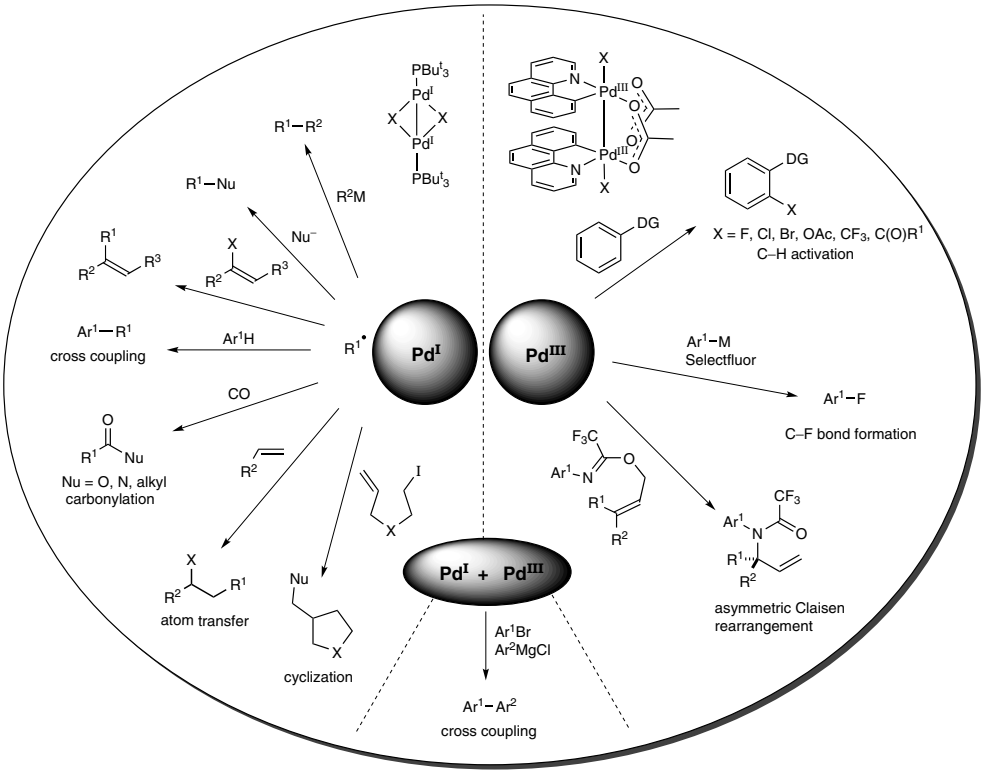
Abstracts

New p 1

1.2.7 **Radical-Based Palladium-Catalyzed Bond Constructions**
Y. Li, W. Xie, and X. Jiang

Palladium(0) and palladium(II) species are frequently used as catalysts and are considered to be active intermediates in traditional palladium-catalyzed coupling reactions, participating in oxidative addition and reductive elimination via two-electron-transfer processes. Meanwhile, the catalytic modes involving palladium(I) and palladium(III) have been gradually developed. Single-electron-transfer pathways are thought to be involved via related catalytic cycles. Various palladium(I) and palladium(III) complexes have been synthesized and characterized. The palladium(I) precatalysts in Suzuki coupling and Buchwald–Hartwig amination exhibit higher reactivity than traditional palladium(0) and palladium(II) catalysts. Palladium-catalyzed single-electron-transfer conditions allow alkyl halides to participate in a series of cross-coupling, carbonylation, atom-transfer, and cyclization reactions, in which the palladium(I) species and various alkyl radicals are thought to be key intermediates. Palladium(III) species have been proposed as active intermediates in various directed C—H activation reactions. Moreover, it has been proved that palladium(III) intermediates can catalyze C—F bond formation and asymmetric Claisen rearrangement reactions. Beyond these systems, it is thought that palladium(I) and palladium(III) species might take part in the same system. In summary, radical-type palladium-catalyzed systems possess new properties which help to realize various otherwise difficult transformations.



Keywords: bond construction · palladium(I) catalysis · palladium(III) catalysis · radical processes

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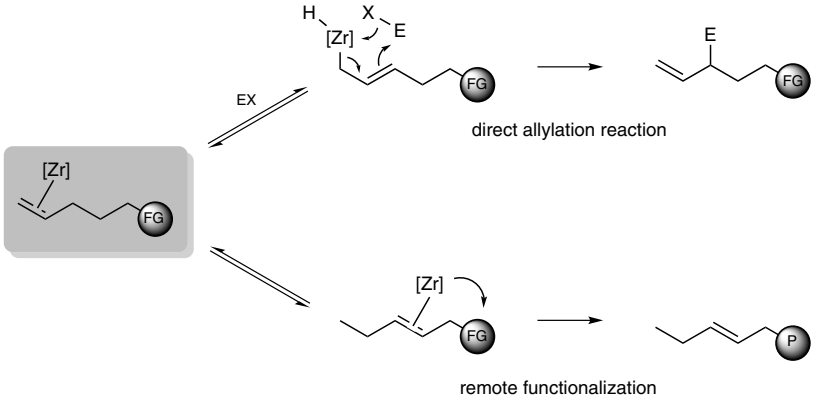
2.11.15 C(sp^3)—H Functionalization by Allylic C—H Activation of Zirconocene Complexes

A. Vasseur and J. Bruffaerts

Zirconocene-assisted allylic C(sp^3)—H activation allows the remote functionalization of alkenes through multipositional migration of the olefinic double bond as a communicative process between two distant sites. The transformation involves the successive formation of zirconacyclopropane species along an alkyl chain. This C—H activation promoted migration proceeds rapidly under mild conditions. Moreover, it occurs in a unidirectional manner if associated with thermodynamically favored termination steps such as elimination, selective carbon–carbon bond activation, or ring expansion. The remotely formed zirconocene species can subsequently react with a variety of electrophilic carbon, oxygen, or nitrogen reagents to give a wide range of added-value products from simple substrates. Transmetalation processes further increase the synthetic potential by allowing the remote formation of a new carbon–carbon bond. The global transformation is not

only stereo- and regioselective, but also enables the relay of stereochemical information. Alternatively, a ziconacyclopropane/crotylzirconocene hydride equilibrium can be promoted under particular reaction conditions, leading to direct regio- and stereoselective allylation reactions with acid chloride, aldehyde, diketone and imine derivatives.



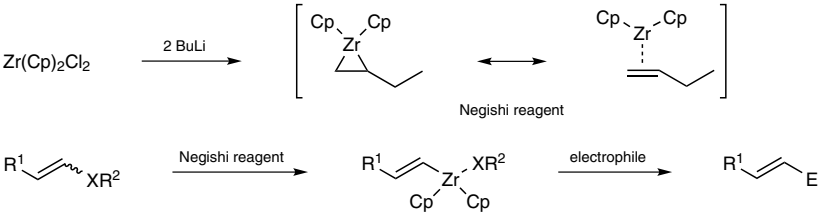
Keywords: zirconocenes · allylic C—H activation · alkenes · conjugated dienes · trienes · homoallylic alcohols · homoallylic amines · alkenylcyclopropanes · cyclopropanols · diastereoselectivity · quaternary stereocenters

New p 147

2.11.16 **Synthesis and Reactivity of Heteroatom-Substituted Vinylzirconocene Derivatives and Hetarylzirconocenes**

J. Bruffaerts and A. Vasseur

Reactive and stereodefined vinylzirconocene derivatives are efficiently prepared from a variety of different heterosubstituted alkenes in the presence of a stoichiometric amount of the Negishi reagent. This chapter describes the synthesis of these compounds along with their applications in the synthesis of various substituted alkenes.



Keywords: organometallic compounds · zirconocenes · alkenes · vinyl compounds · stereoselective synthesis · elimination

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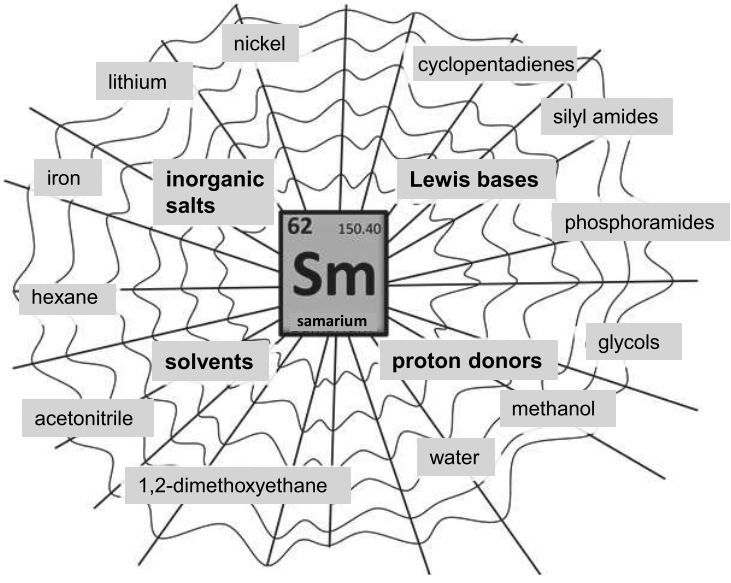
2.12.17 **The Role of Solvents and Additives in Reactions of Samarium(II) Iodide and Related Reductants**

T. V. Chciuk and R. A. Flowers, II

The use of additives with samarium(II) iodide (SmI_2) greatly impacts the rate, diastereoselectivity, and chemoselectivity of its reactions. Additives that are commonly utilized with samarium(II) iodide and other samarium(II)-based reductants can be classified into three major groups: (1) Lewis bases such as hexamethylphosphoric triamide (HMPA) and other electron-donor ligands and chelating ethers; (2) proton donors, such as water, alcohols, and glycols; and (3) inorganic additives such as nickel(II) iodide, iron(III) chloride, and lithium chloride. In addition, the solvent milieu can also play an important role in the reactivity of samarium(II) reductants, predominantly through changes in the coordination sphere of the metal. The main focus of this chapter is on the use of additives and solvent milieu to provide selective and efficient reactions, with at least one example being given for each subclass of samarium(II)-promoted reaction.



Keywords: cross-coupling reactions · electron transfer · hexamethylphosphoric triamide · inorganic additives · intramolecular cyclization · Lewis bases · proton donors · reductive coupling · ring expansion · samarium(II) iodide · solvent effects

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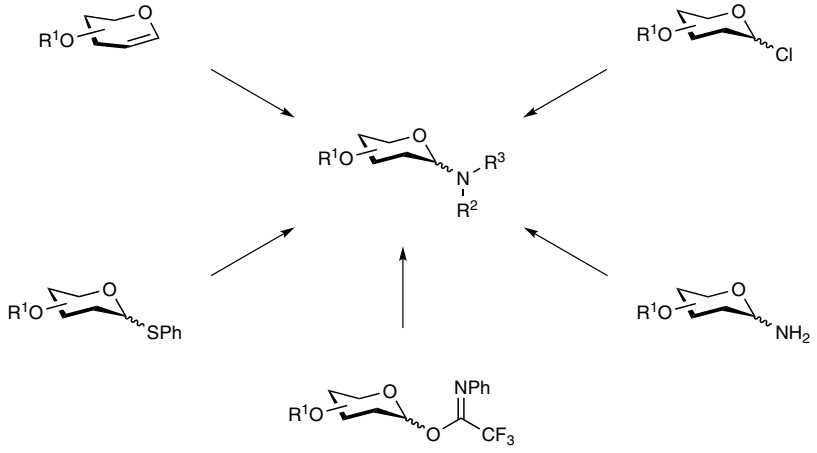
30.1.3 **Carbohydrate Derivatives (Including Nucleosides)**

T. Nokami

O,*N*-Acetals are found in various types of organic molecules and are core motifs in carbohydrates, including nucleosides. This chapter summarizes the synthetic methods to prepare N-linked glycopeptides, ribonucleosides, 2-deoxyribonucleosides, and others. Glycosylation between the anomeric carbon and the nitrogen atom of a nucleophile is a conventional method for the synthesis of these molecules, but stereoselectivity highly depends on the structures of the substrates. Glycosylamines are also important precursors for the stereoselective synthesis of N-linked glycopeptides and ribonucleosides.



Keywords: aminoglycosides · carbohydrates · glycopeptides · glycosylation · nucleosides

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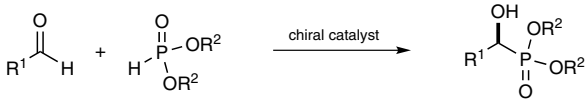
30.2.3 ***O*,*P*-Acetals**

K. Murai and H. Fujioka

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.2) describing methods for the synthesis of *O*,*P*-acetals. It focuses on the literature published in the period 2006–2015. Key methods covered include the addition of phosphorus compounds to carbonyl groups (including enantioselective variations), kinetic resolution of α-hydroxyphosphonates, oxidation of α,β-unsaturated phosphorus compounds, addition of phosphorus compounds to *O*,*O*-acetals, reduction of acylphosphonates and related compounds, and aldol-type reactions of keto phosphonates.



Keywords: *O*,*P*-acetals · asymmetric synthesis · diastereoselectivity · enantioselectivity · kinetic resolution · hydrogenation · organocatalysis · oxidation · epoxidation · reduction · phosphorus compounds · Pudovik reaction

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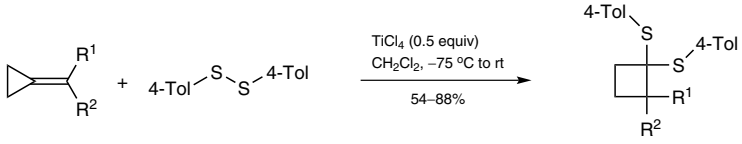
30.3.1.3 **Acyclic *S*,*S*-Acetals**

A. Tsubouchi

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.3.1) describing methods for the preparation of acyclic *S*,*S*-acetals. It focuses on the literature published in the period 2006–2014, presenting complementary information with respect to new developments and transformations. It also contains an important extension of the coverage of the previous contribution. Key methods covered include the thioacetalization of carbonyl compounds using a variety of catalysts, conversion of *O*,*O*-acetals, addition of thiols to C—C multiple bonds, addition of disulfides to methylenecyclopropanes, and ring opening of 1,2-cyclopropanated 3-oxo sugars with thiols.



Keywords: acetals · carbonyl compounds · chemoselectivity · Lewis acid catalysts · *S*,*S*-acetals · supported catalysis · surfactants · thiols · ring opening

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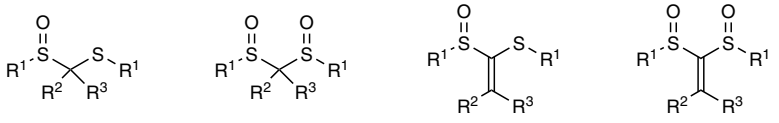
30.3.6.3 **Acyclic and Cyclic *S*,*S*-Acetal *S*-Oxides and *S*,*S*′-Dioxides**

A. Ishii

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.3.6) published in 2007. *S*,*S*-Acetal *S*-oxides and *S*,*S*′-dioxides are synthesized by the reaction of sulfanyl- or sulfinyl-stabilized carbanions with electrophiles or by the (asymmetric) oxidation of *S*,*S*-acetals. Reaction of a carbanion with an aldehyde or ketone followed by dehydration provides ketene *S*,*S*-acetal oxides. Recent advances in synthetic application have been seen in conjugate additions of nucleophiles or radicals to ketene *S*,*S*-acetal oxides and in reactions utilizing reactive sulfonium intermediates generated by treatment with acid anhydrides (Pummerer conditions).



Keywords: sulfur-stabilized carbanions · asymmetric oxidation · condensation · ketene dithioacetals · conjugate addition · cyclopropanation · cross-coupling reaction · hydrolysis · Pummerer conditions · benzo[*b*]chalcogenophenes

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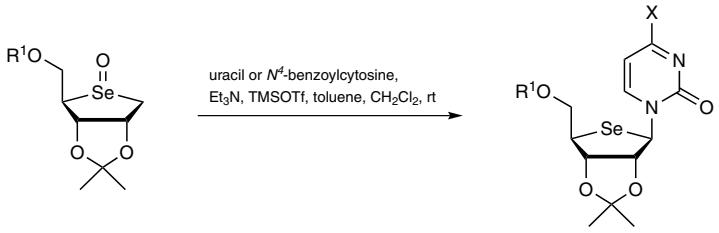
30.5.6 **Selenium- and Tellurium-Containing Acetals**

M. Yoshimatsu

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.5) concerning the synthesis and reactions of selenium- and tellurium-containing acetals. Recent interest has changed to the new field of *Se*,*N*- and *Te*,*N*-acetals including 4′-selenonucleosides, which may be used as unique building blocks for new DNA and RNA analogues. The published methods for *Se*,*N*- and *Te*,*N*-acetals could open up new applications in this field.



Keywords: *Se*,*Se*-acetals · *Se*,*Te*-acetals · *Se*,*N*-acetals · 4′-selenonucleosides · seleno-Pummerer reactions

2016 p 407

30.7.3 ***N*,*P*- and *P*,*P*-Acetals**

T. Kimura

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 30.7) describing methods for the synthesis of *N*,*P*- and *P*,*P*-acetals. It focuses on the literature published in the period 2007–2014. As well as covering the synthesis of the title compounds, their applications in organic synthesis are also briefly reviewed.

Keywords: α-aminophosphonates · hydrophosphorylation · imines · Pudovik addition · Kabachnik–Fields three-component condensation · Horner–Wadsworth–Emmons alkenation · *gem*-bisphosphonates · phospha-Claisen condensation · Michaelis–Becker substitution · Michaelis–Arbuzov rearrangement