

**HANDBOOK OF  
ORGANOPALLADIUM CHEMISTRY  
FOR ORGANIC SYNTHESIS**

**Volume 1**

# HANDBOOK OF ORGANOPALLADIUM CHEMISTRY FOR ORGANIC SYNTHESIS

Volume 1

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# PREFACE

Organic compounds mostly consist of just ten to a dozen non-metallic elements including C, H, N, P, O, S, and halogens. This may be one of the main reasons why chemists, until relatively recently, tended to rely heavily on those reactions involving only non-metallic elements. Many of them including the Diels-Alder reaction, the Claisen and Cope rearrangements continue to be important. Even so, their combined synthetic scope has been rather limited.

Regardless of how one defines metallic elements, more than three quarters of the elements may be considered to be metals. It is therefore not surprising that some of them, mostly main group metals such as Li, Na, K, and Mg, have been used as reagents or components of reagents for many decades primarily for generating carbanionic and other anionic species. Some other main group metals, such as Al and B, have also been used for many years primarily as components of Lewis acid catalysts in the Friedel-Crafts and other acid-catalyzed reactions. The significance of metal's ability to readily provide low-lying empty orbitals has become gradually but widely recognized and led to the development of a modern synthetic methodology involving B, Al, and other predominantly Lewis-acidic main group metals.

Some d-block transition metals (transition metals hereafter) including Ni, Pd, Pt, Rh, Ru, and so on have long been used as catalysts or catalyst components for hydrogenation and other reductions, while some others, such as Cr and Mn, have been used in stoichiometric oxidation reactions. Even some transition metal-catalyzed C—C bond-forming reactions, such as Roelen's oxo process was discovered as early as 1938. However, it was not until the 1950s that the full synthetic potential of transition metals began to be recognized. The discovery and development of the Ziegler-Natta polymerization indicated the ability of some early transition metals, such as Ti and Zr, to serve as superior catalysts for C—C bond formation. Development of the Dewar-Chat-Duncanson synergistic bonding scheme provided a theoretical foundation for the "carbenoidal" characteristic of transition metals, as discussed in **Sect. II.3.1**. The discovery of ferrocene in 1951 and the subsequent clarification of its structure triggered systematic investigations that have made available a wide range of metallocene and related transition metal complexes for reagents and catalysts. In the area of organopalladium chemistry, it is widely agreed that invention of the Wacker oxidation in 1959 may have marked the beginning of the modern Pd-catalyzed organic synthesis (**Sect. I.1**).

Over the last thirty to forty years, compounds containing roughly ten to a dozen transition metals have been shown to serve as versatile and useful catalysts in organic synthesis. Today, they collectively represent the third major class of catalysts, enzymes and non-transition metal acids and bases being the other two. Of various factors, the following two appear to be critically responsible for rendering them superior catalysts and catalyst components. One is their ability to provide readily and simultaneously both filled nonbonding and low-lying empty orbitals. Together, they provide effective frontier orbitals, namely HOMO and LUMO, for concerted and synergistic interactions leading to

low energy-barrier transformations. The other is their ability to undergo simultaneously and reversibly both oxidation and reduction under one set of reaction conditions.

Then, why Pd? This is a very interesting but rather difficult question. Nonetheless, an attempt to answer this question is made in **Sect. I.2**, and the generalization summarized in **Table 2** of **Sect. I.2** is further supported by the experimental results presented throughout this Handbook. In short, Pd simultaneously displays wide-ranging reactivity and high stereo-, regio-, and chemo-selectivities. Its complexes are, in many respects, highly reactive. And yet, they are stable enough to be used as recyclable reagents and intermediates in catalytic processes. These mysteriously favorable characteristics appear to be reserved for just a few late second-row transition metals including Pd, Rh, and Ru that offer a combination of (i) moderately large atomic size and (ii) relatively high electronegativity, both of which render these elements very “soft”, in addition to (iii) ready and simultaneous availability of both filled nonbonding and empty valence-shell orbitals and (iv) ready and reversible availability of two oxidation states separated by two elections mentioned above. The general lack of serious toxicity problems and ease of handling, which may not require rigorous exclusion of air and moisture in many cases are two additional factors associated with them.

The versatility of Pd is very well indicated by the contents of this Handbook listing nearly 150 authored sections spread over ten parts. This Handbook cannot and does not list all examples of the organopalladium reactions. However, efforts have been made to consider all conceivable Pd-catalyzed organic transformations and discuss all known ones, even though it was necessary to omit about ten topics for various unfortunate reasons.

**Part I** discusses the historical background of organopalladium chemistry (**Sect. I.1**) as well as the fundamental properties and patterns of the reactions of Pd and its complexes (**Sect. I.2**). In **Part II**, generation and preparation of Pd complexes are discussed. These discussions are rather brief, as the main focus of this Handbook is placed on Pd-catalyzed organic transformations.

In some of the previously published books on organopalladium chemistry, topics are classified according to the organic starting compounds. This may be a useful and readily manageable classification from the organometallic viewpoint. However, it is envisioned that the prospective readers and users of this Handbook are mostly synthetic organic chemists who are primarily interested in knowing how the organic compounds of their interest might be best prepared by using Pd complexes as catalysts. This perspective, however, does not readily lend itself to an attractive and satisfactory means of classifying the organopalladium chemistry. For both synthetic organic chemists and those who wish to learn more about the organopalladium chemistry from a more organometallic perspective, it appears best to classify the organopalladium chemistry according to some basic patterns of organometallic transformations representing the starting compound—product relationships. As discussed in **Sect. I.2**, formation of carbon—carbon and/or carbon—heteroatom bonds through the use of organotransition metals can be mostly achieved via the following four processes: (i) reductive elimination, (ii) carbometallation, (iii) nucleophilic or electrophilic attack on ligands, and (iv) migratory insertion. As a versatile transition metal, Pd has been shown to participate in them all.

Thus, in **Part III**, the Pd-catalyzed cross-coupling including the carbon-carbon cross-coupling represented by the Negishi, Stille, and Suzuki protocols as well as the Sonogashira alkynylation (**Sect. III.2**) and the more recently developed carbon-heteroatom coupling reactions (**Sect. III.3**) are presented. In most of these reactions, reductive

elimination is believed to be a critical step. This is followed by **Part IV** in which a systematic discussion of carbopalladation represented by the Heck reaction (**Sect. IV.2**) is presented. The scope of carbopalladation, however, extends far beyond that of the Heck reaction, and these other topics are discussed in **Sects. IV.3–IV.11**. There are two major topics that pertain to nucleophilic attack on ligands of organopalladium complexes discussed in **Part V**. One is the Tsuji-Trost reaction. This and related reactions of allylpalladium derivatives are discussed in **Sect. V.2**. The other is the Wacker oxidation. This and related reactions involving Pd  $\pi$ -complexes are discussed in **Sect. V.3**. In **Part VI**, carbonylation and other migratory insertion reactions of organopalladium compounds are discussed. In **Parts III–VI**, the significance of applications of the above-mentioned reactions to the synthesis of natural products (**Sects. III.2.17.1, III.2.18, IV.8, V.2.6, V.3.6, and VI.6**) and polymers of material chemical interest (**Sects. III.2.17.2, VI.4.2, and VI.8**) are recognized and discussed in the sections shown in parentheses.

Aside from the systematic classification mentioned above, the synthetic significance of Pd-catalyzed reduction and oxidation is abundantly clear. Some of those reduction and oxidation reactions that are not discussed in **Parts III–VI** are therefore discussed in **Parts VII and VIII**, respectively. It should be noted, however, that many of the reactions discussed in **Parts III–VI** also leads to oxidation or reduction of organic compounds. Despite the high propensity to undergo concerted reactions, organopalladium derivatives can also serve as sources of carbocationic species as indicated in **Part V**. In some cases, this can lead to skeletal rearrangements similar to the pinacol-pinacolone rearrangement. Other more concerted rearrangements are also observable, as discussed in **Part IX**. These reactions add extra dimensions to the diverse chemistry of organopalladium compounds. Lastly, some significant technological developments including aqueous palladium catalysis (**Sect. X.1**), immobilized Pd catalysts (**Sect. X.2**) and combinatorial organopalladium chemistry (**Sect. X.3**) are making organopalladium chemistry even more important and useful in organic synthesis.

Looking back, it all started when one of my senior colleagues, Professor H. Feuer, repeatedly visited my office several years ago to persuade me to write a book for VCH and later Wiley. Despite my initial firm determination not to write any book, a notion of preparing this Handbook on a topic that has occupied a significant part of my own research career grew in my mind, and I was finally persuaded by him and Dr. Barbara Goldman of Wiley. My life-long mentor and a 1979 Nobel Prize winner, Professor H. C. Brown, has directly and indirectly influenced and encouraged me throughout my career, including this Handbook writing. I wish to dedicate my own contributions to these two senior colleagues at Purdue. I should also like to acknowledge that, through the generosity of Professor and Mrs. Brown, the Herbert C. Brown Distinguished Professorship was established in 1999, of which I have been the very fortunate inaugural appointee. This has had many favorable influences on my involvement in this Handbook preparation. In this and other connections, I am very thankful to my colleagues in the Chemistry Department, especially Dean H. A. Morrison and former Head R. A. Walton.

The actual overall and detailed layout of the Handbook was finalized during my two-month stay in Göttingen, Germany, as an Alexander von Humboldt Senior Researcher Awardee during the summer of 1998. My German host and Associate Editor of the Handbook, Professor A. de Meijere has not only enthusiastically supported my plan but also heavily contributed to the Handbook both as an author and as a member of the editorial board. I am also deeply indebted to the other eight editorial board members,

namely Professors J. E. Bäckvall, S. Cacchi, T. Hayashi, Y. Ito, M. Kosugi, S. I. Murahashi, K. Oshima, and Y. Yamamoto. They all have contributed one or more sections and sacrificed their extremely precious time in the editorial phase. In fact, the ten editorial board members have authored and coauthored nearly one half of all sections.

It is nonetheless unmistakably clear that this Handbook is a joint production by a community or group of 141 chemists and that the great majority of writing and drawing works have actually been performed by the 131 contributors whom I sincerely thank on behalf of the editorial board including myself. Without their massive contributions and cooperation, it would have been absolutely impossible to publish a book of this magnitude. It is my particular pleasure to note that no less than 21 current and former associates of my own research group have made their massive contributions and enthusiastically supported my activities. They are, in the order of appearance, D. Choueiry, L. Anastasia, S. Huo, C. Xu, F. Liu, B. Liao, S. Gagneur, F. Zeng, T. Sugihara, K. Takagi, F. T. Luo, A. Alimardanov, Y. Dumond, Z. Tan, M. Kotoru, T(amotsu) Takahashi, A. O. King, C. Coperet, S. Ma, S. Y. Liou, and H. Makabe.

While I must refrain from mentioning the names of the other 110 contributors, most of them are indeed my long-time colleagues and friends, to whom I deeply thank for their collaborations and contributions. I have also greatly appreciated and enjoyed collaborations with my new colleagues, some of whom I have not yet met. Many of my other esteemed colleagues were too busy to participate in the project. Some of them nevertheless made valuable suggestions that have been very useful in the planning stage.

Typing and a significant part of drawing of our own manuscripts and, more importantly, a seemingly infinite number of correspondences as well as a myriad of other Handbook-related jobs have been handled by Ms. M. Coree (through 2000) and Ms. Lynda Faiola (since 2001). The preparation of this extensive Handbook would not have been possible without their dedicated work for which I am deeply thankful. Many direct and indirect assistances made by my wife, Sumire, and other members of my family are also thankfully acknowledged.

Last but not least, I thank editorial staff members of Wiley, including compositors and freelancers, especially Dr. Barbara Goldman in the initial phase, Dr. Darla Henderson, Amy Romano, and Christine Punzo for their interest, encouragement, and collaboration in this project.

One of the undesirable and yet inevitable consequences of this kind of publication requiring a few years of preparation time is that the book is outdated by at least a few years at the time of publication. There are at least two approaches to cope with this problem. One is to keep publishing as frequently as possible quick and hopefully up-to-date collections of reviews. This approach, however, is not conducive to a systematic, thorough, and penetrating discussion of the chosen topic. Each publication is outdated in due course and forgotten. The other is to publish once a systematic, comprehensive, and well-organized collection of authoritative and penetrating reviews and use it as the foundation for future periodical updating activities. I intend to use this Handbook in this manner. The part and section numbers have therefore been assigned with future updating in mind. They will indeed be retained and used in our future updating. Thus, it is my plan to continue surveying and classifying the Pd-related publications by abstracting them with the use of a computerized abstract form and assigning one to a few pertinent section numbers to each. The classified abstracts may then be published periodically in the conventional book form and/or electronically. Hopefully, these updates will, in turn, continuously revive and reinforce the value of the original Handbook. With the classified updated information, some

seriously outdated sections may be revised and published as supplementary volumes at appropriate times. In this regard, I have already received oral consents from more than a dozen colleagues, and I am currently seeking a dozen or so additional collaborators.

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# ABBREVIATIONS

Ac, Acetyl	Cbz, Carbobenzyloxy
acac, Acetylacetone	CHIRAPHOS, ( <i>R,R</i> )- or ( <i>S,S</i> )- 2,3-
AIBN, Azobis(isobutyronitrile)	Bis(diphenylphosphino)butane
AMPHOS, 2,2'-Bis(diphenylarsino)-1,1'-binaphthyl	COD, Cyclooctadiene
Ar, aryl	Cp, Cyclopentadienyl
9-BBN, 9-Borabicyclo[3.3.1]nonane	CSA, Camphosulfonic acid
BHT, 2,6-Di- <i>tert</i> -butyl-4-methylphenol	Cy, Cyclohexyl
BINAP, (2 <i>R</i> , 3 <i>S</i> ), 2,2'-Bis-(diphenylphosphino)-1,1'-binaphthyl	DABCO, 1,4-Diazobicyclo[2.2.2]octane
BINAPO, 2'-Diphenylphosphino-1,1'-binaphthalenyl-2-ol	DBA (often shown as dba), Dibenzalacetone
BINAS, 2,2'-Bis(diphenylarsino)-1,1'-binaphthyl	DBN, 1,5-Diazabicyclo[4.3.0] non-5-ene
BIPHEMP, 2,2'-Bis(diphenylphosphino)-6,6'-dimethylbiphenyl	DBPF, 1-Bis-di- <i>t</i> -butylphosphinoferrocene
Bipy(BPY), Bipyridine	DBU, 1,8-Diazabicyclo[5.4.0] undec-7-ene
Bn, Benzyl	DCC, 1,3-Dicyclohexylcarbodiimide
Bz, Benzoyl	DCD model, Dewar-Chart-Duncanson model
BNPPA, Binaphthyl-2',2'-dyl hydrogenphosphate	DCE, Dichloroethane
BPPFA, <i>N</i> -Dimethyl-1-[1',2'-bis(diphenylphosphino)ferrocenyl]ethylamine	DDQ, 2,3-Dichloro-5,6-dicyano-1, 4-benzoquinone
BPPFOH, ( <i>R</i> )- $\alpha$ -[( <i>S</i> )-1',2'-Bis(diphenylphosphino)ferrocenyl]ethyl alcohol	DEA, Diethylamine
BPPM, 1- <i>t</i> -Butoxycarbonyl-4-diphenylphosphino-2-(diphenylphosphinomethyl)azolidine	DEAD, Diethylazodicarboxylate
BSA, Bistrimethylsilyl acetamide, <i>N</i> , <i>O</i> -Bis(trimethylsilyl)acetamide	Dec, Decyl
BTMC, Benzyltrimethylammonium carbonate	DFT, Density functional theory
Bu, Butyl	DIBAH, Diisobutylaluminum hydride
<i>c</i> -, Cyclo-	DIBAL-H = DIBAH (sometimes shown as DIBAL)
CAN, Ceric ammonium nitrate	DIEA, Diisopropylethylamine
	DIOP, (4 <i>R</i> ,5 <i>R</i> )- <i>trans</i> -4,5-Bis[(diphenylphosphino)methyl]-2;2-dimethyl-1,3-dioxolane,
	Diphos, See DPE.
	DMA, <i>N,N</i> -Dimethylacetamide
	DMAD, Dimethyl acetylenedicarboxylate
	DMAP, 4-Dimethylaminopyridine
	DME, Dimethoxyethane
	DMF, Dimethylformamide
	DMI, 1,3-Dimethyl-2-imidazolidinone, <i>N,N'</i> -Dimethyl-2-imidazolidinone

- DMSO, Dimethylsulfoxide  
 DP, Degrees of polymerization  
 DPEphos, Bis(*o*-diphenylphosphinophenyl) ether  
 DPEPY, 2-(2-Diphenylphosphinoethyl)pyridine  
 DPMEPY, 2-(Diphenylphosphonomethyl)pyridine  
 DPPB (dppb), 1,4-bis(Diphenylphosphino)butane  
 DPPE (dppe), 1,2-Bis(diphenylphosphino)ethane  
 DPPF (dppf), Bis-(diphenylphosphino)ferrocene  
 DPPP (dppp), 1,3-Bis-(diphenylphosphino)propane  
 EDA, Ethylenediamine  
 EL, Electroluminescence  
 Et, Ethyl  
 EWG, Electron-withdrawing group  
 FBS, Fluorous biphasic system  
 FOS, Formal oxidation state  
 GPC, Gel permeation chromatography  
 Hex, Hexyl  
 HIV, Human immunodeficiency virus  
 HMDS, Hexamethyldisilazane  
 HMPA, Hexamethylphosphoramide  
 HOMO, Highest occupied molecular orbital  
 ICPs, Integrated chemical processes  
*i*-, Iso- *i*-Pr or *i*Pr, Isopropyl  
 L, Ligand  
 LAH, Lithium aluminum hydride, LiAlH<sub>4</sub>  
 LDA, Lithium diisopropylamide  
 LED, Light-emitting diodes  
 LUMO, Lowest unoccupied molecular orbital  
 MCPBA, *m*-Chloroperoxybenzoic acid  
 MCR, Multicomponent reactions  
 Me, Methyl  
 MEM, β-Methoxyethoxymethyl  
 Mes, Mesityl  
 Ms, Mesyl, Methanesulfonyl  
 MOM, Methoxymethyl  
 MOP ligands, 2-(Diphenylphosphino)-2'-methoxy-1,1'-binaphthyl  
*n*-, Normal  
 Naph, Naphthyl  
 NBS, *N*-Bromosuccinimide  
 NCS, *N*-Chlorosuccinimide  
 NDMBA, *N,N'*-Dimethylbarbituric acid  
 NIS, *N*-Iodosuccinimide  
 NIT, Nitronyl nitroxide  
 NMM, *N*-methylmorpholine  
 NMP, *N*-Methylpyrrolidone  
 NMR, Nuclear magnetic resonance  
 NOE, Nuclear Overhauser effect.  
 NORPHOS, 2,3-Bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene  
 Oct, Octyl  
 PAA, Polyacrylamide  
 PCC, Pyridinium chlorochromate  
 PDC, Pyridinium dichromate  
 PEG, Polyethylene glycol  
 Pent, Pentyl  
 PFS, Pentafluorostyrene  
 PG, Prostaglandin  
 Ph, Phenyl  
 PHANEPHOS, 4,12-Bis(diphenylphosphino)[2.2]paracyclophane  
 Phen, 1, 10-Phenanthroline  
 PHOPHOS, 2,2'-Bis(diphenylarsino)-1,1'-binaphthyl  
 PL, Photoluminescence  
 PMHS, Polymethylhydrosiloxane  
 PMP, 1, 2, 6-Pentamethylpiperidine  
 PPA, Polyphosphoric acid  
 PPE, Poly(phenylene ethynylene)  
 PPP, Poly(*para*-phenylene)  
 Pr, *n*-Propyl  
 Py, Pyridine  
 PROPHOS, 1,2-Bis(diphenylphosphino)propane  
 PTA, 1,3,5-Triaza-7-phosphaadamantane  
 PTC, Phase-transfer catalyst  
 PTSA, *p*-Toluenesulfonic acid  
 R, An organic group  
 RAMP, R-(+)-Amino-2-(methoxymethyl)pyrrolidine  
 R<sub>f</sub>, Perfluoroalkyl  
 Red-Al, Na[AlH<sub>2</sub>(MeOCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>]  
 SAMP, S-(−)-Amino-2-(methoxymethyl)pyrrolidine  
 Sec; *s*, Secondary  
*s*-Bu, <sup>t</sup>Bu, *sec*-Bu, Secondary butyl.



SEM, 2-(Trimethylsilyl)ethoxymethyl	THF, Tetrahydrofuran
( <i>S</i> )-( <i>R</i> )-BPPFA, Ferrocenylbisphosphine	THP, Tetrahydropyran(yl)
( <i>S</i> )-( <i>R</i> )-PPFA, Ferrocenylmonophosphine	TIBAH, Triisobutylaluminum
<i>tert</i> , <i>t</i> , Tertiary	TMDHS, Tetramethyldihydrosiloxane
TADDOL $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-4,5- dimethoxy-1,3-dioxolane	TMEDA, Tetramethylethylenediamine
TASF, Tris-(Diethylamino)sulfonium difluorotrimethyl silicate	TMM, Trimethylenemethane
TBAF, Tetrabutylammonium fluoride	TMM-Pd, Trimethylenemethane palladium
TBDMS, <i>tert</i> -Butyldimethylsilyl	TMOF, Trimethyl orthoformate
TBS = TBDMS	TMS, Trimethylsilyl
<i>t</i> -Bu, <sup><i>t</i></sup> Bu, <i>tert</i> -Bu, Tertiary butyl	TMU, <i>N,N,N',N'</i> -Tetramethylurea
TCPP, Tris( <i>p</i> -chlorophenyl)phosphine	TOF, Turnover frequency
TDMPP, Tris(2,6-dimethoxyphenyl) phosphine	Tol, Tolyl
TEBA, Triethylbenzylammonium chloride	Tol-BINAP, 2,2'-Bis(di- <i>p</i> -tolylphosphino)- 1,1'-binaphthyl
Terpy, Terpyridine	TON, Turnover number
Tf, Trifluoromethanesulfonyl, triflyl	TPPTS, Triphenylphosphane <i>m</i> - trisulfonate sodium salt
TFA, Trifluoroacetic acid	Tr, Trityl
TFP, Tris(2-furyl)phosphine	Ts, Tosyl, <i>p</i> -Toluenesulfonyl
	WGS, Water gas shift reaction