratory was Berlin blue, prepared in 1704 by Disbach, so it is obvious that preparative coordination chemistry has an extensive history. At times syntheses were unpredictable, unsuccessful, or unreported. Today, coordination chemists plan their syntheses by applying fundamental chemical principles and theories. For this reason we begin with a chapter describing classical theoretical concepts that are important in the synthesis of coordination compounds before we consider other issues such as solvents, reactive intermediates, reagents, *etc.*

The manuscript was prepared using Microsoft Word 5.1a for the Macintosh®. Figures and Schemes were prepared with Chem Draw Plus® and molecular structures were generated from the original atomic coordinates with Ball&Stick®.

¹*The American Heritage Dictionary*, 2nd edition (Houghton Mifflin, New York, 1985).

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LIST OF ABBREVIATIONS

Ac	acetyl
Alk	alkyl
A _N	acceptor number
Ar	aryl
Bu	butyl
bipy	2,2'-bipyridyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
cod	cycloocta-1,5-diene
cot	cycloocta-1,3,5,7-tetraene
Cy	cyclohexyl
DEA	<i>N,N'</i> -diethylacetamide
DEF	<i>N,N'</i> -diethylformamide
DMA	<i>N,N'</i> -dimethylacetamide
DME	dimethoxyethane
DMF	<i>N,N'</i> -dimethylformamide
DMP	2,2-dimethoxypropane
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
DMSO	dimethyl sulfoxide
D _N	donor number
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
en	ethylenediamine
Et	ethyl
Hacac	acetylacetone
H ₂ acacen	the Schiff base derived from two moles acetylacetone and one mole ethylenediamine
HMP	hexamethylphosphotriamide
H ₂ sal	salicylic acid
H ₂ salen	the Schiff base derived from two moles salicaldehyde and one mole ethylenediamine
H ₂ salophen	the Schiff base derived from two moles salicaldehyde and one mole <i>o</i> -phenylenediamine
H ₂ tpp	5,10,15,20-tetraphenylporphyrin
L	ligand
M	metal or metal ion
Me	methyl
Np	naphthalene
Ph	phenyl
Pr	propyl

LIST OF ABBREVIATIONS, CONTINUED

solv	solvent molecule
phen	1,10-phenanthroline
pic	picoline (methylpyridine)
[PPN] ⁺	μ-nitrido-bis(triphenylphosphorus)(1+)
py	pyridine
TCNE	tetracyanoethylene
TCNQ	tetracyanoquinodimethane
TEOF	triethylorthoformate
THF	tetrahydrofuran
thio	thiourea
TMAO	trimethylamine <i>N</i> -oxide
TMOF	trimethylorthoformate
TMP	trimethylphosphate
TMSO	tetramethylene sulfoxide
trpy	2,2',2''-terpyridyl

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