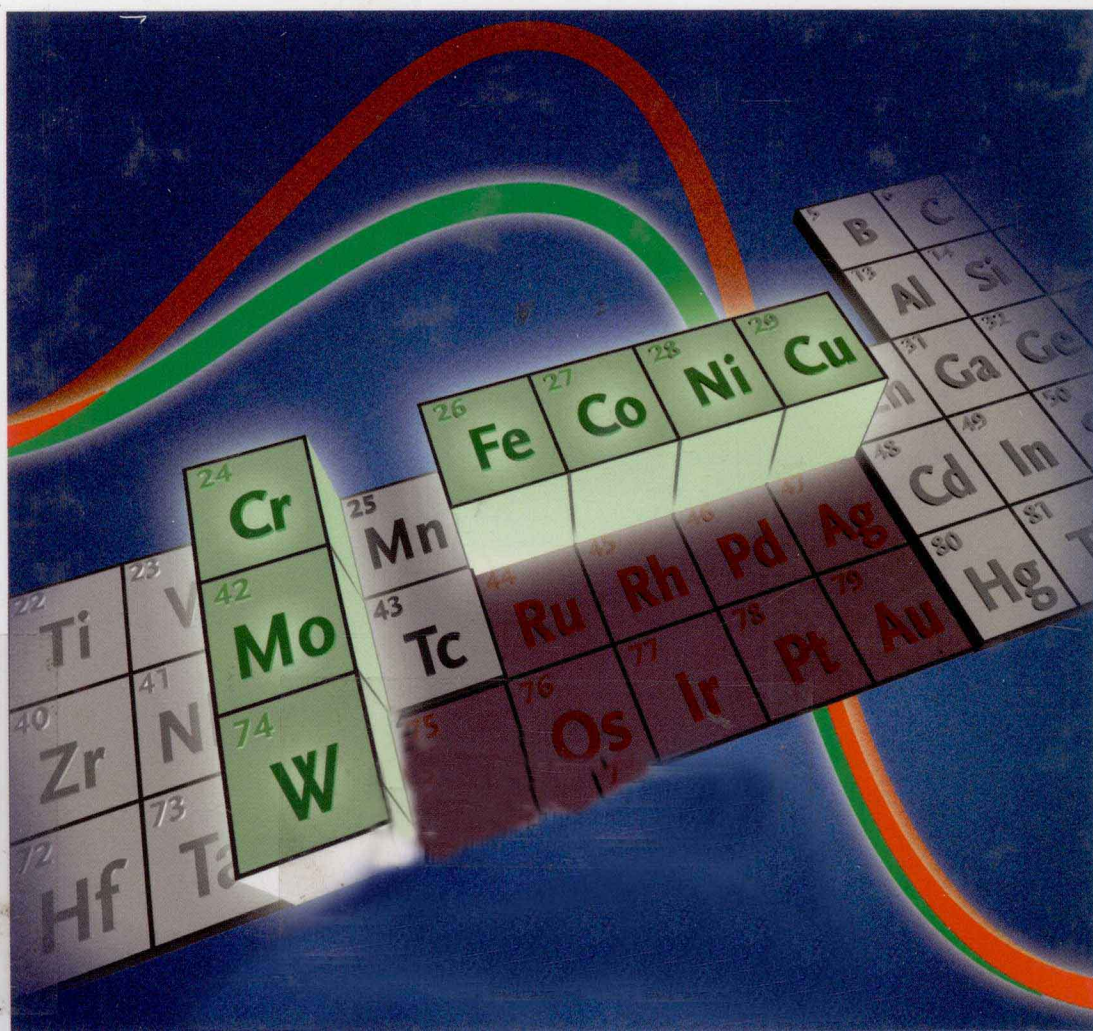


Edited by R. Morris Bullock

 WILEY-VCH

Catalysis Without Precious Metals



Edited by R. Morris Bullock

Catalysis Without Precious Metals



**WILEY-
VCH**

WILEY-VCH Verlag GmbH & Co. KGaA

The Editor

Dr. R. Morris Bullock

Pacific Northwest National
Laboratory
P.O. Box 999, K2-57
Richland, WA 99352
USA

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2010 Wiley-VCH Verlag & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Cover Design Graphik-Design Schulz,
Fußgönheim

Typesetting Toppan Best-set Premedia Limited,
Hong Kong

Printing and Binding Fabulous Printers Pte Ltd,
Singapore

Printed in Singapore
Printed on acid-free paper

ISBN: 978-3-527-32354-8

Preface

Many of the greatest success stories of organometallic and inorganic chemistry are in the application of metal complexes to catalytic reactions. In many cases, precious metals perform the heavy lifting, breaking H–H bonds, forming C–H or C–C bonds, etc. Precious metals have become so familiar in these roles that in some cases the precious metal and their catalytic reactivity seem almost inextricably linked. Wilkinson's catalyst, a rhodium complex, played a pivotal role in our understanding of hydrogenations. More recently, Noyori and co-workers developed remarkably reactive ruthenium complexes for asymmetric catalytic hydrogenations of C=O bonds. Over 150 years have passed since the discovery of a fuel cell that oxidizes hydrogen, yet modern low-temperature fuel cells still require platinum. Many carbon-carbon coupling reactions used extensively in organic synthesis function efficiently with extremely low loadings of palladium catalysts.

Kicking old habits is never easy, despite the allure of significant rewards for making the desired change. Yet we now know that the use of precious metals in catalysis is not always required. The research presented in this book shows how new catalysts that do not require precious metals may ultimately supplant the use of precious metals in some types of reactions. This book also highlights the challenges remaining in the development of catalysts that do not require precious metals. The pathway to devising new types of catalysts using abundant metals often involves scrutiny of reaction mechanisms that could potentially accomplish the desired goal, and finding ways to coerce inexpensive, abundant metals into accomplishing that task. In many cases those mechanisms are altogether different from those used in traditional precious metal catalysts. As can be seen in different chapters in this book, some of the catalytic reactions that use cheap metals are already competitive with well-known reactions that use precious metals. Even in new catalysts that do not yet exhibit rates or lifetimes that compare favorably to long-established and well-optimized precious metal catalysts, fundamentally new reactivity patterns have been discovered, and new classes of catalysts have been developed. This book provides detailed information on many types of reactions that can be catalyzed without the need for precious metals. I hope that these chapters may inspire others to join in the pursuit of "cheap metals for noble tasks."

Research on alternatives to precious metal catalysts has been growing rapidly in recent years, and expected to experience increased growth in the future. The most

obvious reason for replacing precious metals is that they are very expensive, often costing more than 100 or 1000 times the cost of base metals. The high cost is obviously connected to the low abundance of these metals. High cost alone is not the only reason, however; in some cases specialized organic ligands (used in asymmetric catalysis, for example) cost more than the metal. Substantial costs are involved in industrial processes when recovery and recycle of the metal is required. Another attribute of avoiding precious metals is that some metals like iron have a minimal environmental and toxicological impact. Importantly, some large-scale uses in energy storage and conversion currently being considered would require large amounts of precious metals. In automotive transportation, for example, conversion to a “hydrogen economy” based entirely on fuel cells that require platinum would not be feasible, not only due to the high cost, but because there is not enough platinum available to accommodate such a huge scale of usage.

The order of the chapters in this book follows their order in periodic table, starting at the first row of group 6 (Norton’s chapter on chromium catalysts) and continuing to Group 6 metals molybdenum and tungsten. While most of the inexpensive, abundant metals are from the first row of the periodic table, molybdenum and tungsten (from the second and third row of the periodic table) are exceptions, as they are much less expensive than precious metals. Subsequent chapters focus on catalysis by iron (Group 8), cobalt (Group 9), nickel (Group 10) and copper (Group 11). The last chapter highlights new catalysts that have no transition metals at all, using the main group elements phosphorus and boron. The cover highlights the inexpensive, abundant metals that are discussed in this book, with those metals being highlighted in green, and the precious metals of low abundance and high cost being shown in red. Manganese is abundant and inexpensive, and offers appealing opportunities for development into catalytic reactions. But since no chapters in this book focus on Mn, so it was not shown in green on the cover.

This book focuses on homogeneous (molecular) catalysts. There is a need to replace precious metals used in heterogeneous catalysis as well, but that topic is beyond the scope of material that can be covered in one book.

I sincerely thank all of the authors of the chapters in this book. They contributed their expertise and time in the writing of their chapters, and gracefully put up with annoying e-mails and editorial suggestions from me. I appreciate the enthusiasm they share for developing the chemistry of abundant, inexpensive metals as attractive alternatives to precious metals. Paul Chirik and Jack Norton gave me very helpful advice in the planning of this book.

I am deeply indebted to many scientific colleagues who have influenced my thinking, and who helped teach me chemistry over the years. In particular, Carol Creutz (Brookhaven National Laboratory) and Dan DuBois (Pacific Northwest National Laboratory) have both been extremely generous with their time and patient with my questions. I thank my scientific mentors, Chuck Casey and Jack Norton, for invaluable advice on many topics for more than twenty-five years.

It was a pleasure to work with Dr. Heike Nöthe at Wiley-VCH, and with Dr. Manfred Köhl in the early stages of preparations and planning for this book.

I dedicate this book to my wife, Cindy, to my son, Claude, and to my daughter, Lindsay. I thank them for being immensely supportive, including times when I was in the lab or my office rather than at home.

June 2010

R. Morris Bullock

List of Contributors

Ryan D. Baxter

University of Michigan
Department of Chemistry
930 North University Avenue
Ann Arbor, MI 48109-1055
USA

Renee Becker

University of Rochester
Department of Chemistry
Rochester, NY 14627
USA

R. Morris Bullock

Pacific Northwest National Laboratory
Chemical and Materials Sciences
Division
P.O. Box 999
K2-57
Richland, WA 99352
USA

Paul J. Chirik

Cornell University
Department of Chemistry and
Chemical Biology
Baker Laboratory
Ithaca, NY 14853
USA

Daniel L. DuBois

Pacific Northwest National Laboratory
Chemical and Materials Sciences
Division
Richland, WA 99352
USA

M. Rakowski DuBois

Pacific Northwest National Laboratory
Chemical and Materials Sciences
Division
Richland, WA 99352
USA

M. G. Finn

The Scripps Research Institute
Department of Chemistry
10550 North Torrey Pines Road
La Jolla, CA 92037
USA

Valery V. Fokin

The Scripps Research Institute
Department of Chemistry
10550 North Torrey Pines Road
La Jolla, CA 92037
USA

Vernon C. Gibson

Imperial College
Department of Chemistry
South Kensington Campus
London SW7 2AZ
UK

John Hartung

Columbia University
Department of Chemistry
3000 Broadway
New York, NY 10027
USA

Yongwen Jiang

Chinese Academy of Sciences
Shanghai Institute of Organic
Chemistry
State Key Laboratory of Bioorganic
and Natural Products Chemistry
354 Fenglin Lu
Shanghai 200032
China

William D. Jones

University of Rochester
Department of Chemistry
Rochester, NY 14627
USA

Dawei Ma

Chinese Academy of Sciences
Shanghai Institute of Organic
Chemistry
State Key Laboratory of Bioorganic
and Natural Products Chemistry
354 Fenglin Lu
Shanghai 200032
China
Hasnain A. Malik
University of Michigan
Department of Chemistry
930 North University Avenue
Ann Arbor, MI 48109-1055
USA

John Montgomery

University of Michigan
Department of Chemistry
930 North University Avenue
Ann Arbor, MI 48109-1055
USA

Jack R. Norton

Columbia University
Department of Chemistry
3000 Broadway
New York, NY 10027
USA

Richard R. Schrock

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139
USA

Gregory A. Solan

University of Leicester
Department of Chemistry
University Road
Leicester LE1 7RH
UK

Douglas W. Stephan

University of Toronto
Department of Chemistry
80 St. George St.
Toronto
Ontario
Canada M5S 3H6

Contents

Preface XIII

List of Contributors XVII

1 Catalysis Involving the H[•] Transfer Reactions of First-Row Transition Metals 1

John Hartung and Jack R. Norton

- 1.1 H[•] Transfer Between M–H Bonds and Organic Radicals 2
- 1.2 H[•] Transfer Between Ligands and Organic Radicals 4
- 1.3 H[•] Transfer Between M–H and C–C Bonds 7
- 1.4 Chain Transfer Catalysis 11
- 1.5 Catalysis of Radical Cyclizations 15
- 1.6 Competing Methods for the Cyclization of Dienes 19
- 1.7 Summary and Conclusions 20
- References 21

2 Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum 25

Richard R. Schrock

- 2.1 Introduction 25
- 2.2 Some Characteristics of Triamidoamine Complexes 26
- 2.3 Possible [HIPTN₃N]Mo Intermediates in a Catalytic Reduction of Molecular Nitrogen 30
 - 2.3.1 MoN₂ and MoN₂[−] 30
 - 2.3.2 Mo–N=NH 33
 - 2.3.3 Conversion of Mo(N₂) into Mo–N=NH 33
 - 2.3.4 [Mo=N–NH₂]⁺ 35
 - 2.3.5 Mo≡N and [Mo=NH]⁺ 36
 - 2.3.6 Mo(NH₃) and [Mo(NH₃)]⁺ 37
- 2.4 Interconversion of Mo(NH₃) and Mo(N₂) 38
- 2.5 Catalytic Reduction of Dinitrogen 39
- 2.6 MoH and Mo(H₂) 41
- 2.7 Ligand and Metal Variations 44
- 2.8 Comments 47
- Acknowledgements 48
- References 48

3	Molybdenum and Tungsten Catalysts for Hydrogenation, Hydrosilylation and Hydrolysis	51
	<i>R. Morris Bullock</i>	
3.1	Introduction	51
3.2	Proton Transfer Reactions of Metal Hydrides	52
3.3	Hydride Transfer Reactions of Metal Hydrides	54
3.4	Stoichiometric Hydride Transfer Reactivity of Anionic Metal Hydride Complexes	56
3.5	Catalytic Hydrogenation of Ketones with Anionic Metal Hydrides	58
3.6	Ionic Hydrogenation of Ketones Using Metal Hydrides and Added Acid	59
3.7	Ionic Hydrogenations from Dihydrides: Delivery of the Proton and Hydride from One Metal	64
3.8	Catalytic Ionic Hydrogenations With Mo and W Catalysts	65
3.9	Mo Phosphine Catalysts With Improved Lifetimes	69
3.10	Tungsten Hydrogenation Catalysts with N-Heterocyclic Carbene Ligands	70
3.11	Catalysts for Hydrosilylation of Ketones	71
3.12	Cp ₂ Mo Catalysts for Hydrolysis, Hydrogenations and Hydrations	73
3.13	Conclusion	78
	Acknowledgements	78
	References	79
4	Modern Alchemy: Replacing Precious Metals with Iron in Catalytic Alkene and Carbonyl Hydrogenation Reactions	83
	<i>Paul J. Chirik</i>	
4.1	Introduction	83
4.2	Alkene Hydrogenation	86
4.2.1	Iron Carbonyl Complexes	86
4.2.2	Iron Phosphine Compounds	89
4.2.3	Bis(imino)pyridine Iron Complexes	93
4.2.4	α-Diimine Iron Complexes	99
4.3	Carbonyl Hydrogenation	101
4.3.1	Hydrosilylation	101
4.3.2	Bifunctional Complexes	103
4.4	Outlook	105
	References	106
5	Olefin Oligomerizations and Polymerizations Catalyzed by Iron and Cobalt Complexes Bearing Bis(imino)pyridine Ligands	111
	<i>Vernon C. Gibson and Gregory A. Solan</i>	
5.1	Introduction	111
5.2	Precatalyst Synthesis	112

5.2.1	Ligand Preparation	112
5.2.2	Complexation with MX_2 ($\text{M} = \text{Fe}, \text{Co}$)	113
5.3	Precatalyst Activation and Catalysis	115
5.3.1	Olefin Polymerization	115
5.3.1.1	Catalytic Evaluation	116
5.3.1.2	Steric Versus Electronic Effects	116
5.3.1.3	Effect of MAO Concentration	119
5.3.1.4	Effects of Pressure and Temperature	120
5.3.1.5	α -Olefin Monomers	121
5.3.2	Olefin Oligomerization	122
5.3.2.1	Catalytic Evaluation	122
5.3.2.2	Substituent Effects	122
5.3.2.3	Schulz–Flory Distributions	124
5.3.2.4	Poisson Distributions	124
5.3.2.5	α -Olefin Monomers	125
5.4	The Active Catalyst and Mechanism	125
5.4.1	Active Species	125
5.4.1.1	Iron Catalyst	126
5.4.1.2	Cobalt Catalyst	127
5.4.2	Propagation and Chain Transfer Pathways/Theoretical Studies	127
5.4.3	Well-Defined Iron and Cobalt Alkyls	129
5.5	Other Applications	133
5.5.1	Immobilization	133
5.5.2	Reactor Blending and Tandem Catalysis	134
5.6	Conclusions and Outlook	134
	References	136
6	Cobalt and Nickel Catalyzed Reactions Involving C–H and C–N Activation Reactions	143
	<i>Renee Becker and William D. Jones</i>	
6.1	Introduction	143
6.2	Catalysis with Cobalt	143
6.3	Catalysis with Nickel	154
	References	163
7	A Modular Approach to the Development of Molecular Electrocatalysts for H_2 Oxidation and Production Based on Inexpensive Metals	165
	<i>M. Rakowski DuBois and Daniel L. DuBois</i>	
7.1	Introduction	165
7.2	Concepts in Catalyst Design Based on Structural Studies of Hydrogenase Enzymes	166
7.3	A Layered or Modular Approach to Catalyst Design	170
7.4	Using the First Coordination Sphere to Control the Energies of Catalytic Intermediates	171

7.5	Using the Second Coordination Sphere to Control the Movement of Protons between the Metal and the Exterior of the Molecular Catalyst	173
7.6	Integration of the First and Second Coordination Spheres	174
7.7	Summary	178
	Acknowledgements	179
	References	179
8	Nickel-Catalyzed Reductive Couplings and Cyclizations	181
	<i>Hasnain A. Malik, Ryan D. Baxter, and John Montgomery</i>	
8.1	Introduction	181
8.2	Couplings of Alkynes with α,β -Unsaturated Carbonyls	182
8.2.1	Three-Component Couplings via Alkyl Group Transfer—Methods Development	182
8.2.2	Reductive Couplings via Hydrogen Atom Transfer—Methods Development	184
8.2.3	Mechanistic Insights	186
8.2.3.1	Metallacycle-Based Mechanistic Pathway	186
8.2.4	Use in Natural Product Synthesis	189
8.3	Couplings of Alkynes with Aldehydes	191
8.3.1	Three-Component Couplings via Alkyl Group Transfer—Method Development	192
8.3.2	Reductive Couplings via Hydrogen Atom Transfer—Method Development	193
8.3.2.1	Simple Aldehyde and Alkyne Reductive Couplings	194
8.3.2.2	Directed Processes	196
8.3.2.3	Diastereoselective Variants: Transfer of Chirality	197
8.3.2.4	Asymmetric Variants	199
8.3.3	Mechanistic Insights	200
8.3.4	Cyclocondensations via Hydrogen Gas Extrusion	204
8.3.5	Use in Natural Product Synthesis	205
8.4	Conclusions and Outlook	210
	Acknowledgements	210
	References	210
9	Copper-Catalyzed Ligand Promoted Ullmann-type Coupling Reactions	213
	<i>Yongwen Jiang and Dawei Ma</i>	
9.1	Introduction	213
9.2	C–N Bond Formation	213
9.2.1	Arylation of Amines	213
9.2.1.1	Arylation of Aliphatic Primary and Secondary Amines	213
9.2.1.2	Arylation of Aryl Amines	215
9.2.1.3	Arylation of Ammonia	215
9.2.2	Arylation and Vinylation of N-Heterocycles	217

9.2.2.1	Coupling of Aryl Halides and N-Heterocycles	217
9.2.2.2	Coupling of Vinyl Bromides and N-Heterocycles	218
9.2.3	Aromatic Amidation	218
9.2.3.1	Cross-Coupling of aryl Halides with Amides and Carbamates	219
9.2.3.2	Cross-Coupling of Vinyl Halides with Amides or Carbamates	220
9.2.3.3	Cross-Coupling of Alkynyl Halides with Amides or Carbamates	220
9.2.4	Azidation	221
9.3	C–O Bond Formation	222
9.3.1	Synthesis of Diaryl Ethers	222
9.3.2	Aryloxylation of Vinyl Halides	223
9.3.3	Cross-Coupling of Aryl Halides with Aliphatic Alcohols	223
9.4	C–C Bond Formation	224
9.4.1	Cross-Coupling with Terminal Acetylene	224
9.4.2	The Arylation of Activated Methylene Compounds	225
9.4.3	Cyanation	227
9.5	C–S Bond Formation	228
9.5.1	The Formation of Bisaryl- and Arylalkyl-Thioethers	228
9.5.2	The Synthesis of Alkenylsulfides	229
9.5.3	Assembly of aryl Sulfones	229
9.6	C–P Bond Formation	230
9.7	Conclusion	230
	References	231

10 Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) 235

M.G. Finn and Valery V. Fokin

10.1	Introduction	235
10.2	Azide–Alkyne Cycloaddition: Basics	237
10.3	Copper-Catalyzed Cycloadditions	238
10.3.1	Catalysts and Ligands	238
10.3.2	CuAAC with In Situ Generated Azides	244
10.3.3	Mechanistic Aspects of the CuAAC	244
10.3.4	Reactions of Sulfonyl Azides	250
10.3.5	Copper-Catalyzed Reactions with Other Dipolar Species	251
10.3.6	Examples of Application of the CuAAC Reaction	252
10.3.6.1	Synthesis of Compound Libraries for Biological Screening	252
10.3.6.2	Copper-Binding Adhesives	253
10.3.7	Representative Experimental Procedures	255
	Acknowledgements	256
	References	257

11 “Frustrated Lewis Pairs”: A Metal-Free Strategy for Hydrogenation Catalysis 261

Douglas W. Stephan

11.1	Phosphine-Borane Activation of H ₂	263
11.2	“Frustrated Lewis Pairs”	264

XII | *Contents*

11.3	Metal-Free Catalytic Hydrogenation	267
11.4	Future Considerations	273
	Acknowledgements	273
	References	273

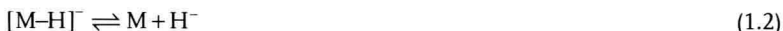
Index	277
--------------	-----

1

Catalysis Involving the H[•] Transfer Reactions of First-Row Transition Metals

John Hartung and Jack R. Norton

The M–H bonds of transition-metal hydride complexes may be cleaved heterolytically (H⁺, H[−] transfer) or homolytically (H[•] transfer). ΔG for the H⁺ transfer in Equation 1.1 is readily quantified by pK_a measurements (see Chapter 3). Analogous measurements for H[−] transfer, or “hydricities”, are difficult because the loss of H[−] generates a vacant coordination site. However, ΔG for Equation 1.2 can be determined indirectly, from electrochemical and pK_a measurements in the appropriate solvent [1, 2], and we can thus compare the “hydricities” of various hydride complexes (see Chapter 3). The lowest values of $\Delta G_{H^{\cdot}}$ (corresponding to the complexes most eager to transfer H[•]) are found for second- and third-row transition metals¹⁾ [3], which is why those (relatively expensive) metals are good H[−] donors and effective catalysts for reactions like ionic hydrogenation [5–10].



The thermodynamics of the homolytic cleavage of an M–H bond (1.3) are also available from electrochemical and pK_a measurements (the thermodynamic cycle in Equations 1.4–1.6). The oxidation potential is that of the one-electron process in Equation 1.5. If the pK_a is measured in CH₃CN, and the potential is measured relative to ferrocene/ferrocenium in that solvent, ΔG for Equation 1.3 in CH₃CN is given by Equation 1.7 [11, 12], while the bond dissociation energy (BDE) for Equation 1.3 (the traditional gas phase “bond strength”) is given by Equation 1.8²⁾.



1) For $[HM(P-P)_2]^+$, experiments show that $\Delta G_{H^{\cdot}}$ decreases in the order Ni > Pt > Pd; see reference [4].

2) The relative and absolute uncertainties in bond strengths determined in this way are discussed in reference [13].

Table 1.1 Bond dissociation energies of some chromium and vanadium hydrides.

Hydride	M–H BDE, kcal mol ^{−1}
CpCr(CO) ₃ H	62.2
dppm(CO) ₄ VH	57.9
dppe(CO) ₄ VH	57.5
dppp(CO) ₄ VH	56.0
dppb(CO) ₄ VH	54.9

$$\Delta G(\text{M–H})(\text{kcal mol}^{-1}) = 1.37\text{p}K_{\text{a}}(\text{M–H}) + 23.06(\text{M}^{\cdot-}/\text{M}^{\cdot}) + 53.6 \quad (1.7)$$

$$\text{BDE}(\text{M–H})(\text{kcal mol}^{-1}) = 1.37\text{p}K_{\text{a}} = 23.06E^{\circ} + 59.5 \quad (1.8)$$

Such measurements show the weakest M–H bonds to be those of first-row transition metals [4], and suggest that these (relatively abundant and cheap) metals are best for catalyzing reactions that involve H[•] transfer. Because most of these metals are nontoxic, their H[•] transfer reactions offer an attractive alternative to the tin-mediated radical chemistry that has become ubiquitous in organic synthesis.

Bond dissociation energies of most M–H bonds lie between 60 and 65 kcal mol^{−1} [4]. A few are much stronger: the Os–H bond of Cp(CO)₂OsH has a BDE ≥82 kcal mol^{−1} [14]. On the other hand V–H bonds are particularly weak. Calculations at the B3LYP level of theory on the hypothetical VH₅ give it the weakest M–H bond (43 kcal mol^{−1}) among neutral “valency-saturated” MH_{*n*} (i.e., among complexes where M forms the maximum number of M–H bonds) [15]. Experimentally Table 1.1 [13] shows very weak V–H bonds for (P–P)(CO)₄VH (P–P = Ph₂P(CH₂)_{*n*}PPh₂, with *n* = 1 (dppm), *n* = 2 (dppe), *n* = 3 (dppp), and *n* = 4 (dppb) [16, 17].

An H[•] transfer, or hydrogen atom transfer (HAT), reaction has been defined by Mayer as “the concerted movement of a proton and an electron ... in a single kinetic step where both ... originate from the same reactant and travel to the same product.” [18] Mayer considers HAT to be “one type of the broad class of proton-coupled electron transfer (PCET) reactions, which also includes reactions where the proton and electron are separated.” The distinction is a matter of ongoing discussion [19, 20], and other acronyms have been proposed [19, 21], but all the reactions to be considered in this chapter can be satisfactorily described as “H[•] transfer”.

1.1

H[•] Transfer Between M–H Bonds and Organic Radicals

HAT reactions from transition-metal hydrides to organic radicals R[•] (1.9) are characterized by second-order kinetics. Second-order kinetics have been

Table 1.2 Bond dissociation energies and rates of H[•] transfer to tris(*p*-*tert*-butylphenyl)methyl radical (extrapolated to room temperature) of several hydrides.

Hydride	BDE, kcal mol ⁻¹	<i>k</i> _H , M ⁻¹ s ⁻¹
Cp(CO) ₂ Fe–H	57 ^{a)}	1.2 × 10 ⁴
Cp(CO) ₃ Cr–H	62 ^{b)}	335
Cp(CO) ₂ Ru–H	65 ^{a)}	1.03 × 10 ³
(CO) ₄ Co–H	59, ^{c)} 67 ^{a)}	1.6 × 10 ³
(CO) ₅ Mn–H	68 ^{a)}	741
Cp(CO) ₃ Mo–H	69 ^{a)}	514
Cp(CO) ₃ W–H	72 ^{a)}	91
(CO) ₄ OsH ₂	78 ^{d)}	15.7

a) Ref [120].

b) Ref [13].

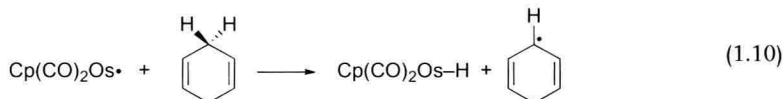
c) Ref [22].

d) Ref [23].

established (the rate constants are shown in Table 1.2) for the transfer of H[•] from a variety of hydrides to the tris(*p*-*tert*-butylphenyl)methyl radical [24–26]. The bulky *t*-Bu substituents keep it entirely monomeric in solution [27, 28]. Additional evidence that H[•] transfers to R[•] obey second-order kinetics is provided by studies of the last step in radical hydrogenation reactions (see Equations 1.14 and 1.15 below). If the hydride L_nM–H in a transfer such as Equation 1.9 is coordinatively saturated (18 electrons), the metalloradical L_nM[•] will have a 17 electron configuration.



Second-order kinetics have also been established for H[•] transfer in the reverse direction, that is, from R–H to M[•]. The rate constant for Equation 1.10, from 1,4-cyclohexadiene to Cp(CO)₂Os[•], has been measured by time-resolved IR spectroscopy as 2.1 × 10⁶ M⁻¹ s⁻¹ (23 °C, hexane) [14]. Intriguingly, H[•] can be abstracted by a photogenerated osmium metalloradical from even stronger C–H bonds, such as those of toluene and THF; photolysis of [Tp(CO)₂Os]₂ (Tp = tris(pyrazolyl) borate) in either of these solvents gives the osmium hydride. (The C–H bonds of toluene (90 kcal mol⁻¹ for the methyl group) and THF (92 kcal mol⁻¹) are considerably stronger than that of cyclohexadiene (77 kcal mol⁻¹) [14, 29].)



Steric factors can be important in H[•] transfer reactions. The rate constant (*k*_H) of H[•] transfer to tris(*p*-*tert*-butylphenyl)methyl radical decreases by a factor of 37 from Cp(CO)₃MoH to Cp^{*}(CO)₃MoH (which has an Mo–H bond of comparable