



# Multifaceted zirconate complexes in organic synthesis

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## Contents

1. Introduction	22
2. Study of zirconates as intermediates	23
3. Reaction of zirconates with proton donors or oxidants	24
4. Reaction of zirconates with electrophiles	25
4.1. Reaction of zirconates with aldehydes	25
4.2. Reaction of zirconates with chloroformates and esters	25
4.3. Reaction of zirconates with cinnamates	27
4.4. Reaction of zirconates with allyl bromides	28
4.5. Mechanistic studies of the reactions of zirconates with electrophiles	29
4.6. Reaction of zirconates with chlorophosphine	29
5. Summary and outlook	30
Acknowledgments	31
References	31

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## ABSTRACT

An ate complex is a salt in which the central atom increases its valence or coordination number and becomes anionic. A significant reaction by the ate complexes is a strong nucleophilicity toward electrophiles to form new chemical bonds, which may lead to useful one-pot synthetic methods for building complex molecules. Zirconocene complexes can have a metal center with 14–18 electrons and a coordination number of 3–5. The 14-electron and 16-electron zirconocene complexes have been explored extensively and many applications have been developed in synthetic chemistry. Zirconate complexes with an 18-electron configuration and five-coordinated number have a higher likelihood of forming new C–C bonds. The present review concentrates on the zirconate complexes used in organic synthesis. When zirconate complexes are treated with *p*-chloranil, aldehydes, chloroformates, esters, cinnamates, allyl bromides, or chlorophosphines, they undergo different types of reactions and various organic products are formed in an efficient manner.

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## 1. Introduction

Ate complexes, which were first introduced by Wittig [1], are defined as salts formed from the stoichiometric reaction between

*Abbreviations:* Ar, aryl; *n*-Bu, *n*-butyl; *t*-Bu, *t*-butyl; Cp,  $\eta^5$ -cyclopentadienyl; DMAD, dimethyl acetylenedicarboxylate; DMAP, 4-dimethylaminopyridine; E<sup>+</sup>, electrophiles; Et, ethyl; *n*-Hex, *n*-hexyl; Me, methyl; *n*-Oct, *n*-octyl; Ph, phenyl; rt, room temperature; TCNE, tetracyanoethylene; TCQ, *p*-chloranil; TMSOTf, trimethylsilyl trifluoromethanesulfonate; *p*-Tol, *p*-tolyl.

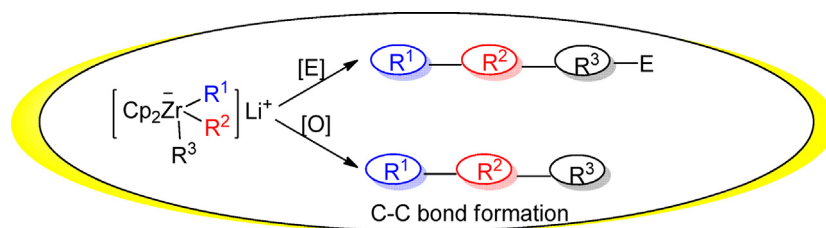
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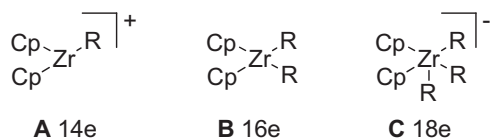
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a Lewis base and a Lewis acid, where the central atom increases its coordination number and becomes anionic. In general, the ate complexes are considered to contain both cationic and anionic moieties with a formula of  $M^{m+}[M'R_n]^{m-}$  [2]. This family of compounds has received much attention from inorganic researchers and organic researchers due to their distinctive and enhanced reactivity compared with their neutral precursors. A significant reaction by ate complexes is a strong nucleophilicity toward electrophiles [2e–g]. Numerous ate complexes have been studied that can be coupled with various electrophiles with high efficiency and high selectivity. In addition, magnesiates, zincates, and aluminates have been utilized successfully in the deprotonation of challenging weakly acidic aromatic C–H bonds (basicity) [2b,3]. In most cases, it is recognized that an ate complex can only transfer one single R group effectively



Scheme 1. Reactivity of zirconates.

Fig. 1. Zirconocene complexes  $\text{Cp}_2\text{ZrR}_n$  (A,  $n = 1$ , B,  $n = 2$ ; C,  $n = 3$ ).

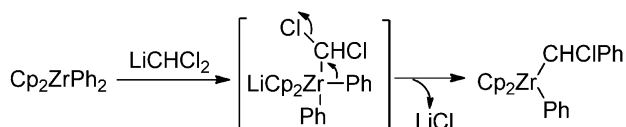
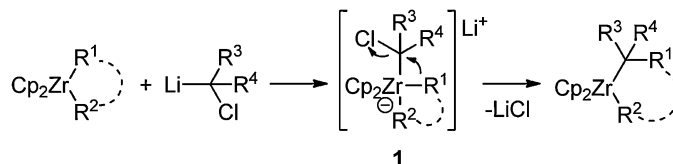
to an electrophilic substrate, whereas the others are discarded as an RM by-product. Another reaction by ate complexes is the reductive elimination of two M–R bonds to form R–R compounds with or without oxidants [4]. The nucleophilicity is lost during reductive elimination. In addition, a novel pathway that comprises a sequence of 1,2- migration and elimination was reported for boronate complexes [5].

Most metals or metalloids can form ate complexes, but previous studies have generally focused on the chemistry of main group elements and late transition metals, such as Mg, B, Al, Cu, and Zn. Thus, there have been few in-depth investigations of the ate complexes of early transition metals. In addition, during recent decades, zirconocene complexes with two cyclopentadienyl ligands as well as 1–3 Zr–R/L bonds have attracted considerable attention due to their fascinating structural features, unique M–C bonding, and unusual capacity for inducing highly selective transformation reactions. The versatile behavior of zirconocene complexes can be explained by their possession of a metal center with 14–18 electrons and a valence coordination number of 3–5, as shown in Fig. 1.

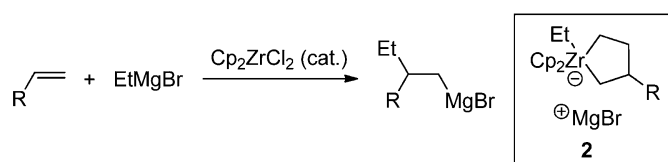
The chemistry of the 14-electron and 16-electron zirconocene complexes (A and B) has been explored extensively and they have numerous applications in synthetic chemistry [6]. The ate complexes of zirconocene (zirconates), which have an 18-electron configuration and five-coordinated number (C), have a higher likelihood of forming new C–C bonds, but to the best of our knowledge, their chemistry has been summarized rarely. In this review, we describe a novel reactivity of the zirconate complexes, where all of the organic moieties on the zirconates are coupled together when the zirconates are attacked by electrophiles or oxidants (Scheme 1). The zirconate complexes exhibit unique characteristics that may facilitate organic synthesis.

## 2. Study of zirconates as intermediates

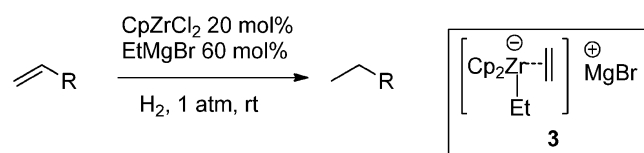
The zirconate complexes were proposed to be key intermediates in a number of reactions. As early as 1989, in a pioneering study, Negishi *et al.* [7] reported the insertion of  $\alpha$ -haloorganolithium into a Zr–C bond *via* migratory insertion to form a new C–C bond (Scheme 2). Whitby *et al.* extended this reaction to acyclic and cyclic

Scheme 2. Insertion of  $\alpha$ -haloorganolithium into  $\text{Cp}_2\text{ZrPh}_2$  [7].

Scheme 3. Insertion of carbenoids into zirconocene complexes [8].



Scheme 4. Zirconium-catalyzed carbometalation of alkenes [9].

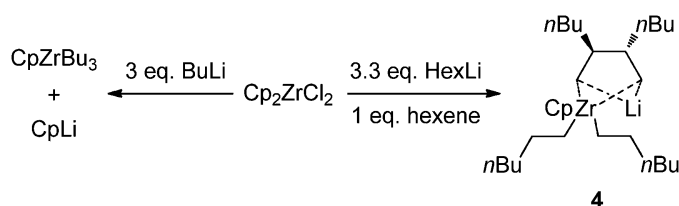


Scheme 5. Zirconium-catalyzed hydrogenation of alkenes [10].

16-electron zirconocene complexes, as well as other 1-halo-1-lithio species such as carbenoids. They proposed the 18-electron zirconate **1** as an intermediate to explain the formation of the insertion products (Scheme 3) [8].

Takahashi *et al.* [9] reported the zirconium-catalyzed carbometalation of alkenes where the zirconate **2** was proposed as an intermediate (Scheme 4). The reaction of  $\text{Cp}_2\text{ZrCl}_2$  with 3 equivalent of  $\text{EtMgBr}$  yielded the zirconate **3**, which can efficiently catalyze the hydrogenation of alkenes (Scheme 5) [10]. It should be noted that a counterion is very important for stabilizing these zirconates. Thus, when organolithiums are employed, the displacement of one cyclopentadienyl ligand and the formation of  $\text{CpZrR}_3$  were observed instead of zirconate **3**. In the presence of an excess amount of organolithium and alkene, a novel zirconate **4** is obtained (Scheme 6) [11].

In general, the aforementioned zirconate complexes bearing alkyl substituents on zirconium are not sufficiently stable to be isolated. In addition, alkynyl zirconate complexes can readily undergo a 1,2- migration reaction on the carbon–carbon triple

Scheme 6. Reaction of  $\text{Cp}_2\text{ZrCl}_2$  with organolithium [11].

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