

Abstracts

New

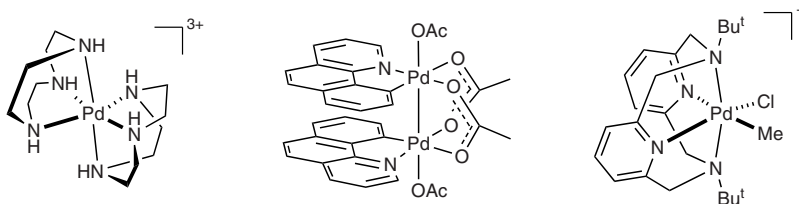
p 1

1.2.5

Product Subclass 5: Palladium(III)-Containing Complexes

D. C. Powers and T. Ritter

Compared with the chemistry of palladium in the 0, I, II, and IV oxidation states, organopalladium(III) chemistry is in its infancy, and complexes containing palladium in the III oxidation state are rare. Despite the scarcity of isolated palladium(III) complexes, recent studies have suggested palladium(III) intermediates may participate in a variety of palladium-catalyzed reactions, including oxidative C–H functionalization and aerobic oxidation reactions. In addition, several new preparative methods toward isolable palladium(III) complexes have been developed, which has allowed direct interrogation of the fundamental organometallic chemistry of organopalladium(III) complexes. Herein, preparative methods for the synthesis of palladium(III) complexes are reviewed and reactions in which palladium(III) intermediates are proposed are discussed.



Keywords: C–H functionalization · organopalladium chemistry · palladium(III) · aerobic oxidation · metal–metal bonds · radical chain reactions

2012

p 33

2.10.20

Organometallic Complexes of Titanium (Update 2)

G. C. Micalizio

This chapter is an update of the earlier *Science of Synthesis* contribution on organometallic complexes of titanium, specifically on titanium alkoxide mediated methods for C–C bond formation. Distinct from the previous contribution, the current work describes developments that enable the realization and control of a broad class of intermolecular reductive cross-coupling reactions between a variety of unsymmetrically substituted π -systems (alkenes, alkynes, allenes, imines, and aldehydes). General principles of reaction design are discussed, successful demonstrations of these reactions are then described for a variety of metallacycle-mediated cross-coupling reactions, and selected applications of these reactions in natural product synthesis are presented. The bulk of the science described is extracted from literature published in the period of 2006 to early 2012.

2012

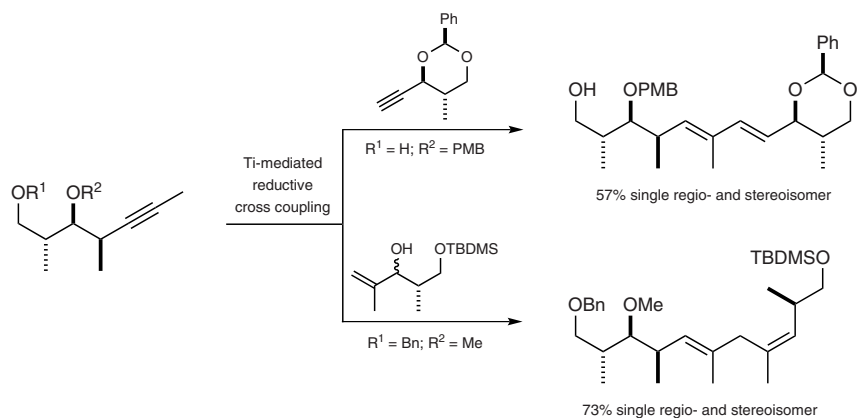
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2012

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Keywords: alicyclic compounds · alkaloids · alkenes · alkyne complexes · alkynes · al-
lenes · allylic alcohols · carbocyclic compounds · carbometalation · C—C bonds · C—C cou-
pling · carbon—metal bonds · chemoselectivity · chiral compounds · complexation · cross-
coupling reactions · diastereoselectivity · dienes · enantioselectivity · enynes · fatty acids ·
Grignard reagents · heterocycles · homoallylic alcohols · homopropargylic alcohols ·
imines · metallacycles · natural products · polyols · pyridines · reductive coupling · regio-
selectivity · stereoselective synthesis · titanium complexes · total synthesis · trienes · um-
pung · unsaturated compounds · vinylsilanes

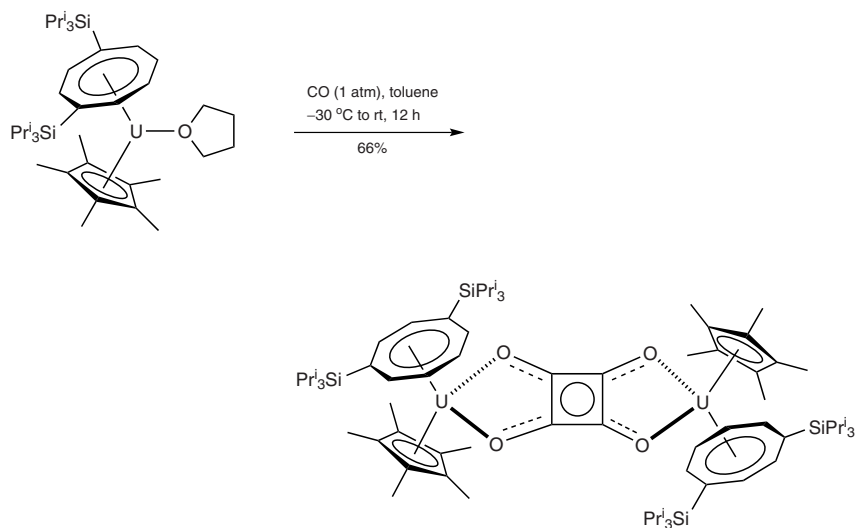
2012

p 99

2.13 Product Class 13: Organometallic Complexes of the Actinides

R. J. Batrice, I.-S. R. Karmel, and M. S. Eisen

This manuscript is a revision of the earlier *Science of Synthesis* contribution describing the methods of synthesis and applications of organoactinide complexes. The preparation of a broad variety of such complexes, along with their catalytic and stoichiometric reactivities, are provided herein. The main focus of this work lies on developments of the past decade; however, earlier works are included for completeness and to provide an adequate background detailing the advances in actinide chemistry.



2012

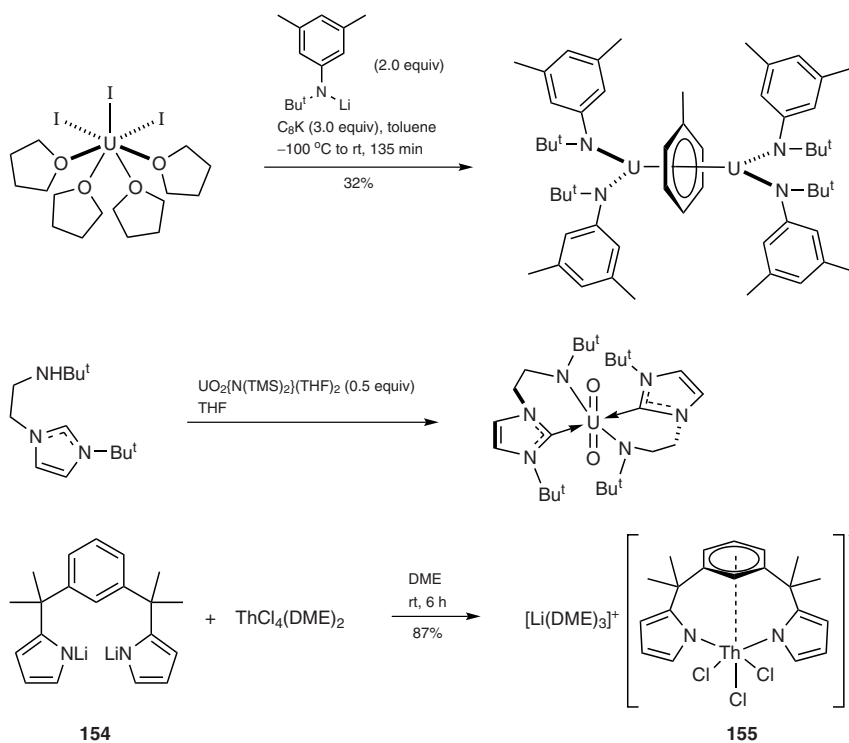
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2012

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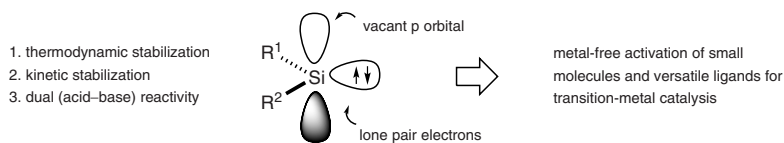
Keywords: organometallics · actinides · cyclopentadienyl ligands · arenes · carbenes · amido ligands · imido ligands · bridged ligands · homobimetallic complexes · heterobimetallic complexes · catalysis

2012

p 213

4.4.3 **Product Subclass 3: Silylenes***S. Inoue and M. Driess*

Silylenes are the heavier analogues of carbenes, bearing divalent silicon atoms. They are far more electron-donating and reactive species than carbenes and thus represent a novel and promising class of steering ligands suitable for the activation of small molecules and for catalysis. Various novel and differently substituted cyclic silylenes have been successfully isolated and characterized, which provide a better understanding of structure–reactivity relationships of stable divalent silicon compounds. This chapter essentially covers the tremendous progress in the chemistry of carbocyclic and heterocyclic silylenes. Their utility as building blocks for the synthesis of novel functional silicon compounds and their role as strikingly versatile coordination ligands toward transition metals is highlighted.



1. thermodynamic stabilization
2. kinetic stabilization
3. dual (acid–base) reactivity

$R^1 = R^2 = \text{H, alkyl, aryl, silyl, alkoxy, halo, amino, phosphino}$

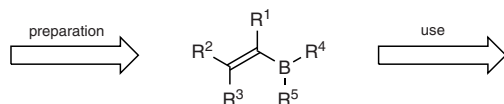
Keywords: catalysis · reduction · silyl halides · cations · insertion reactions · addition reactions · dienes · aldehydes · ketones · imines · alkynes · cyanides · isocyanides · azides · alkenes · silicon · silenes · carbenes · pyridines · oxygen compounds · phosphorus compounds · transition metals

2012

p 297

6.1.28.24 **Vinylboranes***M. Vaultier and M. Pucheault*

Vinylboranes have numerous applications in organic synthesis. This chapter provides an update to the original *Science of Synthesis* contribution on synthesis and applications of this scaffold. New and modified routes to vinylboranes are detailed and further transformations of vinylborane synthons, exploiting the reactivity of the C–B bond or the C=C bond, are also described.



Keywords: vinylboranes · catalysis · C=C bonds · borylation · hydroboration · silaboration · transmetalation

2012

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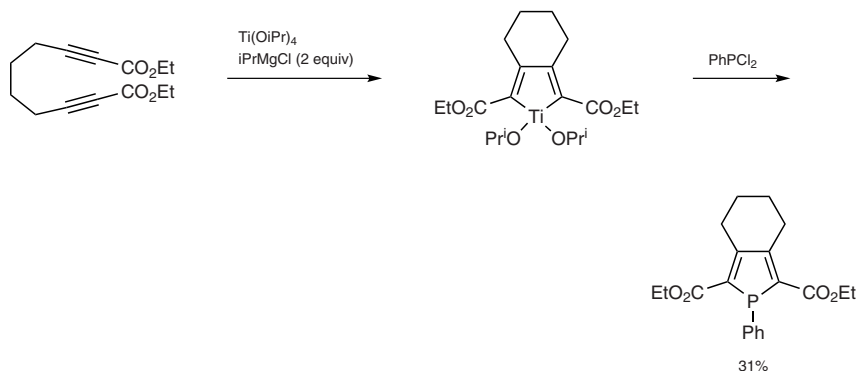
2012

p 341

9.14.4 Phospholes

F. Mathey

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of phospholes, phospholide ions, and phosphametalloenes. It focuses on the literature published in the period 2001–2012.



Keywords: phospholes · phospholide ions · phosphametalloenes · phosphoferrocenes · aromaticity · [1,5]-sigmatropic shifts

New

p 365

40.1.1.5.6 Transition-Metal-Catalyzed Functionalization of C(sp³)–H Bonds of Amines

J. Ipaktschi and M. R. Saidi

This chapter describes the recent literature dealing with the selective functionalization of C(sp³)–H bonds adjacent to the nitrogen atom of amines or amides. The transition-metal-catalyzed transformation of a C–H bond into a C–C or carbon–heteroatom bond enables strategically new approaches to complex organic compounds including biologically active agents and functional organic materials. Straightforward and operationally economical solutions for target-oriented synthesis of complex structures are presented.

Particularly useful methods discussed are the transition-metal-catalyzed oxidation of α-C(sp³)–H bonds of tertiary N-methylamines and amides, transition-metal-catalyzed cross-dehydrogenative coupling (CDC) reaction of C(sp³)–H bonds at the α position of amines, transition-metal-catalyzed hydroaminoalkylation, functionalization of amines via transition-metal-catalyzed hydride transfer cyclization, and the synthesis of non-natural amino acids via functionalization of α-C(sp³)–H bonds of tertiary amines. Further methods discussed are the C–C bond formation at the γ-position of amines and the appli-

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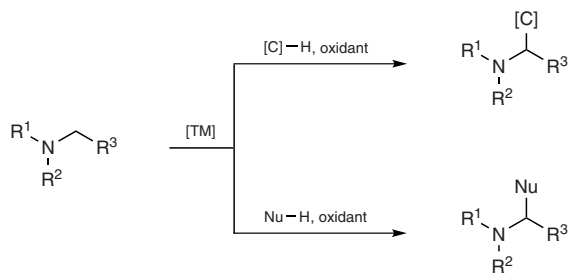
2012

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cation of cooperative metal and organocatalysis for the C(sp³)–H bond activation of amines, which is otherwise impossible with a metal catalyst or an organocatalyst alone. An example is the cross-dehydrogenative coupling reaction of glycine esters with unmodified ketones cooperatively catalyzed by copper(II) acetate and pyrrolidine.



[TM] = transition-metal complex; [C] = C(sp), C(sp²)

Keywords: C–H activation · transition-metal catalysis · oxidation · cross-dehydrogenative coupling · organocatalysts · Mannich reaction · aza-Henry reaction · aerobic oxidative coupling · Petasis–Mannich reaction · photoredox reaction · phosphonation · amino acids · hydroaminoalkylation