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#### 1.3.6 Organometallic Complexes of Platinum

A. Nomoto and A. Ogawa

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 1.3) describing methods for the synthesis of organometallic complexes of platinum and related applications in catalytic reactions using organoplatinum complexes. Recently, organometallic complexes of platinum have been used in many areas, including as medical or luminescent materials.

$$\begin{array}{c|c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

**Keywords:** Diels–Alder cycloaddition  $\cdot$  allene complexes  $\cdot$  dinuclear complexes  $\cdot$  anticancer agents  $\cdot$  allyl complexes  $\cdot$  metallacycles  $\cdot$  alkyne complexes  $\cdot$  catalytic reactions  $\cdot$  selenaplatinacycles  $\cdot$  dicationic complexes

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#### Organometallic Complexes of Iridium

H. Li and C. Mazet

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 1.6) that covers literature from 1999 to the first half of 2013. While Section 1.6 provided a fantastic overview of the different types of organometallic complexes of iridium and their preparation, this contribution aims at focusing more on their applications in homogeneous catalysis.

 $BARF^{-} = [3,5-(F_3C)_2C_6H_3]_4B^{-}$ 

**Keywords:** iridium complexes  $\cdot$  catalysis  $\cdot$  borylation  $\cdot$  oxidation  $\cdot$  hydroamination  $\cdot$  dehydrogenative coupling  $\cdot$  hydrogenation  $\cdot$  transfer hydrogenative coupling  $\cdot$  transfer hydrogenation  $\cdot$  allylic substitution  $\cdot$  isomerization  $\cdot$  oligomerization

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 13.13) describing methods for the synthesis of 1,2,3-triazoles. Recent interest in this area has mainly been generated by the discovery that copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) and ruthenium(II)-catalyzed azide–alkyne cycloaddition (RuAAC) regioselectively afford 1,4- or 1,5-disubstituted 1,2,3-triazoles in high yields under mild conditions. This review focuses on the contributions published between 2002 and 2013.

$$R^{1}N_{3} + R^{2} = \begin{bmatrix} Cu^{i} \end{bmatrix}$$

$$R^{1}N_{3} + R^{2} = \begin{bmatrix} Ru^{i} \end{bmatrix}$$

$$R^{2} = \begin{bmatrix} Ru^{i} \end{bmatrix}$$

$$R^{2} = \begin{bmatrix} Ru^{i} \end{bmatrix}$$

$$R^{2} = \begin{bmatrix} Ru^{i} \end{bmatrix}$$

**Keywords:** 1,2,3-triazoles  $\cdot$  azides  $\cdot$  alkynes  $\cdot$  click chemistry  $\cdot$  Huisgen reaction  $\cdot$  1,3-dipolar cycloadditions  $\cdot$  copper catalysts  $\cdot$  ruthenium catalysts

#### 16.10.5 **Phthalazines**

T. J. Hagen and T. R. Helgren

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 16.10) concerning the synthesis and reactions of phthalazines. Literature from 2004 to early 2014 has been considered. The major focus since the initial publication involves phthalazine substituent modification rather than the synthesis of phthalazine rings.

**Keywords:** phthalazines  $\cdot$  2,3-dihydrophthalazine-1,4-diones  $\cdot$  multicomponent reactions  $\cdot$  cyclization  $\cdot$  heteroarylation  $\cdot$  cross coupling  $\cdot$  hypervalent iodine

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#### 16.13.5 Quinazolines

F.-A. Kang and S.-M. Yang

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 16.13) describing methods for the synthesis of quinazolines. It summarizes new technologies and surveys the literature published in the period 2002–2012.

**Keywords:** quinazolines  $\cdot$  quinazolinones  $\cdot$  quinazolinediones  $\cdot$  nitriles  $\cdot$  isocyanides  $\cdot$  annulation  $\cdot$  rearrangement  $\cdot$  multicomponent condensation  $\cdot$  cyclization  $\cdot$  ionic liquids  $\cdot$  copper(I) iodide  $\cdot$  solid-phase synthesis  $\cdot$  C—H insertion  $\cdot$  carbon dioxide fixation  $\cdot$  solvent free

## 24.4.2.3 1-(Organooxy)alk-1-ynes and 1-(Heterooxy)alk-1-ynes

M. H. Larsen, M. Cacciarini, and M. Brøndsted Nielsen

This manuscript is an update to the earlier *Science of Synthesis* contribution (Section 24.4.2) describing methods for the synthesis of 1-(organooxy)alk-1-ynes and 1-(heterooxy)alk-1-ynes. The original contribution describes the synthesis of six subgroups: alk-1-ynyl *N*,*N*-dialkylcarbamates, carboxylates, ethers, sulfonates, and dialkyl phosphonates as well as 1-siloxyalk-1-ynes. However, during the period covered in this update (2005–2014), new contributions have only been made in the field of alk-1-ynyl ethers and 1-siloxyalk-1-ynes. These methodologies, primarily methods centering on elimination reactions, are covered in this chapter, along with a short description of the applications of these two types of compound.

$$R^1O \xrightarrow{X} R^2 \xrightarrow{\text{elimination}} R^1O \xrightarrow{} R^2$$

 $\textbf{Keywords:} \ alkynyl\ ethers \cdot siloxyalkynes \cdot elimination \cdot Meyer-Schuster\ rearrangement \cdot metal\ catalysis$ 



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# 24.4.4.4 1-Nitrogen-Functionalized Alk-1-ynes

K. Banert

This chapter is an update of the earlier *Science of Synthesis* contributions (Sections 24.4.4.1–24.4.4.3) describing methods for the synthesis of ynamines, and especially those alk-1-yn-1-amines that bear electron-withdrawing units such as N-acyl and N-sulfonyl groups. Compounds with  $C \equiv C$  bonds directly connected to azido or nitro functionalities are likewise updated, whereas the chemistry of N-alk-1-ynyl-substituted sulfoximines and isocyanates is described for the first time. The update focuses on new developments published in the period 2004–2014.

$$R^{1} = + HN X$$

$$R^{2}$$

$$R^{2}$$

$$R^{2}$$

$$R^{1} = + HN X$$

$$R^{2}$$

$$R^{1} = + HN X$$

$$R^{2}$$

$$R^{2}$$

$$R^{2}$$

$$R^{2}$$

**Keywords:** alkynes  $\cdot$  alkynylation  $\cdot$  amines  $\cdot$  azides  $\cdot$  carboxamides  $\cdot$  copper catalysis  $\cdot$  dehydrohalogenation  $\cdot$  isocyanates  $\cdot$  nitro compounds  $\cdot$  oxazolidinones  $\cdot$  sulfonamides  $\cdot$  sulfoximines

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#### 24.4.5.3 1-Phosphorus-Functionalized Alk-1-ynes

M. Cacciarini, M. H. Larsen, and M. Brøndsted Nielsen

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 24.4.5) describing methods for the synthesis of 1-phosphorus-functionalized alk-1-ynes. The focus is on the literature published in the period 2006–2014.

$$R^{1} = + \begin{array}{c} O \\ \parallel \\ P \\ O \\ O \\ \end{array} \xrightarrow{Q} \begin{array}{c} Cu \text{ source (cat.)} \\ \stackrel{\text{air}}{\longrightarrow} \end{array} \qquad R^{1} = \begin{array}{c} O \\ P \\ O \\ R^{2} \\ \end{array}$$

**Keywords:** alkynylation  $\cdot$  oxidative coupling  $\cdot$  metal catalysis  $\cdot$  (alk-1-ynyl)benziodoxolone reagents  $\cdot$  alkynyl protecting groups



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#### 33.4.2.3 1-Nitrosoalkenes

H.-U. Reissig and R. Zimmer

This chapter deals with the generation of nitrosoalkenes from suitable precursors and their application as synthetically useful key intermediates in organic synthesis, including the synthesis of natural products and biologically active compounds. This is an update to Section 33.4.2, covering selected relevant literature that has been reported since 2007.

R<sup>3</sup> = H, SiR<sup>8</sup><sub>3</sub>; Hal = Br, Cl

**Keywords:** nitrosoalkenes  $\cdot$  dehydrohalogenation  $\cdot$  halooximes  $\cdot$  nitroalkene reduction  $\cdot$  [4 + 2] cycloaddition  $\cdot$  [3 + 2] cycloaddition  $\cdot$  hetero-Diels–Alder  $\cdot$  *N*-hydroxypyrroles  $\cdot$  natural products

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# **1,2-Dihydrophosphetes and Derivatives**

Gy. Keglevich and A. Grün

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 33.5.7) describing methods for the synthesis of 1,2-dihydrophosphetes. It focuses on the literature published in the period 2004–2015.

$$\begin{array}{c|c} CI & SPh \\ \hline R^1 & & & \\ \hline \end{array} \begin{array}{c} 2 \, \text{Ti}(Cp)_2 \{P(OEt)_3\}_2 \\ \hline \\ R^1 & & \\ \end{array} \begin{array}{c} Cp \\ \hline \\ Cp-Ti \\ \hline \\ R^1 & & \\ \end{array} \begin{array}{c} 1. \, PhPCI_2 \\ \hline \\ 2. \, O_2 \\ \hline \\ R^1 & & \\ \end{array} \begin{array}{c} O \\ II \\ Ph-P \\ \hline \\ R^1 & & \\ \end{array}$$

**Keywords:** vinyl compounds  $\cdot$  titanium complexes  $\cdot$  phosphorus heterocycles  $\cdot$  phosphine oxides  $\cdot$  metallacycles



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## 33.5.8.2 **2,3-Dihydro-1***H*-phospholes and Derivatives

Gy. Keglevich and A. Grün

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 33.5.8) describing methods for the synthesis of 2,3-dihydro-1*H*-phospholes. It focuses on the literature published in the period 2004–2015.

**Keywords:** zirconium complexes  $\cdot$  phosphorus heterocycles  $\cdot$  phosphines  $\cdot$  metallacycles  $\cdot$  metalhesis

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## 33.5.9.2 **1,2,3,4-Tetrahydrophosphinines and Derivatives**

Gy. Keglevich and A. Grün

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 33.5.9) describing methods for the synthesis of 1,2,3,4-tetrahydrophosphinines. It focuses on the literature published in the period 2004–2015.

**Keywords:** enamines  $\cdot$  bromine compounds  $\cdot$  phosphorus heterocycles  $\cdot$  phosphonium salts  $\cdot$  cyclization





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## 33.5.10.2 1,4-Dihydrophosphinines and Derivatives

Gy. Keglevich and A. Grün

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 33.5.10) describing methods for the synthesis of 1,4-dihydrophosphinines. It focuses on the literature published in the period 2004–2015.

**Keywords:** phosphorus heterocycles  $\cdot$  phosphinic acids  $\cdot$  unsaturated compounds  $\cdot$  ring expansion  $\cdot$  carbenes

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### 35.1.1.1.9 Synthesis by Substitution of Hydrogen

J. Iskra and S. S. Murphree

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.1.1.1) summarizing methodology for the chlorination of non-activated C—H bonds, with a particular focus on regioselectivity.

**Keywords:** chlorination  $\cdot$  halogenation  $\cdot$  chlorine compounds  $\cdot$  halo compounds  $\cdot$  chlorides  $\cdot$  halides  $\cdot$  alkanes  $\cdot$  carbon—halogen bonds



# 35.2.1.1.8 Synthesis by Substitution of Hydrogen I. Iskra

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.2.1.1) summarizing methodology for the bromination of non-activated C—H bonds, with a particular focus on regioselectivity.

**Keywords:** bromination  $\cdot$  halogenation  $\cdot$  bromine compounds  $\cdot$  halo compounds  $\cdot$  bromides  $\cdot$  halides  $\cdot$  alkanes  $\cdot$  carbon—halogen bonds

# 35.3.1.1.6 Synthesis by Substitution of Hydroger J. Iskra

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.3.1.1) summarizing methodology for the iodination of non-activated C—H bonds, with a particular focus on regioselectivity.

$$\begin{array}{c} \text{OH} \\ \text{OO} \\ \text{OO} \\ \\ \text{R}^2 \\ \text{R}^3 \\ \text{H} \end{array}$$

**Keywords:** iodination  $\cdot$  halogenation  $\cdot$  iodine compounds  $\cdot$  halo compounds  $\cdot$  iodides  $\cdot$  halides  $\cdot$  alkanes  $\cdot$  carbon—halogen bonds

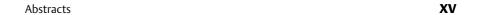
# 35.3.1.2.7 Synthesis by Substitution of Metals

M. C. Elliott and B. A. Saleh

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.3.1.2) describing methods for the synthesis of alkyl iodides from organometallic reagents, generally by addition of iodine, although other iodide sources have been used. It focuses on the literature published in the period 2005–2014.

$$R^1-M$$
  $\xrightarrow{I_2}$   $R^1-I$ 

 $\textbf{Keywords:} \ iodoalkanes \cdot alkyl \ iodides \cdot iodination \cdot organometallic \cdot organomercury \cdot organozinc \cdot organozin$ 





#### 35.3.1.3.8 Synthesis by Substitution of Carbon Functionalities

B. A. Saleh and M. C. Elliott

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.3.1.3) describing methods for the synthesis of alkyl iodides from carboxylic acids and related compounds. It focuses on the literature published in the period 2005–2014.

**Keywords:** iodoalkanes  $\cdot$  alkyl iodides  $\cdot$  iodination  $\cdot$  decarboxylation  $\cdot$  hypervalent iodine

### 35.3.1.4.6 Synthesis by Substitution of Other Halogens

F. V. Singh and T. Wirth

lodoalkanes are versatile reagents and precursors in a variety of organic reactions such as nucleophilic substitution, elimination, and metal-catalyzed C—C bond-forming reactions. In this chapter, various halogen-exchange approaches for the synthesis of iodoalkanes from other haloalkanes are described. The methods described cover the literature published in the period 2007–2014.

**Keywords:** halogen-exchange reaction  $\cdot$  iodoalkanes  $\cdot$  bromoalkanes  $\cdot$  chloroalkanes  $\cdot$  sodium iodide  $\cdot$  phase-transfer catalyst

# 35.3.1.5.7 Synthesis by Substitution of Oxygen Functionalities

F. V. Singh and T. Wirth

Iodoalkanes are important synthetic intermediates in organic chemistry. These compounds undergo various reactions such as nucleophilic substitution, elimination, and metal-catalyzed C—C bond-forming reactions. This chapter describes various synthetic approaches available for the generation of C—I bonds from different oxygen functionalities and covers the literature published in the period 2007–2014.

$$\begin{array}{ccc}
 & OR^3 & & I \\
 & R^1 & R^2 & & R^1 & R
\end{array}$$

**Keywords:** iodoalkanes  $\cdot$  iodination  $\cdot$  ionic liquids  $\cdot$  silicaphosphine  $\cdot$  polymethylhydrosiloxane  $\cdot$  iodotrimethylsilane  $\cdot$  alcohols  $\cdot$  ethers  $\cdot$  phosphate esters  $\cdot$  sulfonate esters  $\cdot$  microwave irradiation



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## 35.3.1.8.7 Synthesis by Addition to $\pi$ -Type C—C Bonds

U. Hennecke

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.3.1.8) describing methods for the synthesis of iodoalkanes by addition reactions to  $\pi$ -type C—C bonds (mostly alkenes). It focuses mainly on the literature published in the period 2007–2014.

$$R^1$$
 $R^3$ 
 $R^4$ 
 $R^3$ 
 $R^4$ 
 $R^3$ 

**Keywords:** alkyl iodides  $\cdot$  carbocyclization  $\cdot$  carbocyclic compounds  $\cdot$  carboiodination  $\cdot$  electrophilic additions  $\cdot$  iodo compounds

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# 35.3.5.1.5 Synthesis by Addition across C=C Bonds

U. Hennecke

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 35.3.5.1) describing methods for the synthesis of 1-iodo-2-heteroatom-substituted alkanes by addition reactions across C=C bonds. The chapter also covers the synthesis of 1-iodo-3-heteroatom-substituted alkanes including saturated 3-iodo-substituted heterocycles. It focuses mainly on the literature published in the period 2007–2014.

**Keywords:** alkyl iodides  $\cdot$  electrophilic additions  $\cdot$  iodination  $\cdot$  iodo compounds  $\cdot$  iodohydrins  $\cdot$  iodolactonization  $\cdot$  piperidines  $\cdot$  Prins reaction