1.7 Product Class 7: Organometallic Complexes of Iron

G. R. Stephenson

This chapter is a revision of the previous Science of Synthesis contribution describing methods for the synthesis of organometallic complexes of iron with hapticities between $\eta^6$ (arene complexes) and $\eta^1$ (carbene complexes and $\sigma$-bonded complexes).

The main methods surveyed are the direct complexation of ligands, nucleophile addition to cationic complexes (which reduces the hapticity by one), protonation of unsaturated but non-coordinated sections of ligands or ligands bearing leaving groups (which increases the hapticity by one), and functional-group transformations of substituents on the haptyl ligand (which leaves the hapticity unchanged). Access to nonracemic complexes and the use of iron complexes in total synthesis are discussed.

Keywords: iron complexes · arene complexes · cyclohexadienyl complexes · diene complexes · $\pi$-allyl complexes · alkene complexes · alkyne complexes · metal–carbene complexes · carbonyl complexes · nucleophilic addition · regioselectivity · diastereoselectivity · asymmetric synthesis · enantioselectivity · enantiomeric resolution · kinetic resolution · total synthesis
This chapter is an update to the earlier *Science of Synthesis* Section 1.7.8 describing methods for the synthesis of ferrocenes. The focus is on the literature published between 2000 and early 2013. The main methods discussed are direct complexation of ligands, modification of cyclopentadienyl rings by electrophilic substitution or directed lithiation, and functional-group transformations in ferrocenyl side-chains. The access to nonracemic ferrocenes and to ferrocenes with configurationally defined side-chain chirality is discussed.

**Keywords:** iron complexes · ferrocenes · cyclopentadienyl complexes · acylation · lithiation · materials synthesis · bioorganometallic chemistry · diastereoselectivity · asymmetric synthesis · enantioselectivity · enantiomeric resolution · kinetic resolution · asymmetric catalysis
Zinc salts are abundant, inexpensive, nontoxic, and exhibit environmentally benign properties. As a result, organic chemists have been interested in using zinc salts as catalysts in organic synthesis during the last three decades. In this chapter, the main contributions on zinc-catalyzed organic synthesis are summarized and discussed. Many name reactions with zinc as catalyst are included, as well as zinc-catalyzed reduction and oxidation reactions.

**Keywords:** zinc catalysts · organic synthesis · asymmetric synthesis · C—C bond formation · C—N bond formation · C—O bond formation · reduction · oxidation

This chapter describes methods for the synthesis of siloles and benzannulated analogues (benzosiloles and dibenzosiloles). Classical routes to siloles involve the nucleophilic attack of a carbanion onto the silicon atom, but more recent developments involving different approaches are included as well.

**Keywords:** siloles · benzosiloles · dibenzosiloles · reductive cyclization · C—C bond formation · transmetalation
20.5.2 2,2-Diheteroatom-Substituted Alkanoic Acid Esters
T. L. March and P. J. Duggan

This chapter is an update to the earlier Science of Synthesis contribution describing methods for the preparation of 2,2-diheteroatom-substituted alkanoic acid esters, and covers the literature published in the period 2007–2012. A major focus has been on the development of stereoselective Reformatsky and conjugate addition reactions, while atom-transfer radical addition and cyclization methods continue to attract strong interest.

![Chemical structure](image)

**Keywords:** carbon—halogen bonds · carbon—heteroatom bonds · chlorination · conjugate addition · coumarins · esters · fluorine compounds · Friedel–Crafts acylation · halalkylation · halogenation · hetero-Diels–Alder reaction · atom-transfer radical addition · atom-transfer radical cyclization · Reformatsky reaction

26.8.4 Aryl Ketones
J. D. Sellars

This chapter is an update to the earlier Science of Synthesis contribution describing methods for the synthesis of aryl ketones. It focuses on the literature published in the period 2003–2013.

![Chemical structure](image)

**Keywords:** aryl ketones · arynes · C—H activation · Friedel–Crafts acylation · Fries rearrangement · hydroacylation · organometallic reagents · supported catalysis

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