
R—X + R'—M
Pd°
R—R'
Handbook of
Palladium-Catalyzed
Organic Reactions
Pd°
R'
R
R—Pd—X
R—Pd—R'
R'—M
M—X
Jean-Luc Malleron
Jean-Claude Fiaud
Jean-Yves Legros
Foreword by H. Kagan
AP
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PRESS

Handbook of Palladium-Catalyzed Organic Reactions

Synthetic Aspects and Catalytic Cycles

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Foreword

Palladium chemistry and its application to the synthesis of organic compounds already has a long history. It was involved in the shift of raw C_2 materials from coal chemistry via acetylene to oil chemistry via ethylene. For years the Wacker process (which is palladium catalyzed) provided several million tons per year of acetaldehyde from ethylene. From the 1960s, homogeneous catalysis by palladium complexes started to be applied to more complicated organic molecules (Tsuji-Trost allylic substitution, Heck, Stille, Neghishi or Suzuki coupling reactions, Bäckvall functionalization of dienes, etc.). In the last 10 years, organic transformations catalyzed by palladium complexes have become one of the most active fields in homogeneous organometallic catalysis as judged by the number of publications per year. They are used routinely in multi-step total syntheses, as well as in fundamental research (e.g. the recent developments in asymmetric catalysis). Mechanistic details of the various catalytic cycles are reasonably well understood.

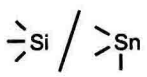
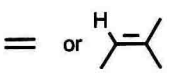
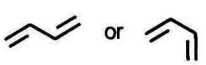
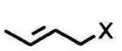
It is therefore opportune that this handbook is offered to those synthetic organic chemists wishing to take advantage of the rich chemistry of palladium for solving their problems. This handbook has been prepared for practitioners by Dr. J.-L. Malleron, an industrial chemist (Rhône-Poulenc-Rorer Co., Vitry, France), and Prof. J.-C. Fiaud and Dr. J.-Y. Legros from Université Paris-Sud (Orsay, France). For each class of reaction, a mechanism taken from the most recent literature is included which aids understanding and optimization of a given process. This handbook originates from a computerized database of more than 3,000 references which has been created and organized by Dr. Malleron.

The aim of the book is to provide the user with the main organic transformations catalyzed by palladium complexes, with a choice of references, in order to find the closest example for solving a given problem. To that end, structural features of the reactants as well as some experimental parameters are indicated in the tables. The reactions are numbered from RXN1 to RXN84. This large number of transformations shows the power of palladium homogeneous catalysis. This handbook offers the synthetic organic chemist in either industry or academia an impressive source of inspiration and information. The manipulation of this handbook is not difficult and is helped by the instructions given by the authors. It is also very useful for the reader to have access to the corresponding database on diskette. This greatly extends the scope of the book since it allows searching by keywords.

In conclusion it is very fortunate that this important work of selection and classification of data on palladium-catalyzed reactions originally from an industrial chemist, is now available to the scientific community. I congratulate the authors and wish them every success in their enterprise.

H. KAGAN

Abbreviations and Symbols

[Red.]	reducing agent
[Ox.]	oxidizing agent
L	ligand
BQ	benzoquinone
H_2BQ	dihydrobenzoquinone
dba	dibenzylideneacetone
dppb	bis(diphenylphosphino)butane
Tf	trifluoromethylsulfonyl (triflyl)
M, M'	metal
Nu	nucleophile
E	electrophile
$(\,)_n$	$(CH_2)_n$
RF	polyfluorinated alkyl chain
	RR'R"-Si / RR'R"-Sn
	alkene
	1,3-diene
	allene
	alkyne
	allylic derivative
	allylic epoxide
	diphosphine

NOTES

The references are given with abbreviations from the CAS source index. They are indicated as follows:

name of the main author, abbreviation of the journal, year, first page

or, when necessary,

name of the main author, abbreviation of the journal, year, volume, first page

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I- INTRODUCTION

Organometallic chemistry is widely used by organic chemists and palladium chemistry is probably one of their most versatile tools. For synthetic and economic reasons, catalyzed reactions are preferred to stoichiometric reactions. It is very important to have a good knowledge of the synthetic aspects of organic chemistry, promoted by palladium complexes and of the catalytic cycles involved. In spite of excellent reviews and series having been published on this topic, it appears difficult to quickly and easily find complete information in this area.

This review provides a compilation of the most well-known catalytic reactions related to organo-palladium chemistry. The references have been covered up to November 1995. The mechanisms are generally described with respect to the data in the literature and by the use of information found mainly in publications. For each catalytic cycle, the chemical parameters are listed and one or more related references are given. As an example, for the cross-coupling reactions between RX and R'M, the identity of R, R', X, and M parameters are defined. The references which are quoted contain at least one example of these parameters . A few palladium-catalyzed reactions are not reported in this review because of insufficient data concerning the mechanism or because the reaction affords a complex mixture of products.

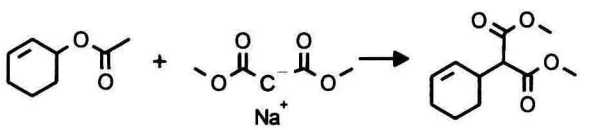
For classification, a name has been assigned to each reaction related to a reaction number (RXN) and these have been listed. With this classification, for any general mechanism presented here, it is possible to identify very quickly to which class the reaction belongs from the table of contents.

The first chapter presents the graphical abstracts for all the reactions (reaction numbers) which are described in this handbook. Thus it is easy to search for a reaction type and then look at the literature references in the tables.

In addition, the catalytic cycles and the corresponding chemical parameters have been entered into a database of palladium-catalyzed reactions. As well as the various examples quoted in the publications, it is possible to view either the general catalytic cycle (RXN) related to each reference or all the chemical parameters related to a reaction number. For each reference, one or more examples have been selected with respect to the reaction. ISIS software (version 1.2) from MDL, EXCEL software (version 5.0c) and WORD software (version 6.0c) from MICROSOFT have been used. At the present time, this database is made available to many research centres by the Rhône-Poulenc company. An example of the database form is shown over the page.

Any remaining errors and inaccuracies are solely the responsibility of the authors.

23/03/1995	*PALLADIUM DATABASE*	Chem. Parameters	Zoom	Mechanism



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Yield (%) :	75.0
Exp. Conditions :	
N_2/ 20°C/ 48h	

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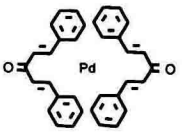
1	THF	1	Pd(dba)2 dppe



Step: 1

RXN Code: RXN32

Comments:

Several examples.

References:

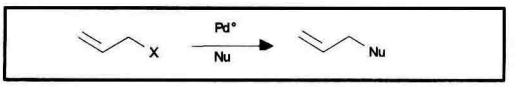
FIAUD J.-C., MALLERON J.-L., TETRAHEDRON LETT., 1980, 21, 4437

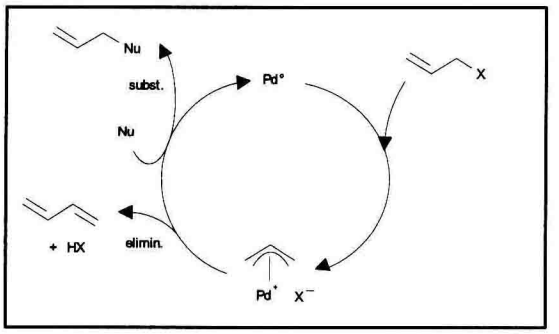
RXN type:

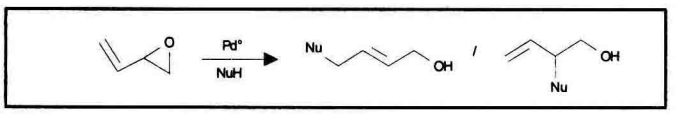
Substitution, Addition and Elimination on Pro-π-Allyl Substrates

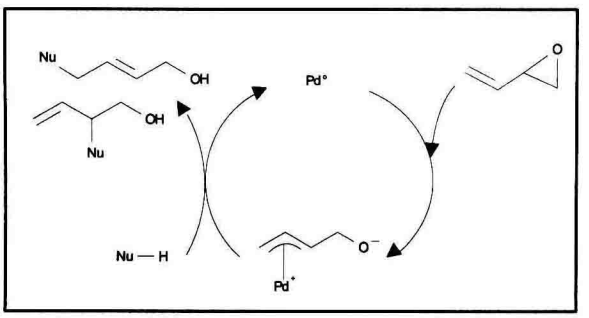
Substitution, Addition and Elimination on Pro-π-Allyl Substrates

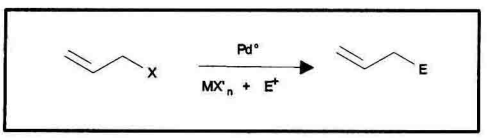
RXN32

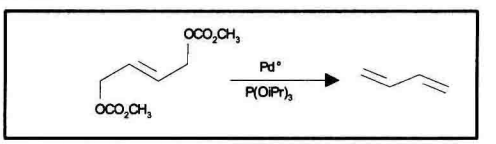


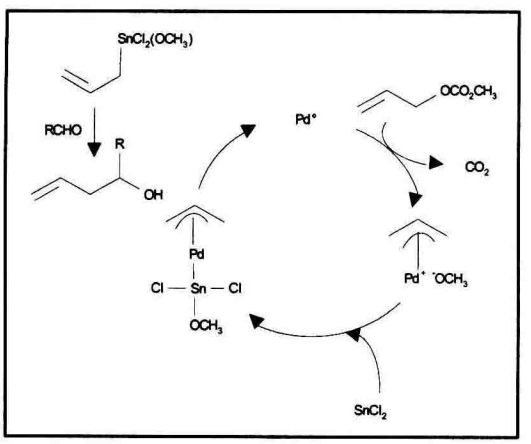


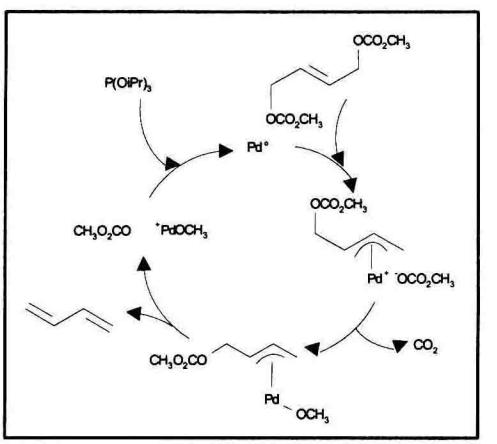












Leaving Group	References
OH	Atkins K.E., *Tetrahedron Lett.*, 1970; 3821 Bergbreiter D.E., *J. Chem. Soc., Chem. Commun.*, 1989; 883 Miura M., *J. Chem. Soc., Perkin Trans. 1*, 1992; 2833 Sakakibara M., *Tetrahedron Lett.*, 1994; 8013
OR	Klumpp G.W., *Tetrahedron Lett.*, 1988; 3579 Takahashi K., *Bull. Chem. Soc. Jpn.*, 1972; 230 Kusama T., *Chem. Pharm. Bull.*, 1992; 1718
OC_6H_5	Fiaud J.C., *J. Organomet. Chem.*, 1978; 154, 175 Takahashi K.; *Bull. Chem. Soc. Jpn.*, 1972; 230 Tsuji J., *Tetrahedron Lett.*, 1978; 2075 (elimination)
OAc	Trost B.M., *J. Am. Chem. Soc.*, 1976; 630 Sinou D., *Tetrahedron Lett.*, 1991; 2025 Trost B.M., *J. Am. Chem. Soc.*, 1994; 4089 (asymmetric catalysis) Andersson P. G., *Organometallics*, 1995; 14, 1 (elimination) Trost B.M., *Tetrahedron Lett.*, 1979; 2301 (elimination)
OCOtBu	Fiaud J.C., *J. Org. Chem.*, 1990; 4840

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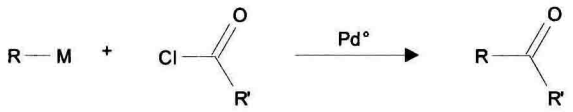
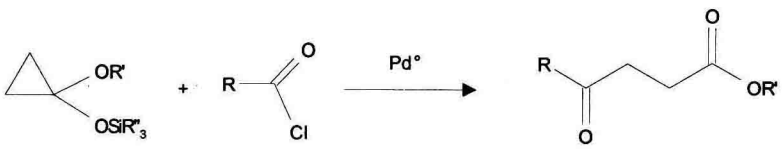
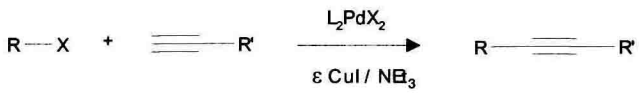
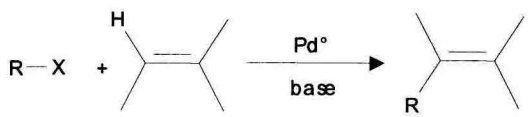
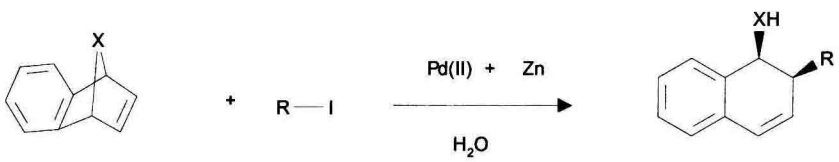
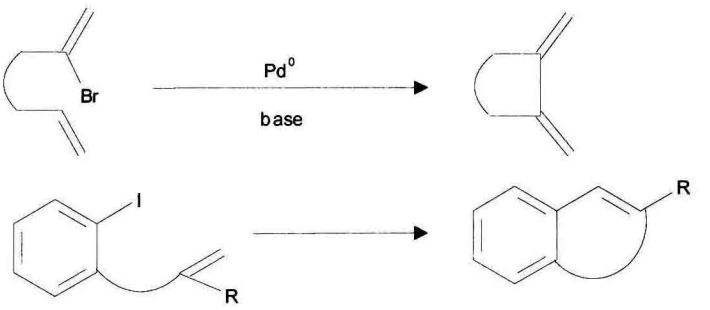
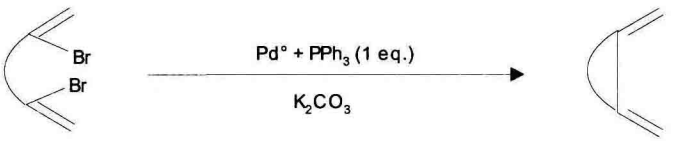
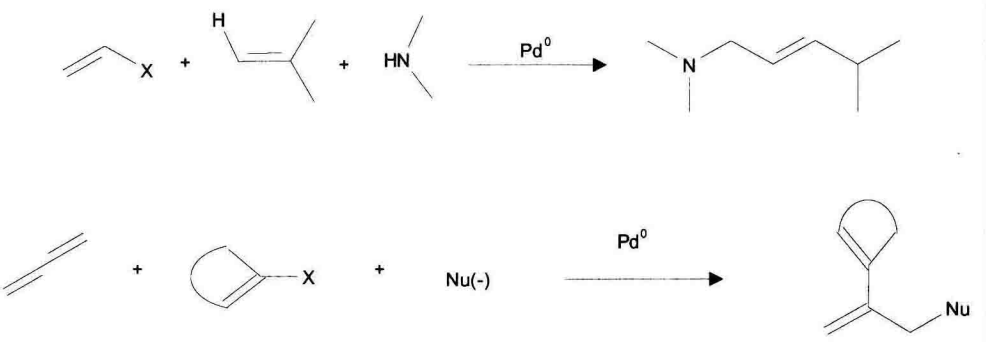
II- GRAPHICAL ABSTRACTS OF REACTION NUMBERS

Reaction number	Graphical abstracts
RXN1	
RXN2	
RXN3	
RXN4	
RXN5	 

RXN6	
RXN7	
RXN8	
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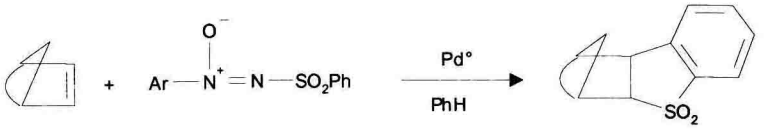
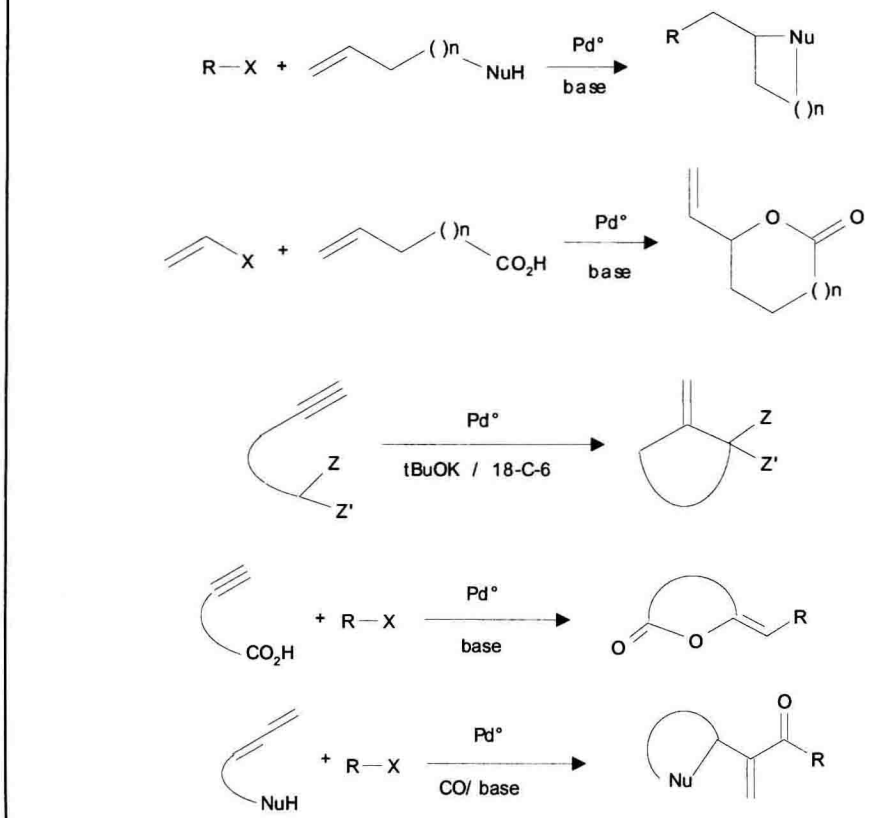
RXN10	

RXN11



RXN12