

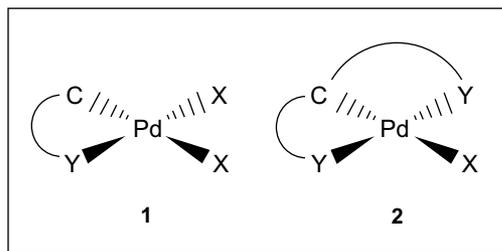
“Palladacycles: Synthesis, Characterization and Applications”

EDITED BY J. DUPONT (UFRGS, Institute of Chemistry, Brazil) and M. PFEFFER (Université Louis Pasteur, France), Wiley-VCH, Weinheim, Germany, 2008, 431 pages, ISBN 978-3-527-31781-3, £120, €144, U.S.\$200

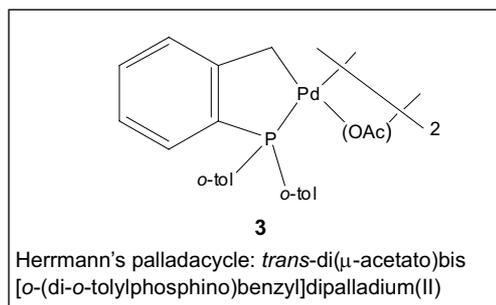
Reviewed by Chris Barnard

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Palladium compounds containing chelating ligands with at least one palladium–carbon bond are commonly known as palladacycles. Related compounds exist for other late transition metals. There are two distinct types of palladacycle where the ligand is either an anionic four-electron donor (Structure 1) or a six-electron donor (Structure 2).



These types of compound were first characterised in the 1960s (1, 2), but came to prominence in the 1990s when their potential as catalysts for cross-coupling reactions was highlighted by Herrmann (3); Herrmann's palladacycle is shown in Structure 3. The compounds have high thermal stability, permitting them to be used with low cost, but poorly reactive, aryl chloride substrates. There are many variations on the basic structural types shown in Structures 1 and 2, differing both in the nature of the supporting donor atom Y (commonly Y = nitrogen, phosphorus or sulfur) and the size of the chelate ring, ranging from three to ten atoms. Compounds containing five- and six-membered rings are the most easily prepared. The compounds may be neutral or charged, and dimeric compounds related to Structure 1 with bridging ligands X (such as chloride, or acetate as in Structure 3) are common.



There have been increasing numbers of papers related to palladacycles in recent years and this book provides a timely review of this literature. There are fifteen chapters contributed by authors interested in the field, which describe the formation, characterisation, properties and applications of palladacycles. They are most commonly formed by activation of an aryl carbon–hydrogen bond (less commonly, reaction can also occur at an aliphatic C–H bond). This transformation has attracted much interest, since C–H activation is key to the efficient utilisation of hydrocarbon natural resources, and has been the focus of both practical and theoretical studies (4). Although palladacycles show excellent thermal stability with respect to decomposition to Pd metal, they are far from inert. This has led to their exploitation as catalysts for cross-coupling reactions. Initially it was thought that these compounds might be stable to reduction to Pd(0) and so a catalytic cycle involving Pd(II) and Pd(IV) was proposed, but to date clear experimental evidence to support this idea has not been obtained, and it is believed that in many cases palladacycles act as steady-state sources of colloidal Pd nanoparticles as the catalytically active species. This application of

palladacycles is rightly placed at the heart of the book and is divided into two chapters, one on Heck and Sonogashira coupling and the other dealing with Suzuki coupling and Buchwald-Hartwig amination. There is also a further chapter describing a range of other synthetic applications of palladacycles.

The book is completed by a number of chapters describing alternative applications of palladacycles. The thermal stability of these compounds arising from the chelating ligand structure allows them to be melted without the decomposition that is typical of many organometallic compounds. This has encouraged their study as liquid crystals. Their stability also makes palladacycles an interesting topic for study in thermomorphic systems, where highly temperature-dependent solubility allows effective recovery and recycling of these materials, and makes them useful for functionalising dendrimer structures. The incorporation of chiral centres into palladacycles allows them to be used as resolving agents for racemic mixtures of ligands. Other chapters deal with the photophysical properties of palladacycles and their similarities to and interactions with biological systems and possible anticancer action.

Overall, the editors of this book are to be congratulated on delivering a well-organised,

interesting and readable overview of this topic. Certainly, palladacycles will continue to provide many opportunities for further study and new applications for years to come and this book will provide an excellent introduction to the subject for those deciding to contribute to this work.

References

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The Reviewer



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