

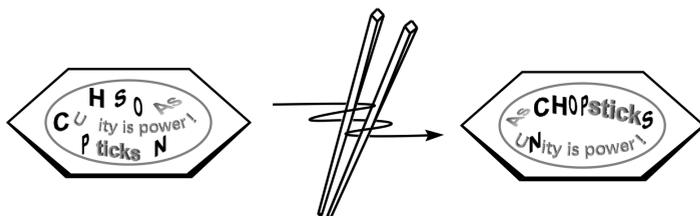
## Abstracts

p 1

### 2.1.1 General Principles of Metal/Organocatalyst Dual Catalysis

Z. Shao and Y.-H. Deng

Metal/organocatalyst dual catalysis is a privileged catalytic strategy which involves both a metal-based catalyst and an organocatalyst to catalyze the organic transformation. Based on the type of activation of substrates with both catalysts, there are seven kinds of dual catalysis; namely cooperative catalysis, cascade catalysis, sequential catalysis, double activation catalysis, restorative catalysis, bifunctional catalysis, and multiple relay catalysis. The generic activation of the metal-based catalyst and the organocatalyst applied in the dual-catalytic system is summarized. In these dual-catalytic approaches, the advantages of both metal catalysis and organocatalysis are converged to achieve many transformations that were previously inaccessible or challenging by any single-catalyst paradigm, to develop new reactions, to discover unique reaction mechanisms, and even to allow for stereodivergent synthesis.



**dual catalysis as chopsticks: unity is power!**

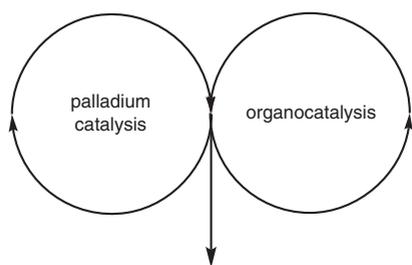
**Keywords:** metal catalysts · organocatalysts · dual catalysis · asymmetric catalysis · stereodivergent synthesis

p 59

### 2.1.2 Palladium/Organocatalyst Dual Catalysis

M. R. Vitale

This chapter describes the recent development of original asymmetric transformations based on the synergistic merger of palladium catalysis with organocatalysis. Thanks to this association, the orthogonal and complementary activation of different reaction partners has proven to be key to the discovery of efficient enantioselective catalytic processes that would not otherwise be possible. To illustrate this, several selected examples are discussed. The combination of  $\pi$ -allylpalladium catalysis with organocatalysis allows a considerable widening of the scope of enantioselective allylic alkylation reactions of carbonyl-containing compounds. Moreover, innovative asymmetric arylation of aldehydes, ketones, and alkenes has also been developed. Finally, palladium/organocatalyst dual catalysis constitutes a unique opportunity for the discovery of new cycloaddition processes.



- development of original reactivities
- new methods for controlling enantioselectivity

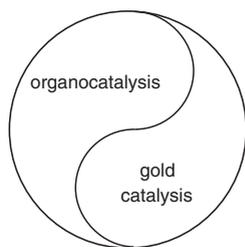
**Keywords:** palladium catalysis • organocatalysis • dual catalysis • synergistic catalysis • allylic alkylation • arylation • cycloaddition

— p 87 —

### 2.1.3 Gold/Organocatalyst Dual Catalysis

*X. Shi and J. Wang*

Since the beginning of the 21st century, gold catalysis and organocatalysis have become two important branches in modern synthetic methodology thanks to the tremendous efforts the synthetic chemistry community have devoted to these two fields. While gold catalysis demonstrates superior capability in the activation of C–C multiple bonds, organocatalysis has been a remarkable tool for the activation and functionalization of carbonyl compounds, such as aldehydes and ketones, in a stereoselective fashion. Combining these two powerful, yet complementary, catalytic modes in a dual-catalytic manner will lead to even more-efficient and sophisticated catalytic systems and, thus, dual gold/organocatalysis has become a hot topic in the past decade. In this chapter, a summary of reported examples of dual gold/organocatalysis are discussed, including gold/aminocatalysis, gold/Brønsted acid catalysis, and gold/hydrogen-bonding catalysis.

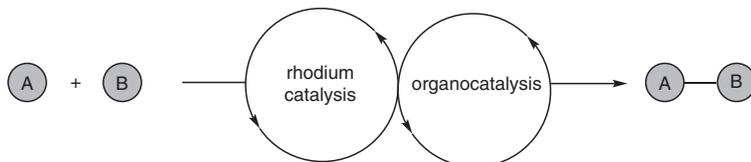


**Keywords:** dual catalysis • gold catalysis • organocatalysis • aminocatalysis • enamines • imines • iminium ions • Brønsted acid • chiral phosphoric acids • hydrogen-bonding catalysts

### 2.1.4 Rhodium/Organocatalyst Dual Catalysis

*F. A. Cruz and V. M. Dong*

This chapter reviews the combined use of rhodium and organocatalysis. The combination of two catalysts enables new reactivity and selectivity.



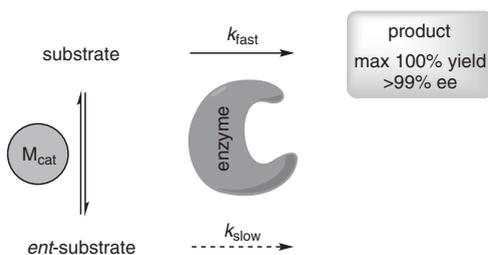
**Keywords:** dual catalysis · asymmetric catalysis · C–H bond activation · C–C bond activation · Brønsted acids · carbene complexes · carbenes · enamines · imines · Lewis acid catalysts · Lewis base catalysts · rhodium catalysis · organocatalysis · aldol-type reaction · Mannich-type reaction · semipinacol rearrangement · Michael addition · C–H activation

### 2.2 Metal/Biocatalyst Dual Catalysis

*M. Diéguez, J.-E. Bäckvall, and O. Pàmies*

Chemoenzymatic dynamic kinetic resolution (DKR) and dynamic kinetic asymmetric transformation (DYKAT) processes have become some of the most appealing transformations for the preparation of chiral molecules. In this review, we present the huge advances made in the combination of a metal racemization catalyst and a biocatalyst for the synthesis of enantiopure alcohols, amines, and other relevant compounds.

chemoenzymatic dynamic kinetic resolution (DKR)



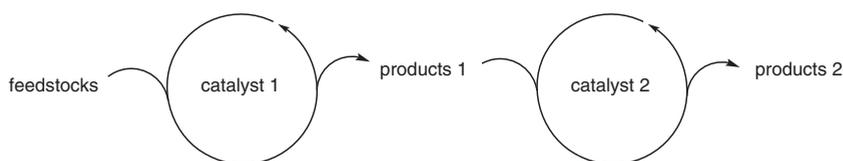
**Keywords:** metal catalysts · biocatalysts · dynamic kinetic resolution · dynamic kinetic asymmetric transformation · chiral alcohols · chiral amines · chiral allenes · chiral carboxylic acids

### 2.3 Dual Catalysis with Two Organocatalysts

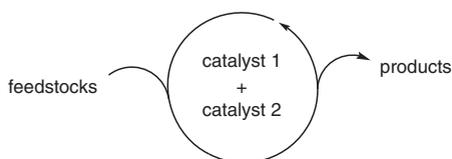
*H.-Y. Wang and G. Zhao*

The field of asymmetric organocatalysis has attracted the attention of chemists due to the environmentally benign conditions, particularly for the synthesis of chiral molecules, bioactive compounds, natural products, and drugs. Besides the conventional approaches using a single organocatalyst in asymmetric reactions, dual catalysis with two organocatalysts has emerged as an important strategy for resolving existing challenging problems, including the synthesis of complex molecules, improvement of enantioselectivities, and the development of new catalytic mechanisms. In this review, selected recent examples of the combination of two organocatalysts are covered in detail. Moreover, future perspectives are also described.

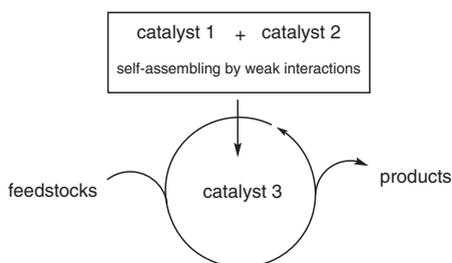
#### multicatalysis with two organocatalysts



#### cooperative catalysis with two organocatalysts



#### supramolecular catalysis with two organocatalysts



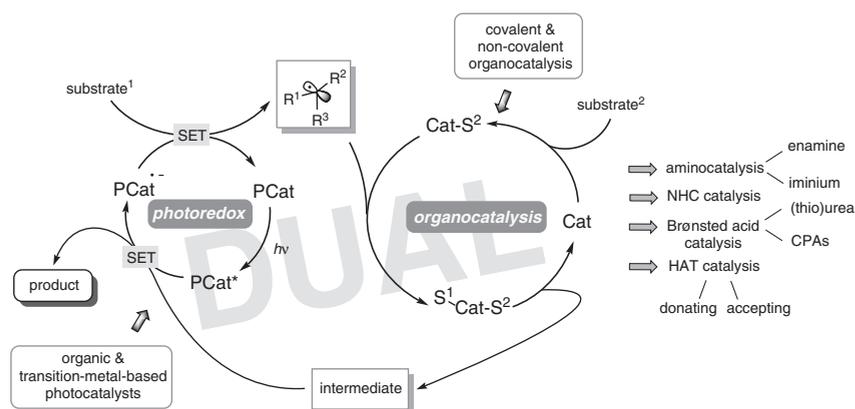
**Keywords:** dual catalysis · asymmetric catalysis · organocatalysis · enamines · imines · nucleophilic pyridines · organophosphines · thioureas · hydrogen bonding · N-heterocyclic carbenes

## 2.4 Organocatalyst/Photocatalyst Dual Catalysis

K. Zeitler

Recent advances in dual-catalytic methods combining organocatalysis with (visible-light) photocatalysis are detailed within this chapter. It summarizes general aspects together with selected state-of-the-art procedures, highlighting both pioneering examples and current developments.

The merger of organocatalysis with photocatalysis has proven to be enormously powerful, not only because it provides a synthetic platform to readily access radical intermediates within an organocatalytic manifold and its potential to alter the reactivity of typical organocatalytic intermediates, but also due to the new opportunities in asymmetric synthesis. The synergistic dual combination with organocatalysis enables photocatalytic reactions to be conducted in an enantioselective fashion and thereby has had a profound influence on several fields of current chemical research, including radical chemistry.

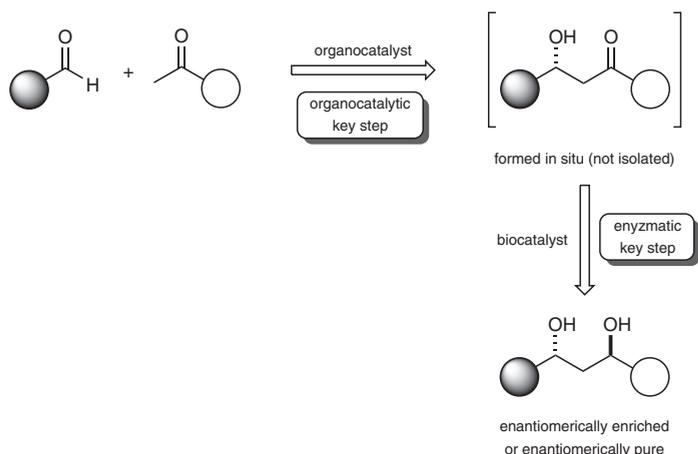


**Keywords:** dual catalysis · organocatalysis · photocatalysis · photoredox catalysis · visible light · asymmetric catalysis · aminocatalysis · enamines · iminium ions · ammonium enolates · isothioureas · N-heterocyclic carbene (NHC) catalysis · Brønsted acid catalysis · chiral phosphoric acids (CPA) · hydrogen-bonding catalysis · thioureas · amidinium · radicals · single-electron transfer (SET) · proton-coupled electron transfer (PCET) · hydrogen-atom transfer (HAT) · radical reactions · ketyl radicals · thiyl radicals · arylation · amination · alkylation · C–H functionalization · activation of C–H bonds · umpolung

## 2.5 Organocatalyst/Biocatalyst Dual Catalysis

Y. Yamashita and H. Gröger

The combination of catalysts from the fields of organocatalysis and biocatalysis toward chemoenzymatic one-pot syntheses is an attractive concept for enabling efficient enantioselective synthetic processes for chiral building blocks without the need for isolation of intermediates, thus avoiding time-consuming as well as waste-producing work-up steps.



**Keywords:** dual catalysis · asymmetric catalysis · biocatalysis · organocatalysis · chemo-enzymatic synthesis · chiral resolution · enantiomeric resolution · enzyme catalysis · one-pot synthesis · organocatalysts · racemization · aldol reaction · nitroaldol reaction · Mannich reaction · Michael addition

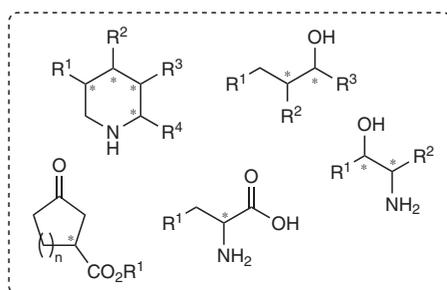
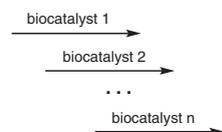
p 365

## 2.6 Dual Catalysis with Two or More Biocatalysts

*F. Parmeggiani, J. L. Galman, S. L. Montgomery, and N. J. Turner*

The remarkable activity, selectivity, and stability of many commercially available or easily prepared biocatalysts, along with their simple operative conditions and the intrinsic “greenness” of biocatalytic processes, have all contributed to a rapidly accelerating expansion of the research area dedicated to the design and development of one-pot multistep synthetic approaches involving two or more enzymes and/or microbial cells. A brief survey of the literature is presented, focusing mainly on efficient protocols that are generally applicable to a broad range of substrates and relevant to the synthesis of small, often chiral, organic molecules as synthons for the pharmaceutical and fine-chemical industries.

one-pot multistep  
biocatalytic processes



**Keywords:** dual catalysis · biocatalysis · enzymes · microorganisms · green chemistry · cascades · multistep processes · asymmetric synthesis · resolution · deracemization · functional-group interconversion