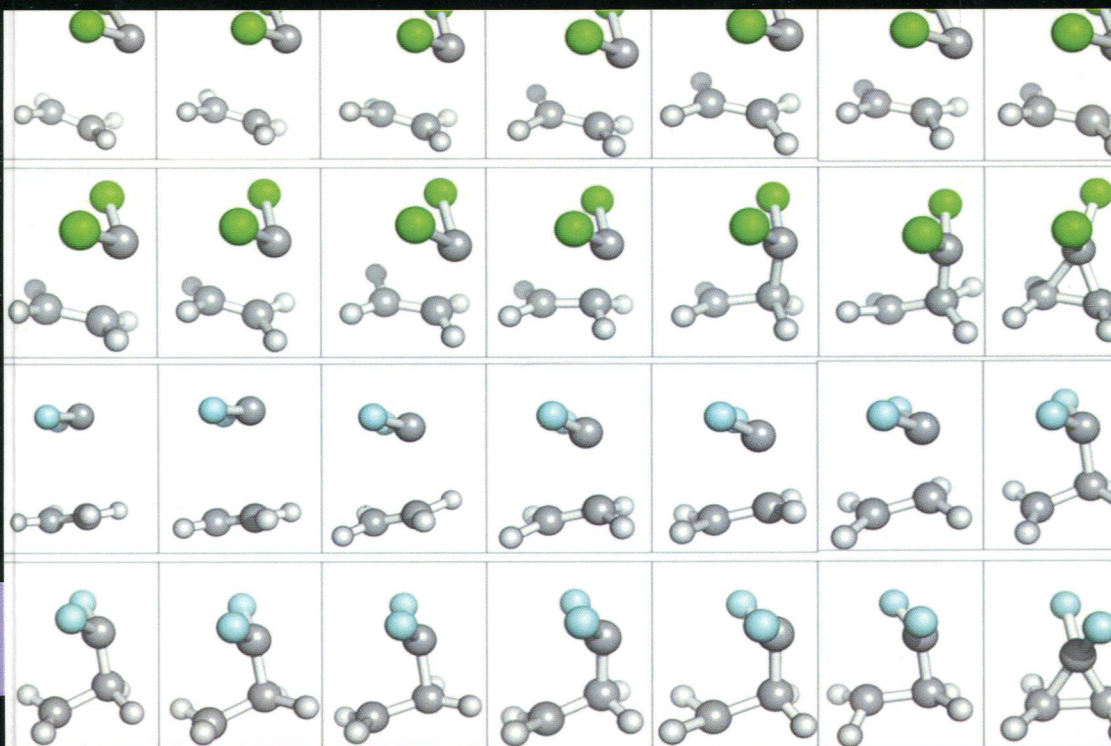


Wiley Series on Reactive Intermediates
in Chemistry and Biology

Steven E. Rokita, Series Editor

CONTEMPORARY CARBENE CHEMISTRY

Edited by Robert A. Moss and Michael P. Doyle



VOLUME SEVEN

WILEY

CONTEMPORARY CARBENE CHEMISTRY

Edited by

**ROBERT A. MOSS
MICHAEL P. DOYLE**

WILEY

Copyright © 2014 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

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, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Moss, Robert A., author.

Contemporary carbene chemistry / Robert A. Moss, Michael P. Doyle.
pages cm. – (Wiley series of reactive intermediates in chemistry and biology)

Includes bibliographical references and index.

ISBN 978-1-118-23795-3 (hardback)

1. Carbenes (Methylene compounds) 2. Carbon compounds. I. Doyle, Michael P., author. II. Title.

QD305.H5M67 2014

547'.01-dc23

2013023529

Printed in the United States of America

10 9 8 7 6 5 4 3 2

CONTENTS

PREFACE TO SERIES	xiii
PREFACE	xv
CONTRIBUTORS	xix
PART 1 PROPERTIES AND REACTIONS OF CARBENES	1
1 Carbene Stability	3
<i>Scott Gronert, James R. Keeffe, and Rory A. More O'Ferrall</i>	
1.1 Introduction	3
1.2 Background	4
1.2.1 Measures of Carbene Stability	4
1.2.2 Bonding and Orbital Interactions in Carbenes	6
1.2.3 Determining Carbene Stability	8
1.3 Carbene Stability	11
1.3.1 Hydrocarbon-Substituted Carbenes	11
1.3.2 Substituted Phenylcarbenes	16
1.3.3 Heteroatom-Substituted Carbenes	20
1.3.4 Conjugated Heterocyclic Carbenes	24
1.3.5 Carbenes with Other Electron-Withdrawing Groups	27
1.3.6 Carbenes versus Ylides	29
1.4 Correlations Involving Carbene Stability	30
1.4.1 CSE versus Singlet-Triplet Gap	30

1.4.2	CSE(Singlet) versus Proton Affinities	31
1.4.3	CSE(Singlet) versus Carbene Reaction Rates	32
1.5	Conclusion and Outlook	35
	Suggested Reading	35
	References	36
2	Stable Carbenes	40
	<i>Jonathan P. Moerdyk and Christopher W. Bielawski</i>	
2.1	Introduction	40
2.2	Types of Stable Carbenes	41
2.2.1	Push–Push Carbenes	42
2.2.2	Push–Pull Carbenes	48
2.2.3	Abnormal Carbenes	49
2.3	Spectroscopic Characteristics	50
2.4	Chemical Reactivity	52
2.4.1	Heteroallenes/Electrophilic Traps	55
2.4.2	Lewis Acids: Boryl Compounds	56
2.4.3	Alkenes, Alkynes, and Nitriles	56
2.4.4	Carbon Monoxide and Isonitriles	59
2.4.5	X–H Activation	60
2.4.6	Homodiatomic Bond Activation	63
2.4.7	Elemental Allotropes and other Reactive Species	65
2.5	Conclusions and Outlook	65
	Suggested Reading	67
	References	67
3	Acid–Base Chemistry of Carbenes	75
	<i>AnnMarie C. O’Donoghue and Richard S. Mussey</i>	
3.1	Introduction	75
3.2	Solution pK_a s of the Conjugate Acids of Carbenes	76
3.2.1	Experimental Methods in Aprotic Solvents	77
3.2.2	Experimental Methods in Aqueous Solution	80
3.2.3	Substituent Effects on pK_a	85
3.2.4	Solvent Effects on pK_a	91
3.3	Gas-Phase Basicities and Proton Affinities of Carbenes	92
3.3.1	Experimental Methods	93
3.3.2	Heteroatom-Stabilized Carbenes	94
3.3.3	Alkyl- and Aryl-Substituted Carbenes	100
3.3.4	Halocarbenes	102
3.4	Conclusion and Outlook	103
	Suggested Reading	104
	References	104

4 Computational Methods for the Study of Carbenes and their Excited States	107
<i>Hoi Ling Luk, Shubham Vyas, and Christopher M. Hadad</i>	
4.1 Introduction	107
4.2 Carbenes	109
4.3 Rearrangement in Excited States (RIES)	111
4.4 Advances in Computational Investigations of Carbenes	115
4.4.1 Configuration Interaction	117
4.4.2 Complete Active Space Self-Consistent Field (CASSCF) Theory	118
4.4.3 Coupled-Cluster Theory with Resolution-of-the-Identity Approximation (RI-CC2)	121
4.4.4 Time-Dependent Density Functional Theory (TD-DFT)	121
4.4.5 Molecular Dynamics (MD)	123
4.5 Theoretical Studies of the Photochemistry of Carbene Precursors	123
4.6 Conclusion and Outlook	127
Suggested Reading	128
References	128
5 Dynamics in Carbene Reactions	131
<i>Dina C. Merrer, K. N. Houk, and Lai Xu</i>	
5.1 Introduction	131
5.1.1 Carbenes	131
5.1.2 Nonstatistical Reaction Dynamics	133
5.2 Dynamics of Carbene Cycloadditions to Alkenes and Alkynes	136
5.2.1 Carbene Additions to Unstrained Alkenes	136
5.2.2 Carbene Additions to Strained π Systems	144
5.2.3 Carbene Additions to Strained σ Systems	152
5.3 Dynamics of Other Carbene-Mediated Reactions	153
5.3.1 Wolff Rearrangement	153
5.3.2 Photochemical Carbene Formation	156
5.4 Conclusion and Outlook	159
Suggested Reading	159
References	160
6 Ultrafast Kinetics of Carbene Reactions	166
<i>Gotard Burdzinski and Mathew S. Platz</i>	
6.1 Introduction	166
6.2 Ultrafast UV-Vis Studies of the Intermolecular Reactivity of <i>p</i> -Biphenylcarbene (BpCH)	167

6.3	Rearrangements in the Excited State of the Carbene Precursor	171
6.4	Dynamics of Carbene Vibrational Cooling and Solvation	173
6.5	Influence of Solvent on Carbene Intersystem Crossing Rates	176
6.6	Electronically Excited (Open Shell) Singlet Carbenes	179
6.7	Parent Phenyl diazirine—Mechanistic Aspects of Singlet Carbene Formation	179
6.8	Influence of Halo-Substituent Electron-Donating Capacity on Diazirine Decay in the First Excited Singlet State	183
6.9	The Influence of Excitation Wavelength on the Photochemistry of Diazirines	186
6.10	Conclusion and Outlook	189
	Suggested Reading	190
	References	191
7	Tunneling in the Reactions of Carbenes and Oxacarbenes	193
	<i>Dennis Gerbig and Peter R. Schreiner</i>	
7.1	Introduction: Light- and Heavy-Atom Tunneling	193
7.2	Alkyl- and Halocarbenes	197
7.2.1	Cyclopropylcarbenes	197
7.2.2	Ethylidene and Phenylmethylcarbene	200
7.2.3	Methylchlorocarbene and Benzylchlorocarbene	201
7.2.4	<i>tert</i> -Butylchlorocarbene	202
7.2.5	1-Methylcyclobutylfluorocarbene	202
7.2.6	Noradamantylchlorocarbene	203
7.3	The Formose Reaction and Hydroxycarbenes	203
7.3.1	Hydroxymethylene	203
7.3.2	Methylhydroxycarbene and Tunneling Control	205
7.3.3	Arylhydroxycarbenes	206
7.3.4	Cyclopropylhydroxycarbene	209
7.4	Conclusion and Outlook	210
	Suggested Reading	211
	References	211
8	Carbodicarbenes	216
	<i>Gernot Frenking and Ralf Tonner</i>	
8.1	Introduction	216
8.2	Carbodicarbenes with <i>N</i> -Heterocyclic Ligands C(NHC) ₂	218
8.3	Tetraaminoallenes and “Hidden” Carbodicarbenes	225
8.4	Bent Allenes	228
8.5	Related Compounds	233
8.6	Conclusion and Outlook	234
	Suggested Reading	234
	References	234

Catalytic Reactions with *N*-Mesityl-Substituted *N*-Heterocyclic Carbenes **237**

Jessada Mahatthananchai and Jeffrey W. Bode

9.1	Introduction	237
9.1.1	Historical Background	238
9.1.2	State of the Art Prior to 2004	238
9.1.3	<i>N</i> -Mesityl Catalysts as the Key Innovation	239
9.2	The <i>N</i> -Mesityl Group: A Mechanistic Aspect	242
9.2.1	Catalytic Generation of Reactive Species via <i>N</i> -Mesityl NHCs	242
9.2.2	The Kinetic Effect of the <i>N</i> -Mesityl Group	243
9.3	NHC Catalysis by Class of Reactive Intermediates	246
9.3.1	Acyl Anion Equivalent	246
9.3.2	Homoenolate Equivalent	248
9.3.3	Enolate Equivalent	254
9.3.4	Activated Carboxylate Equivalent	257
9.3.5	α,β -Unsaturated Activated Carboxylate Equivalent	264
9.4	Conclusion and Outlook	268
	Suggested Reading	268
	References	268

10 Supramolecular Carbene Chemistry **274**

Udo H. Brinker, Jean-Luc Miesusset, and Murray G. Rosenberg

10.1	Introduction	274
10.2	Types of Hosts Used in Supramolecular Carbene Chemistry	276
10.2.1	Cyclodextrins	276
10.2.2	Hemicarcerands	276
10.2.3	Resorcin[4]arene-Based Cavitanes	278
10.2.4	Octa Acid	278
10.2.5	Cucurbit[n]urils	278
10.2.6	Zeolites	280
10.3	Choosing the Right Carbene Guest	283
10.4	Diazirines as Suitable Supramolecular Carbene Precursors	285
10.5	Architecture of the Guest@Host Complex	287
10.6	Case Studies	291
10.6.1	Carbenes with Available 1,2-H Shifts	291
10.6.2	(2-[1,3-Dioxolan-2-yl]phenyl)(4-phenylphenyl)-carbene	294
10.6.3	4-Oxocyclohexa-2,5-dienylidene	295
10.6.4	Dichlorocarbene	296
10.6.5	Adamantylidene	296
10.6.6	3-Oxobicyclo[3.2.1]octan-8-ylidene	302
10.6.7	<i>endo</i> -3-Hydroxybicyclo[3.2.1]octan-8-ylidene	304
10.6.8	Ring Fragmentation and Expansion	305
10.6.9	Aryl(halo)carbenes	308

10.6.10	Fluoro(phenoxy)carbene	312
10.6.11	Persistent Triplet Carbenes	312
10.7	Conclusion and Outlook	313
	Acknowledgments	315
	Suggested Reading	315
	References	315
PART 2	METAL CARBENES	325
11	Modern Lithium Carbenoid Chemistry	327
	<i>Vito Capriati</i>	
11.1	Introduction	327
11.2	Structural Features of Lithium Carbenoids	328
11.3	Lithium Halide Carbenoids	329
11.3.1	Thermal and Kinetic Stability	329
11.3.2	Configurational Stability and Stereochemistry of the Coupling Reactions with Electrophiles	331
11.4	Structure–Reactivity Relationships	342
11.5	Lithium–Oxygen Carbenoids	344
11.6	Lithium–Nitrogen Carbenoids	352
11.7	Conclusion and Outlook	355
	Suggested Reading	357
	References	357
12	Rhodium Carbenes	363
	<i>Huw M. L. Davies and Brendan T. Parr</i>	
12.1	Introduction	363
12.2	Overview of Rhodium–Carbenoid Intermediates and Chiral Catalysts	364
12.3	Enantioselective Cyclopropanation	367
12.4	Cascade Sequences Initiated by Rhodium-Catalyzed Cyclopropanation	370
12.5	Enantioselective Cyclopropanation	373
12.6	C–H Functionalization By Carbenoid-Induced C–H Insertion	375
12.7	Combined C–H Activation/Cope Rearrangement (CHCR)	380
12.8	Formation and Reactions of Rhodium-Bound Ylides	383
12.9	Vinyllogous Reactions of Rhodium– Vinylcarbenoids	392
12.10	Conclusions and Future Outlook	397
	Suggested Reading	397
	References	398

13 Ruthenium Carbenes	404
<i>Steven T. Diver and Jonathan M. French</i>	
13.1 Introduction	404
13.2 Improved Mechanistic Understanding	405
13.2.1 Background	406
13.2.2 Identification of Ruthenacyclobutane Intermediates in Alkene Metathesis	410
13.2.3 Conformational Dynamics “Windshield Wiper”	412
13.3 Catalyst Development	413
13.3.1 Development of Phosphine-Free Catalysts	413
13.3.2 Decomposition of the Grubbs’ Complex	417
13.4 Achieving Selectivity in Alkene Metathesis	424
13.4.1 Enantioselective Metathesis with Ruthenium Carbenes	424
13.4.2 Site Selectivity Using Relay Ring-Closing Metathesis	426
13.4.3 Z-Selective Alkene Metathesis	429
13.5 Applications	432
13.5.1 Selected Examples of Alkene Metathesis in the Total Synthesis of Natural Products	432
13.5.2 Applications of Metathesis in Aqueous Systems	438
13.5.3 Applications in Diversity-Oriented Synthesis	441
13.6 Conclusion and Outlook	444
Suggested Reading	445
References	446
14 Nucleophilic Carbenes of the Chromium Triad	452
<i>Zachary J. Tonzetich</i>	
14.1 Introduction	452
14.1.1 Discovery	453
14.1.2 Spectroscopic Properties	455
14.1.3 Metathesis Reactivity	455
14.2 Chromium Carbenes	457
14.2.1 Cr(VI) Carbenes	457
14.2.2 Nucleophilic Cr(III) Carbenes	459
14.2.3 Supported Cr(IV) Carbenes	459
14.3 Molybdenum Carbenes	460
14.3.1 Mo(VI) Imido-Alkylidene-bis-Alkoxide Compounds	461
14.3.2 Mo(VI) Imido-Alkylidene Pyrrolide Compounds	468
14.3.3 Other Nucleophilic Mo Carbenes	471
14.3.4 Supported Mo Alkylidenes	473
14.4 Tungsten Carbenes	476
14.4.1 W(VI) Imido-Alkylidene-bis-Alkoxide Compounds	476

14.4.2	W(VI) Imido-Alkylidene Pyrrolide Compounds	477
14.4.3	Other Nucleophilic Tungsten Carbenes	480
14.5	Conclusions and Outlook	484
	Suggested Reading	485
	References	485
15	Cobalt-Mediated Carbene Transfer Reactions	491
	<i>Xin Cui and X. Peter Zhang</i>	
15.1	Introduction	491
15.2	Cobalt-Catalyzed Cyclopropanation Reactions	494
15.2.1	Cobalt Dioximate and Cobalt Ketoiminato Catalysts	494
15.2.2	Cobalt Salen Catalysts	496
15.2.3	Cobalt Porphyrin Catalysts	501
15.2.4	Cobalt Catalysts with Other Supporting Ligands	512
15.2.5	Mechanistic Studies	514
15.3	Other Cobalt-Catalyzed Carbene Transfer Reactions	517
15.3.1	Cyclopropanation	517
15.3.2	Carbonylation	518
15.3.3	Olefination	519
15.4	Conclusion and Outlook	520
	Acknowledgments	522
	Suggested Reading	522
	References	522
16	Gold Carbenes	526
	<i>Liming Zhang</i>	
16.1	Introduction	526
16.2	Nature of the Au–Carbon Double Bond	528
16.2.1	Experimental Studies	528
16.2.2	DFT Calculations	529
16.3	Generation and Reactions of Gold Carbenes	530
16.3.1	Gold Carbenes with Dative or Alkyl Substituents	530
16.3.2	Generation and Reactions of α -Oxo Gold Carbenes	534
16.3.3	Generation and Reactions of α -Imino Gold Carbenes	542
16.3.4	Generation and Reactivities of Gold Carbenes via Carbene Transfer	545
16.3.5	Generation and Reactivities of 1,3-Dipolar Gold Carbenes from Allenes	545
16.4	Conclusion and Outlook	547
	Suggested Reading	548
	References	548
	Index	552