

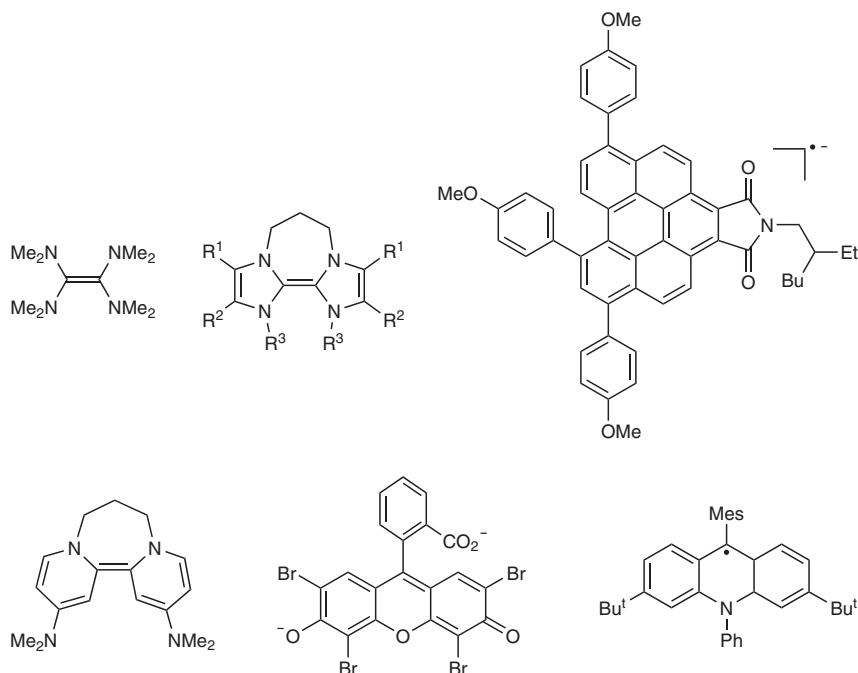
## Abstracts

p 1

### 2.1 Organic Electron Donors in Electron-Transfer Reactions

K. F. Clark, D. Dimitrova, and J. A. Murphy

The field of organic electron donors is large and diverse, both in terms of the structures of the donors and the structures of the acceptors. In the past 15 years, organic donors have been developed that show remarkable strength, with ground-state or excited-state oxidation potentials rivalling even the most reactive metals. At the other end of the scale of reactivity, highly reactive oxidizing agents are now available upon photoactivation of a number of organic structures. The first part of this chapter reviews organic electron donors that are based upon an alkene that is activated by strongly electron-releasing substituents; these donors can be active in the ground and/or excited states. The chapter also covers anionic organic donors that emerged in the field of  $S_{RN}1$  and base-induced homolytic aromatic substitution (BHAS) reactions, as well as substrate-based anionic donors including borates and silicates. The use of photoexcited organic dyes as electron donors is described and, finally, some of the recent research with very weak organic donors is highlighted.

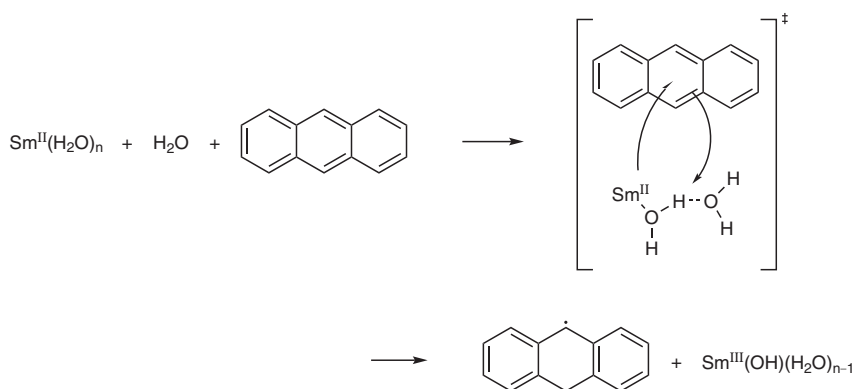


**Keywords:** organic electron donors • radicals • radical anions • reduction • tetrakis(dimethylamino)ethene (TDAE) • tetrathiafulvalene (TTF) •  $S_{RN}1$  reactions • base-induced homolytic aromatic substitution (BHAS) reactions •  $\text{tert}$ -butoxide • organic dyes • eosin Y • rhodamines • acridinium salts • photoexcitation

## 2.2 Samarium-Mediated Reductions


*R. A. Flowers, II, T. V. Chciuk, C. O. Bartulovich*

Samarium(II)-based reductants have been shown to be a group of very powerful reagents whose reactivity can be tuned significantly by the use of additives. The use of additives has been shown to greatly impact the rate, diastereoselectivity, chemoselectivity, and mechanism by which these reactions proceed, making these systems extremely useful and versatile. These reagents have been shown to promote several reactions including reductions of a range of functional groups and a variety of carbon–carbon bond forming reactions. More recently, initial work has demonstrated catalytic reactions of samarium(II)-based reductants. This chapter focuses on the chemistry of samarium diiodide ( $\text{SmI}_2$ ) and a few other samarium(II)-based reductants, with examples of the reactions they promote, both with and without the use of additives. Additionally, recent work on the mechanistic understanding of catalytic reactions using terminal reductants and a novel example of an approach employing radical relay that negates the use of a terminal reductant are presented.

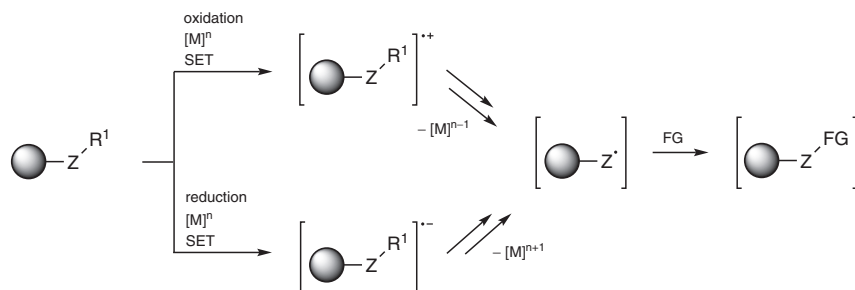


**Keywords:** samarium • electron transfer • proton donors • hexamethylphosphoric triamide (HMPA) • Lewis bases • additives • lithium halide additives • cyclizations • reductions • reductive coupling • catalysis

### 2.3 Single-Electron-Transfer Oxidation and Reduction Involving Metal Complexes other than Samarium

M. Cormier and J.-P. Goddard 



Recent advances in the field of radical organic chemistry involving single-electron transfer (SET) are highlighted in this chapter. The focus is on processes between organic molecules and metal complexes that facilitate the creation of challenging covalent bonds. A selection of oxidation and reduction reactions is reported, with special attention paid to enantioselective reactions. Mechanistic discussions are also provided.



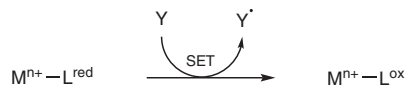
Z = C, N, O, P

**Keywords:** radical chemistry · organic synthesis · oxidation · reduction · single-electron transfer · metal complexes · enolate coupling · atom-transfer radical addition (ATRA) · C–H oxidation · amination · fluorination · enantioselective reactions · hydrofunctionalization · aryl coupling · phosphorylation

### 2.4 Redox-Active Ligands in Catalysis for Single-Electron-Transfer Processes

Y. Ren, A. Das, , C. Hessin, and M. Desage-El Murr 

Redox-active ligands are well known for their ability to stabilize electronic density on their scaffolds, and coordination complexes with such ligands are often stable, open-shell species. This property can be used as a means to favor single-electron transfer (SET) with external sources and devise catalytic radical manifolds. This chapter highlights selected representative reactions resulting in efficient and broad-scope catalytic methodologies. It covers nitrene and carbene radical reactivity, as well as radical trifluoromethylation.



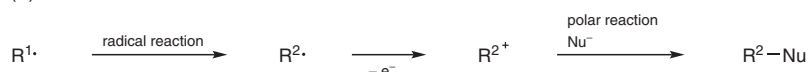
**Keywords:** redox-active ligands · radicals · single-electron transfer · nitrenes · carbenes · trifluoromethylation · aziridines · cyclopropanes · C–H functionalization · porphyrins · transition-metal complexes

## 2.5 Radical–Polar Crossover Reactions

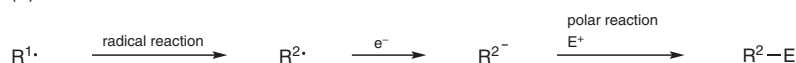
*F. Chemla and A. Pérez-Luna*

Radical–polar crossover reactions, that is, single-electron redox events allowing for the interconversion between radical and ionic intermediates, make it possible to connect radical and polar processes in the same synthetic transformation. Such a combination is the basis of much original synthetic methodology, which is particularly useful in the context of domino, tandem, or multicomponent reactions. This chapter comprehensively covers the field of radical–polar crossover reactions, with a primary emphasis on transformations wherein both the radical and polar processes provide synthetic elaboration.

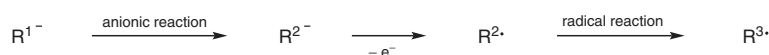
(A) radical-to-cation crossover



(B) radical-to-anion crossover



(C) anion-to-radical crossover

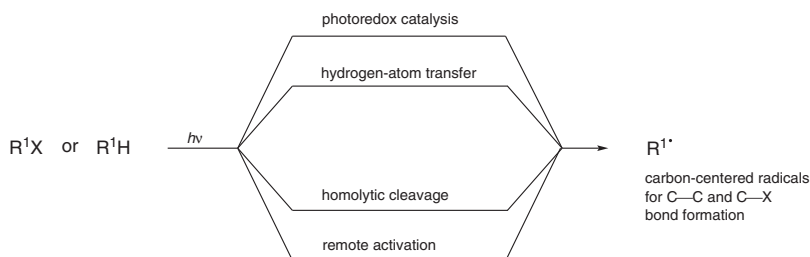


**Keywords:** radical–polar crossover reactions • anionic reagents • carbocations • domino reactions • multicomponent reactions • organometallic reagents • oxidation • photochemistry • radical addition • radical cyclization • radical reactions • radicals • reduction • tandem reactions

## 2.6 Generation of Carbon-Centered Radicals by Photochemical Methods

*M. Fagnoni, D. Ravelli, and S. Protti*

A selection of the recent literature describing the light-driven generation and subsequent exploitation of carbon-centered radicals for synthetic purposes is presented in this chapter. The aim is to showcase to organic (photo)chemistry practitioners the impressive potential of photocatalytic and photochemical strategies in terms of versatility, efficiency, and sustainability.

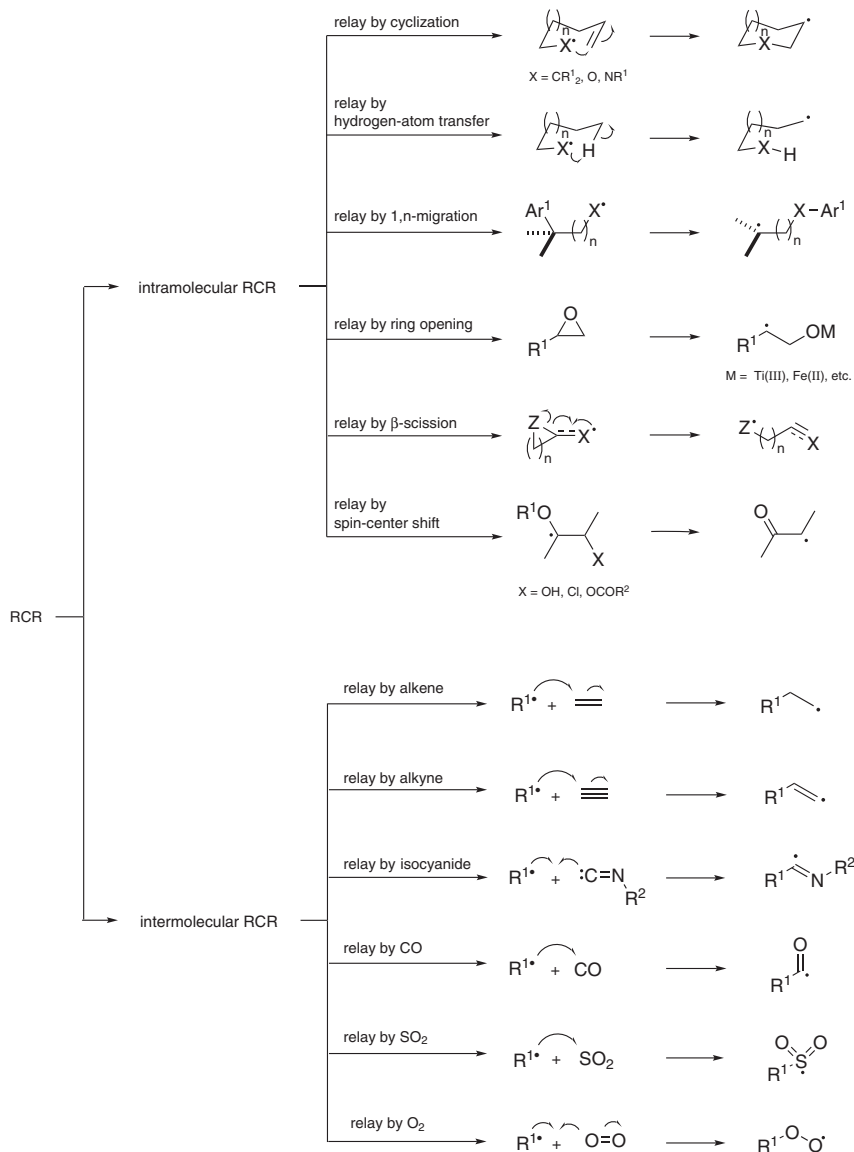


**Keywords:**  $C-C$  bond formation • photocatalysis • photochemistry • radical ions • radicals

## 2.7 Radical Cascade Reactions

Z.-Q. Liu 

This chapter briefly summarizes the concept of radical cascade reactions (RCR). The chapter is divided into two main parts, describing intramolecular and intermolecular radical cascade reactions, which are further classified based on the six types of relay manner (intramolecular RCR) and six commonly used relay molecules (intermolecular RCR), respectively. This simple classification allows readers to understand this area easily and quickly. Features of radical cascade reactions include step-economy and waste minimization, which endow these radical cascades with a bright future.

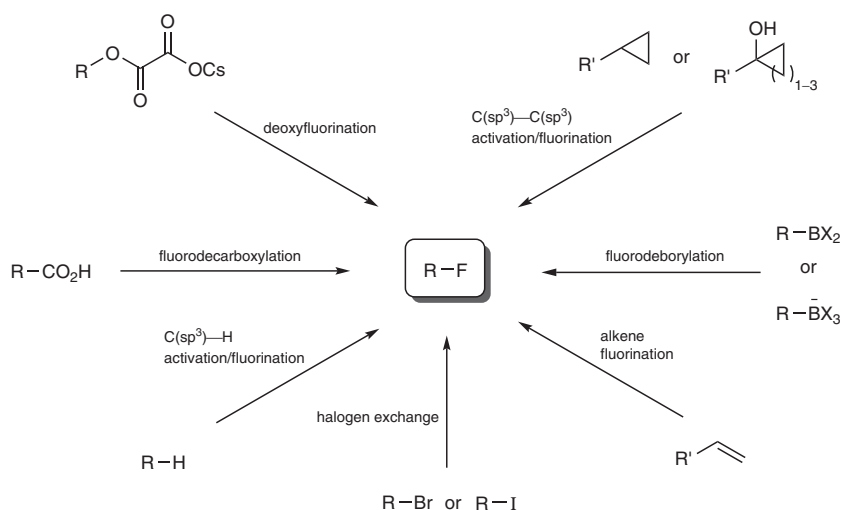


**Keywords:** free radicals · radical cascade reactions (RCR) · domino reactions · synthetic methods

## 2.8 Selective Radical Fluorinations

T. G. Bolduc, B. Thomson, and G. M. Sammis

Fluorine atoms are found in numerous industrially relevant materials, including pharmaceuticals, agrochemicals, and plastics. In the pharmaceutical industry alone, more than 20% of all therapeutics and a majority of the top-grossing drugs contain fluorine. The ubiquity of fluorinated compounds in industry has necessitated the development of new methods for selective fluorination. Historically, selective fluorination has relied upon electrophilic or nucleophilic processes. Recently, breakthroughs in the discovery of mild radical fluorine-transfer reagents have led to a renaissance in selective radical fluorinations. This review provides a brief overview of the known fluorine-transfer reagents, including molecular fluorine, hypofluorites, xenon difluoride, electrophilic N-F reagents, and metal-F reagents. A survey of a range of radical fluorination reactions is covered, including fluorodecarboxylation, fluorination of alkenes, fluorination of boronic acid derivatives, C-H activation and fluorination, C-C activation and fluorination, deoxyfluorination, and halogen-exchange reactions. This review primarily focuses on advances in the last ten years, with an emphasis on the most practical methods.

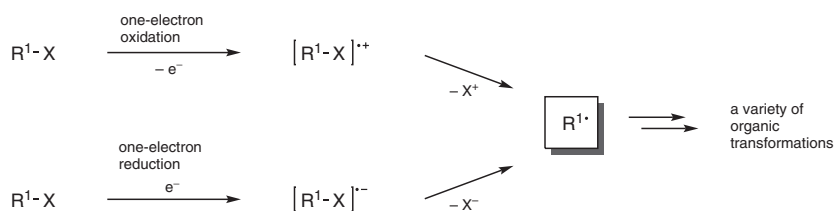


**Keywords:** selective radical fluorinations · fluorine-atom transfer · Selectfluor · *N*-fluorobenzenesulfonimide (NFSI) · fluorine · hypofluorites · xenon difluoride · metal fluorides · fluorodecarboxylation · fluorination of alkenes · fluorodeborylation · C(sp<sup>3</sup>)-H fluorination · C(sp<sup>2</sup>)-H fluorination · C(sp<sup>3</sup>)-C(sp<sup>3</sup>) activation and fluorination · deoxyfluorination · halogen exchange · photocatalysis · electrochemistry

## 2.9 Electrochemical Organic Synthesis via Radical Species

*K. Mitsudo and S. Suga*

An electrochemical single-electron-transfer reaction is a promising method to generate reactive radical species in organic synthesis. One-electron oxidation of a neutral compound gives a radical cation, which usually breaks down into a radical and a cationic species; conversely, one-electron reduction of a neutral compound affords a radical anion, which forms a radical and an anionic species. The radical species generated in this way can be used for a variety of transformations. In this chapter, selected recent electrochemical transformations that involve electrogenerated radical species are collected and described.



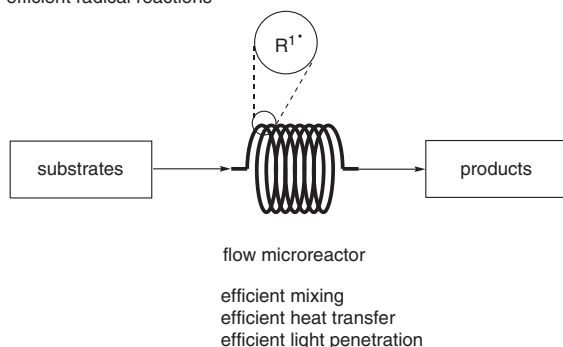
**Keywords:** electrochemistry · electroorganic chemistry · radical species · single-electron-transfer reaction · one-electron oxidation · one-electron reduction · electrochemical oxidation · electrochemical reduction · nitrogen-centered radicals · sulfur-centered radicals · carbon-centered radicals

## 2.10 Radical Chemistry in Flow

*S. Sumino, T. Fukuyama, and I. Ryu*


The past two decades have witnessed a rapid growth in flow-based organic synthesis and synthesis involving radical reactions in flow systems is no exception. Flow microreactors have large surface-to-volume ratios that become available by the employment of tiny channels, and this allows radical reactions to occur with efficient heat transfer and diffusion. Flow photomicroreactors with thin, glass-made channels allow for efficient light penetration, which enables highly efficient photo-radical reactions. This chapter highlights recent advances in both thermal and photo-induced radical reactions, which have achieved increased efficiency by using flow reaction systems.

efficient radical reactions



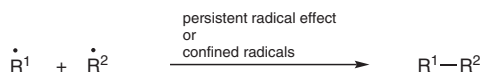
**Keywords:** radical reaction · flow chemistry · microreactors · radical reduction · radical cyclization · radical carbonylation · radical halogenation · radical C–H functionalization · photo-radical reaction

## 2.11 Radical–Radical Cross-Coupling Reactions

M. Zhou and T. Qin 

Due to nearly diffusion-limited radical–radical coupling, synthetically useful, selective radical–radical cross-coupling reactions remain challenging. However, different radical lifetimes and various radical initiation approaches now provide the possibility for radical–radical cross-coupling. In this chapter, recent advances in radical–radical cross-coupling reactions are described. In the first part, a basic kinetic phenomenon called the persistent radical effect is briefly reviewed and explained. The remainder of the chapter presents a series of case studies, illustrating several types of radical–radical cross couplings in a variety of disparate settings.

radical–radical cross coupling

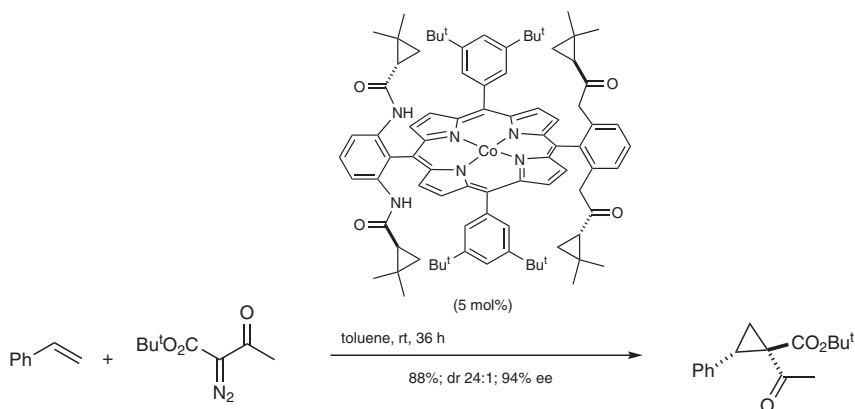


**Keywords:** radical–radical cross coupling (RRCC) • persistent radicals • transient radicals • persistent radical effect • single-electron transfer • C–C bond formation • metal-free coupling • radical–metal crossover

## 2.12 Asymmetric Catalysis of Radical Reactions

H. Subramanian and M. P. Sibi

Synthetic methodologies based on radical chemistry are efficient and powerful tools for the construction of carbon–carbon and carbon–heteroatom bonds. This chapter highlights the significance of asymmetric catalysis in free-radical reactions. Several asymmetric catalytic principles, ranging from early chiral Lewis acid and organocatalytic activation to recent photoredox and transition-metal-based asymmetric catalytic systems, are discussed.

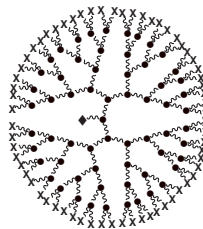
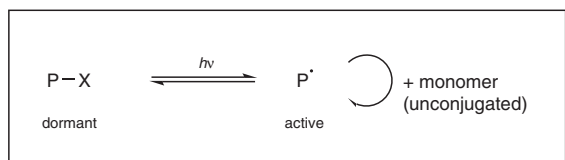


**Keywords:** asymmetric catalysis • radical reactions • chiral Lewis acids • hydrogen-atom transfer • chiral aluminum Lewis acids • chiral Brønsted acids • organocatalysis • photoredox catalysis • transition-metal catalysis • single-electron transfer • chiral porphyrins • chiral N-heterocyclic carbenes



**2.13 Recent Developments in Reversible Deactivation Radical Polymerization***S. Yamago and Y. Lu*

Recent developments in reversible deactivation radical polymerization, which is also called controlled or living radical polymerization, are summarized in this chapter. In particular, this chapter focuses on (1) broadening the range of applicable monomers from conjugated monomers to unconjugated monomers, (2) the expansion of the polymer structure from linear polymers to highly branched polymers, and (3) the use of light, in particular low-intensity and inexpensive visible light, to enable a higher degree of polymerization control under environmentally benign polymerization conditions.



**Keywords:** reversible deactivation radical polymerization · living radical polymerization · unconjugated monomers · highly branched polymers · hyperbranched polymers · photoactivation · photoredox catalysts