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"Metal Catalyzed Cascade Reactions"

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Reviewed by Ron Grigg
MIDAS Centre, University of Leeds, Leeds LS2 9JT, U.K.; E-mail: r.grigg@leeds.ac.uk

Cascade reactions, also known as domino reactions, are multibond-forming processes in which the first reaction creates the functionality/geometry necessary for the second reaction to proceed, and so on. Volume 19 of the Topics in Organometallic Chemistry series comprises eight chapters written by experts in the relevant areas and is heavily weighted towards palladium(0)-catalysed processes (5 chapters). Additionally, there is an excellent chapter on the Pauson-Khand reaction (mainly cobalt catalysis) and on metathesis (ruthenium).

Chapter 1 (by E. Negishi, G. Wang and G. Zhu) reviews Pd(0)-catalysed cyclisation-carbopalladation and acylpalladation cascades. A logical organisational framework enables systemisation of the sprawling literature, and adequate references to pertinent reviews and early work are provided. The role of proximal alkene and alkyne functionalities in facilitating oxidative insertion of Pd(0) into aryl/vinyl C–halogen bonds is noted. Carbopalladation comprises the major part of this chapter, and the versatility of such processes is amply demonstrated by processes involving polyenes, polyenynes, enylallenes and ynylallenes for the assembly of a bewildering array of fused, bridged and spirocyclic ring systems. The majority of the cascades are one- or two-component processes involving the formation of up to five rings.

The following Chapter 2 (by P. von Zezschwitz and A. de Meijere) covers sequential and cascade combinations of the Heck reaction with 6π-electrocyclisations or Diels-Alder and 1,3-dipolar cycloadditions. The importance of the relative rates of reaction of the substrates and of temperature in cascade design involving three or more components, which in adverse circumstances leads to the sequential one-pot option, is noted. The development of bicyclopropylidene as a cyclopropyl-1,3-diene source in the three-component Heck-Diels-Alder processes is well reviewed, as is the use of allenes in three-component Heck-Diels-Alder and Heck-1,3-dipolar cycloaddition cascades. The latter provide access to a substantial array of heterocycles. Catalytic cross-coupling with ensuing thermal 6π-electrocyclisations, which results in the annulation of 6-membered carbo- or heterocyclic rings onto various core rings including [2,2]-paracylcophanes, is well exemplified.

A survey of Pd(0)-catalysed cascades involving π-allylpalladium(II) species is given in Chapter 3 (by N. T. Patil and Y. Yamamoto), which is essentially a review of Yamamoto's contributions to the area. The major focus is on π-allyl generation from allylic systems, including vinyl oxiranes, thiiranes, aziridines and 1,3-dienes. Generation of π-allyl species from allenes is only fleetingly mentioned. The emphasis is on one- and two-component processes and examples of both carbo- and heterocycle formation are given, including Yamamoto's three-component Pd(0)-Cu(I)-catalysed triazole and tetrazole syntheses from allylic carbonates, trimethylsilyl azide ($TMSN_3$) and an alkyne or nitrile.

Metal-promoted cyclisative cascade reactions which incorporate Michael addition as a key step are the focus of Chapter 4 (by G. Balme, D. Bouyssi and N. Monteiro). The major emphasis is on Pd-promoted processes but examples of copper(I)-, scandium(III)-, yttrium(III)- and rhodium(I)-promoted processes are included. The review is nicely organised and mainly surveys formation of 5- and 6-membered carbocycles and

heterocycles, with a strong emphasis on 5-membered oxygen heterocycles in the latter case. Both Michael initiated and terminated sequences are reviewed and exemplified by unimolecular and two- and three-component cascades involving a variety of metal activated intermediates (π-allylpalladium, π-complexed alkynes, alkenes and enolates).

Chapter 5 (by T. J. J. Müller) reviews a series of sequential Pd-catalysed processes initiated by Heck reactions, allylic substitution, amination, Sonogashira coupling, metallation (for example, *in situ* formation of Stille and Suzuki reagents, Pd migration/insertion into C–H bonds) and cycloisomerisation sequences. Given the huge and buoyant literature, this chapter, of necessity, presents a 'bird's-eye' view of a dynamic field.

The 100% atom economic Pauson-Khand reaction (PKR), a formal [2+2+1]-cycloaddition reaction involving an alkyne, an alkene and carbon monoxide, together with related processes, are covered in Chapter 6 (by J. Pérez-Castells). The concise introduction benefits the non-specialist reader. The current limitations of the catalytic PKR are discussed and the wide range of metal complexes employed are illustrated, as are the various approaches and strategies for chiral induction. The interfacing of the Nicholas reaction (alkylation of Co-stabilised α-carbocationic alkynes) with the PKR and bimetallic Pd-Rh catalysis to generate and process the PKR substrate *in situ* are illustrated, as are *in situ* sources of carbon monoxide. A wide variety of cascade PKRs, including combination with Diels-Alder and photochemical [2+2]-reactions, are also reviewed in this excellent chapter.

Access to complex polycyclic compounds from acyclic precursors is the concern of Chapter 7 (by C. Aubert, L. Fensterbank, V. Gandon and M. Malacria). Inevitably there is some overlap with the other chapters, particularly Chapters 1 and 2. The review is divided into two broad classes: those involving non-carbenoid intermediates and those involving metallo carbenoids. The non-carbenoid processes involve cycloaddition, cycloisomerisation or ene-type reactions in which a simple change in temperature often drives the process to completion. Topics covered include the Kinugasa reaction, the Cu(I)-catalysed β-lactam synthesis from an alkyne plus a nitrone and the coupled Rh(I)-catalysed alkylation of π-allyl species – carbocyclisations which provide a facile access to bicyclic systems. Examples accessing three or more rings include those involving nickel enolates, rhodium- or silver-catalysed Alder-ene processes and Co-catalysed Conia-ene reactions. Processes involving metallo carbenoids focus on α-diazocarbonyl compounds and illustrate how rhodium, ruthenium, nickel and tungsten react with these to generate bridged, fused and spirocyclic ring systems. Other non-carbenoid routes to complex cyclopropanes are also illustrated.

The final Chapter 8 (by C. Bruneau, S. Dérien and P. H. Dixneuf) is concerned with cascade and sequential Ru-catalysed metathesis processes. The cascade processes, which are only briefly reviewed, are enyne metathesis and alkene metathesis, and are largely examples involving Grubbs 2nd generation Ru heterocyclic carbene catalyst and Hoveyda's catalyst. The metathesis area is so fast moving that reviews have a short 'shelf life'.

Overall, this would not be considered a volume for personal libraries but is well worth consulting when appropriate. It is to be recommended on that basis.

The Reviewer

Professor Ron Grigg is Director of the Centre for Molecular Innovation, Diversity and Automated Synthesis (MIDAS Centre) at the University of Leeds, U.K. His current interests include cascade reactions catalysed by palladium, iridium, rhodium and ruthenium, and their applications to medicinal chemistry.