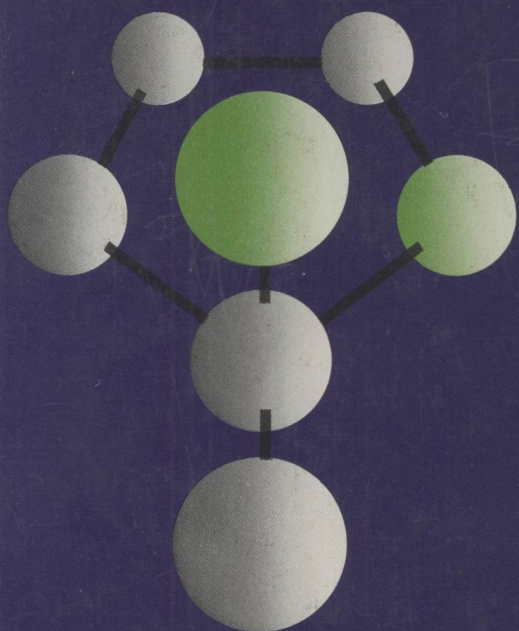
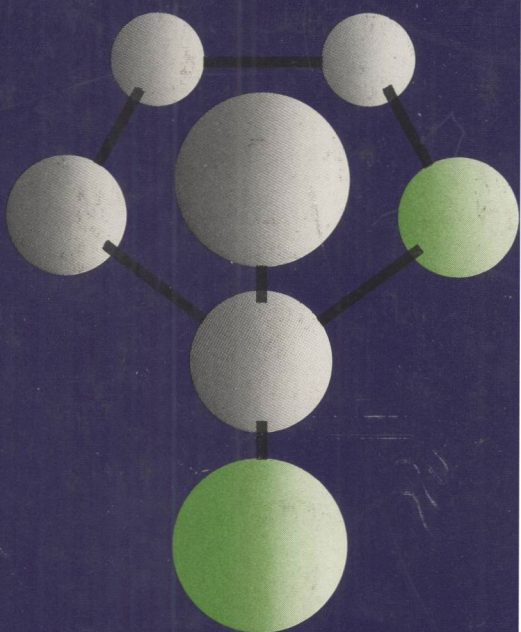


stereochemistry of organometallic and inorganic compounds



Volume 3: Chemical Bonds - Better Ways to Make Them and Break Them

Ivan Bernal (editor)



Elsevier

stereochemistry of organometallic and inorganic compounds 3

Chemical Bonds Better Ways to Make Them and Break Them

Edited by

IVAN BERNAL

Department of Chemistry, University of Houston, Houston TX 77004, U.S.A.



ELSEVIER

Amsterdam — Oxford — New York — Tokyo 1989

ELSEVIER SCIENCE PUBLISHERS B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands .

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
655, Avenue of the Americas
New York, NY 10010, U.S.A.

ISBN 0-444-88082-8

© Elsevier Science Publishers B.V., 1989

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V./ Physical Sciences & Engineering Division, P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Special regulations for readers in the USA – This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the publisher.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

Printed in The Netherlands

stereochemistry of organometallic and inorganic compounds 3

Chemical Bonds—Better Ways to Make Them and Break Them

Preface to Volume 3

As the twenty first century approaches us, a new era appears in the horizon--the era of the environmentalist-- or so it seems to me.

In this dawning era, our need to survive in an esthetically satisfying environment will place heavy demands on our future treatment of our planet, and nowhere will that demand be greatest than in our handling of our chemical industry. We can no longer live without it-- the question is "can we learn to live, safely and well, with it"?

There is a difference between an ordinary ballet performance and watching Moira Shearer dancing in *Tales of Hoffmann* or *The Red Shoes*-- it is elegance! The movements are the same, but the outcome is not, and the difference is what provides such joy to watch.

So it must be with our future chemistry-- it can no longer be only effective, it must be elegant so as to safely and efficiently provide for our most subtle needs.

The authors of the five chapters of this volume have reviewed for us how to understand the making and breaking of bonds at the dawn of what I perceive to be a more sophisticated era-- one in which we efficiently make and break bonds, but do so in a stereochemically correct manner, when such requirement is needed. These authors have summarized for us how to better understand bonds and the ways for making them and breaking more elegantly-- hopefully, some day, as elegantly and esthetically pleasing as Ms. Shearer's terpsichorean art.

Chapter 4 summarizes the fundamentals of bonding in organometallic clusters and provides the basis for the making and breaking bonds which, efficiently, do your bidding; i.e, they have, or do, the right chemistry and stereochemistry.

In Chapter 1, Braunstein and Rose show us how to create clusters which are either chemically and stereochemically correct,

or correctly catalyze the formation of new bonds. The rules for understanding the making and breaking of such bonds, either for syntheses or catalyses, are discussed by Osella and Raithby in Chapter 4.

Some of the art of making and breaking bonds is discussed in Chapters 2, 3 and 5. Blackburn, Davies and Whittaker discuss the stereochemistry of a class of organometallics which the senior author has made into an effective group of smooth and efficient, stereospecific catalysts.

The use of solar energy is one of the imperatives of the new era. Thus, an understanding of photochemical processes for making and breaking bonds, in sophisticated new ways, is one of our pressing needs. Stufkens, in Chapter 3, addresses the problem of understanding the mechanism(s) of creating photoproducts which are useful or can do useful chemistry and stereochemistry for us.

Finally, one of the active participants in documenting the power and sophistication of the Sakurai Reaction kindly agreed to review it for this volume. His contribution appears in Chapter 5.

I hope readers agree that the dawn of the era of elegance are clear in these pages. Hopefully, subsequent volumes will measure to the standards of this one and educate us in the existence of sophistication in other areas of organometallic and inorganic chemistry yet unexplored by this series.

Finally, I should mention that this volume should have appeared in the Fall of 1988. This delay was caused by unexpected responsibilities and to the extent it caused anxiety to the authors, and dated by a few months their reviews, I apologize and thank them for their forbearance.

May 16th, 1989

The Editor.

Contributors to this Volume

B.K. Blackburn

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QY, United Kingdom

P. Braunstein

Département de Chimie, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal,
F-67070 Strasbourg, France

S.G. Davies

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QY, United Kingdom

D. Osella

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino,
Via P. Giuria 7, 10125 Torino, Italy

P.R. Raithby

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom

J. Rose

Département de Chimie, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal,
F-67070 Strasbourg, France

N. Sasaki

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan 980

D.J. Stufkens

Anorganisch Chemisch Laboratorium, University of Amsterdam, J.H. van 't Hoff Instituut,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

M. Whittaker

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QY, United Kingdom

Y. Yamamoto

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan 980

TABLE OF CONTENTS

Preface to Volume 3	V
Contributors to this Volume	IX

Chapter 1

Heterometallic Clusters in Catalysis

P. Braunstein and J. Rose

1. General Introduction	5
2. Heterometallic Clusters in Homogeneous Catalysis	9
3. Hybrid Catalysts Prepared from Molecular Mixed-Metal Clusters	64
4. Heterometallic Clusters in Heterogeneous Catalysis	76
5. Acknowledgements	119
6. References	124

Chapter 2

**Conformational Analysis for Ligands Bound to the Chiral Auxiliary
[(C₅H₅)Fe(CO)(PPh₃)]**

B.K. Blackburn, S.G. Davies and M. Whittaker

1. Introduction	143
2. The Chiral Auxiliary [(C ₅ H ₅)Fe(CO)(PPh ₃)]	143
3. Conformational Analysis for [(C ₅ H ₅)Fe(CO)(PPh ₃)CH ₂ R]	146
4. Conformational Analysis for [(C ₅ H ₅)Fe(CO)(PPh ₃)CH ₂ XR]	161
5. Conformational Analysis for [(C ₅ H ₅)Fe(CO)(PPh ₃)CHRR']	168
6. Stereoelectronic Effects	175
7. Conformational Analysis for [(C ₅ H ₅)Fe(CO)(PPh ₃)C(OMe)R] ⁺	177
8. Conformational Analysis for [(C ₅ H ₅)Fe(CO)(PPh ₃)COR]	184
9. Stereoselective Reactions of Ligands Attached to the Chiral Auxiliary [(C ₅ H ₅)Fe(CO)(PPh ₃)]	193
10. The Chiral Auxiliary [(C ₅ H ₅)Re(NO)(PPh ₃)]	208
11. Conclusions	218
12. Acknowledgements	219
13. References	219

Chapter 3

**Steric and Electronic Effects on the Photochemical Reactions of Metal-Metal
Bonded Carbonyls**

D.J. Stufkens

1. List of Abbreviations	226
2. Introduction	227
3. M ₂ (CO) ₁₀ (M = Mn, Re)	228
4. M ₂ (CO) ₈ (diimine) (M = Mn, Re)	262
5. Cp ₂ M ₂ (CO) ₆ (M = Mo, W)	268
6. Cp ₂ Fe ₂ (CO) ₄	277
7. Heterodinuclear Metal Carbonyls	286
8. Concluding Remarks	290

Chapter 4**Stereochemical Aspects of Organometallic Clusters. A View of the Polyhedral Skeletal Electron Pair Theory***D. Osella and P.R. Raithby*

1. Introduction	304
2. Synthesis	305
3. Structures of and Rationalisation of Bonding in Alkyne-substituted Clusters	317
4. Reactivity	331
5. Dynamics	347
6. Conclusion	354
7. Acknowledgements	354

Chapter 5**The Stereochemistry of the Sakurai Reaction***Y. Yamamoto and N. Sasaki*

1. Introduction	365
2. Intermolecular Reactions	371
3. Intramolecular Reactions	407
4. Optically Active Allylsilanes	415
5. Other Reactions	419
6. Concluding Remarks	426
7. References and Notes	427
8. Added in Proof	438
 SUBJECT INDEX	 443

HETEROMETALLIC CLUSTERS IN CATALYSIS

P. Braunstein and J. Rose

HETEROMETALLIC CLUSTERS IN CATALYSIS

P. BRAUNSTEIN and J. ROSE

Département de Chimie, Institut Le Bel
Université Louis Pasteur
4, rue Blaise Pascal
F-67070 Strasbourg (France)

1. GENERAL INTRODUCTION
2. HETEROMETALLIC CLUSTERS IN HOMOGENEOUS CATALYSIS
 - 2.1. INTRODUCTION
 - 2.2. HYDROGENATION REACTIONS
 - 2.2.1. HYDROGENATION AND ISOMERIZATION OF CARBON-CARBON MULTIPLE BONDS
 - 2.2.2. CO HYDROGENATION
 - 2.3. WATER-GAS SHIFT REACTION
 - 2.4. HYDROFORMYLATION REACTIONS
 - 2.5. CARBONYLATION REACTIONS
 - 2.6. METHANOL HOMOLOGATION
 - 2.7. NORBORNADIENE DIMERIZATION
 - 2.8. BUTADIENE OLIGOMERIZATION
 - 2.9. HYDROSILATION REACTIONS
 - 2.10. CONCLUSION
3. HYBRID CATALYSTS PREPARED FROM MOLECULAR MIXED-METAL CLUSTERS
 - 3.1. INTRODUCTION
 - 3.2. CATALYSIS BY IMMOBILIZED MIXED-METAL CLUSTERS ON INORGANIC OXIDES
 - 3.3. CATALYSIS BY IMMOBILIZED MIXED-METAL CLUSTERS ON FUNCTIONALIZED SUPPORTS
 - 3.4. BIMETALLIC CLUSTERS IN ZEOLITES
 - 3.5. CONCLUSION
4. HETEROMETALLIC CLUSTERS IN HETEROGENEOUS CATALYSIS
 - 4.1. INTRODUCTION
 - 4.2. PREPARATION OF MIXED-METAL CLUSTER-DERIVED CATALYSTS
 - 4.3. INTERACTIONS OF MIXED-METAL CLUSTERS WITH CATALYTIC SUPPORTS
 - 4.4. OCCURRENCE OF HETEROMETALLIC INTERACTIONS IN MIXED-METAL CLUSTER-DERIVED CATALYSTS

4.5. REACTIONS INVOLVING HETEROGENEOUS MIXED-METAL CLUSTER-DERIVED CATALYSTS

4.5.1. HYDROCARBON SKELETAL REARRANGEMENTS

4.5.2. HYDROGENATION REACTIONS

4.5.2.1. Hydrogenation of Carbon-Carbon Multiple Bonds

4.5.2.2. Hydrogenation of CO and CO₂

4.5.2.3. Hydrogenation of Ketones

4.5.3. HYDROFORMYLATION OF OLEFINS

4.5.4. REDUCTIVE CARBONYLATION OF NITRO DERIVATIVES

4.5.5. HYDRODESULFURIZATION

4.6. CONCLUSION

5. ACKNOWLEDGEMENTS

6. REFERENCES

ABBREVIATIONS

acac	acetylacetonato
Bu	butyl
COANE	cyclooctane
COD	cyclooctadiene
COENE	cyclooctene
Cp	η^5 -cyclopentadienyl (η -C ₅ H ₅)
Cy	cyclohexyl
DMF	dimethylformamide
DPAE	1,2-bis(diphenylarsino)ethane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
Et	ethyl
Me	methyl
<i>o</i> -MeC ₆ H ₄	<i>o</i> -tolyl
MMCD	mixed-metal cluster-derived catalyst
NBD	norbornadiene
OAc	acetate
Ph	phenyl
Py	pyridine
PPN	bis(triphenylphosphine)iminium
R.T.	room temperature
THF	tetrahydrofuran
TMBA	trimethyl(benzyl)ammonium
TOF	turnover frequency
Tol	tolyl
[M _x M' _y]	heterogeneous catalyst prepared from a molecular cluster of metal core composition M _x M' _y
WGS	water gas shift reaction

1. GENERAL INTRODUCTION

Metal cluster chemistry, which involves compounds displaying direct metal-metal interactions, provides a shining example of the fruitful interactions that can occur between various disciplines and of the subsequent cross-fertilization in the frontier areas. Cluster compounds are encountered in molecular and solid state chemistry; they belong to organometallic and inorganic chemistry and their properties arouse the interest of physicists (*e.g.*, superconductivity), of biochemists (*e.g.*, multimetallic redox centers), of academic and industrial researchers studying new materials and catalysts, and of course, of the chemists themselves. They encompass interests in main group elements or transition metals, in synthetic organic or inorganic chemistry, in theoretical, mechanistic or analytical chemistry. These areas of scientific activity do not constitute a restricted list but they already explain the exponential growth that cluster chemistry has enjoyed over the last 15 years [170].

In order for new materials to be evaluated and for new properties to emerge, the synthetic chemist must have first created the new molecules or materials of interest. Cluster chemists have displayed great skill and imagination in the synthesis and structural characterization of novel and complex molecules. Rational synthetic methods have emerged which allow, in many instances, the designed synthesis of molecules containing, *e.g.*, a specific number of different metal atoms bonded to each other or to given ligands in an unusual mode of attachment [249, 292, 303]. Beautiful achievements include tetrahedral clusters with four different metal atoms [247] (Fig. 1.1), and thus inherently chiral, and large bimetallic clusters, *e.g.*,

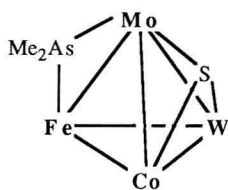


Fig. 1.1. Metal core structure of $\text{FeCoMoW}(\mu_3\text{-S})(\mu\text{-AsMe}_2)(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_7$, the first cluster with four different metal atoms [247].

$[\text{Ag}_{12}\text{Au}_{13}\text{Cl}_6(\text{PPh}_3)_{12}]^{m+}$ [294] (Fig. 1.2), $[\text{Ag}_{19}\text{Au}_{18}\text{Br}_{11}\{\text{P}(p\text{-Tol})_3\}_{12}]^{2+}$ [295a] and $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$ ($n = 5,4$) [72] (Fig.1.3), a molecular model of "cherry" crystallites studied in heterogeneous catalysis.

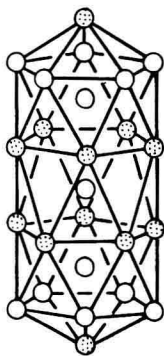


Fig. 1.2. Metal core of $[\text{Ag}_{12}\text{Au}_{13}\text{Cl}_6(\text{PPh}_3)_{12}]^{m+}$ [294].

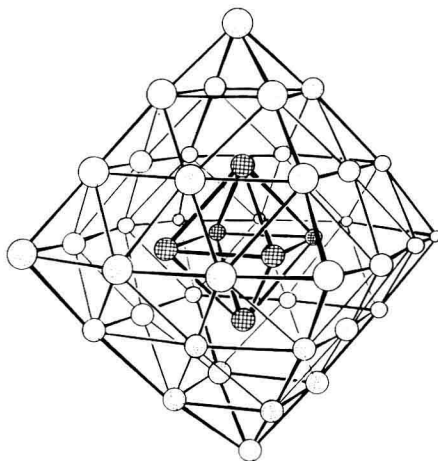


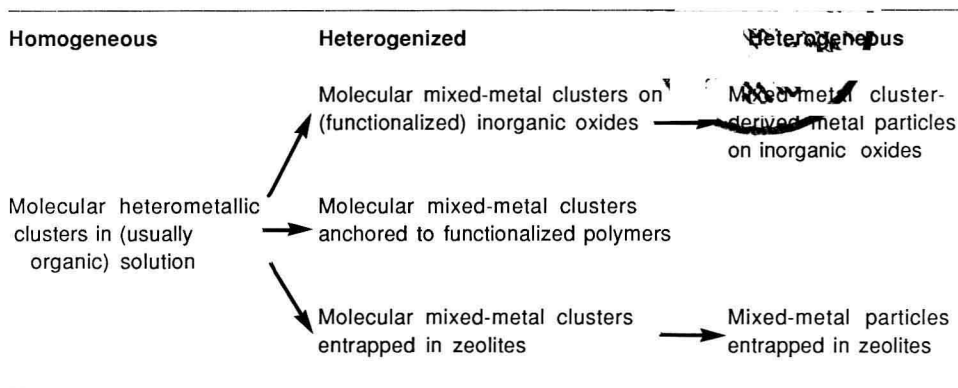
Fig. 1.3. Metal core of $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$ ($n = 5,4$) [72].

Obviously, the diversity and complexity of clusters containing more than one metal type are considerable and largely justify the current efforts to better understand their synthesis, structures and physical and chemical (stoichiometric and catalytic) properties.

The goal of this chapter is to evaluate the achievements and potential in catalysis of heterometallic transition metal clusters (including heterodinuclear complexes), *i.e.*, of well-defined and characterized molecular compounds containing at least two different transition metal atoms in their core. Bimetallic catalysis has become an area of major interest and applies to homogeneous, heterogenized or heterogeneous processes [320], as shown in Scheme 1.1.

SCHEME 1.1.

Uses of Mixed-Metal Clusters in Catalysis.



The concept of synergism in homogeneous catalysis has been discussed by Golodov [132]: "Synergism may be defined as a disproportionate increase in reaction rate observed upon mixing two catalytic systems, both of which will individually catalyze the reaction in question" [98]. However, caution must be taken when interpreting the enhanced rate effects caused by added metal complexes [291]. On the other hand, the increased diversity and availability of mixed-metal clusters, for which many high-yield syntheses have been reported and will continue to appear in series such as *Inorganic Syntheses*, have stimulated a considerable academic and industrial research interest for their catalytic properties [126]. These efforts are encouraged by the exact knowledge of the molecular structure and stereochemistry of an increasing number of mixed-metal clusters. The importance of heterometallic clusters for catalysis is based on the following reasons: (i) the adjacent metal centers offer the possibility for cooperative reactivity and the intrinsic polarity of heterometallic bonds [49] can direct the selectivity of substrate-cluster interactions [264]. This may lead to

new, more active, or more selective homogeneous or heterogenized (by attachment of the clusters to solid supports) catalysts; (ii) the metal core of these clusters constitutes a well defined unit, which may be viewed as a molecular microalloy and which can be used as a precursor of novel heterogeneous catalysts. Stripping off the ancillary ligands is expected to provide catalytic materials with improved control of both particle size and composition; (iii) the knowledge of the precise structural and spectroscopic properties of atoms or ligands bound to the metal frameworks allows one to establish and evaluate conceptual and comparative models for understanding the coordination of these species, *e.g.*, H, N, NH, O, S, C, CO, CH, CH₂, CH₃, C₂H₃, to metal surfaces.

In this chapter, we shall restrict ourselves to studies in which well-characterized mixed-metal cluster compounds of the transition metals (including Cu, Ag and Au) have been used in catalysis. We will therefore not discuss situations where a mixture of homonuclear complexes of different metals has been used, except when comparisons have been made with the corresponding heterometallic precursors. We recognize that this distinction is somewhat arbitrary as mixed-metal complexes are often likely to fragment into homonuclear species under the catalytic conditions while, conversely, they may be produced *in situ* upon mixing of the individual metal complexes. Similarly, alloy formation may occur during catalysis with heterogeneous catalysts prepared from different homonuclear systems. Furthermore, it has been shown that the presence of a mixture of homonuclear, even mononuclear, complexes of different metals can be most beneficial for a given catalytic process, consecutive elementary steps occurring at each metal center. This is particularly notable, *e.g.*, in the formation of ethylene glycol from CO and H₂, catalyzed by Ru/Rh systems [97] and in the methanol homologation reaction, catalyzed by Ru/Co systems [128]. Other approaches consisting of, *e.g.*, using metal vapor chemistry for preparing metal clusters and catalysts [181, 222] will not be considered here.

The following Sections are organized according to the ways of utilizing mixed-metal clusters in catalysis, as summarized in Scheme 1.1.