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Review

Advances in transmetalation reactions originated from organozirconium compounds

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ABSTRACT

Transmetalation is a fundamental reaction in organometallic chemistry. It provides common and useful methods for preparing various organo-transition metal complexes, which are either used as reagents or catalyst in organic synthesis. Organozirconium complexes have attracted considerable attention owing to their fascinating structural features and unique Zr–C bonding. As the booming development of the organozirconium chemistry, transmetalation of organozirconium with other metallic reagents afforded various new types of organometallic complexes, which showed a remarkable advantage in modern organic synthesis. In this review, we would like to summarize the typical examples of transmetalation reactions that originated from organozirconium compounds, which mainly include organic species or ligands from organozirconocenes to *p*-block elements and transition-metals. In addition, transmetalation reactions beyond the organozirconocenes system, such as zirconium carbene complexes, zirconium pincher complexes, and arylzirconium complexes would be also introduced. Transmetalation reactions that originated from organozirconium included (i) Direct transfer; (ii) Tandem transfer; (iii) Catalytic transfer.

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Abbreviations: Acac, acetylacetonate; Ar, aryl; Bcat, catecholboryl; Bpin, pinacolboryl; ⁿBu, *n*-butyl; ^tBu, *t*-butyl; Cp, η⁵-cyclopentadienyl; ebi, 1,2-ethylene-1,1'-bis(η⁵-indenyl); Et, ethyl; EWG, electron-withdrawing groups; IPr, (2,6-diisopropylphenyl)imidazol-2-ylidene; nb, norbornene; Me, methyl; NMI, neomenthylindenyl; Ph, phenyl; TBS, tributylsilyl; tmp, 2,2,6,6-tetramethylpiperidyl.

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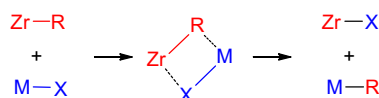
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1. Introduction

Transmetalation is a type of organometallic reaction that involves the transfer of organic groups or ligands from one metal to another [1]. As one of fundamental reactions in organometallic chemistry, it provides common and useful methods for preparing various organo-transition metal complexes. Moreover, transmetalation is a key elementary reaction of many important cross-coupling reactions, such as the Suzuki reaction, Negishi reaction, Sonogashira reaction and so on [2]. In the most cases, the transfer of one organic group or neutral ligand was conducted from main group metal to transition metal. For examples, various alkyl, aryl, and alkynyl transition metals' complexes are prepared from the reaction of organolithiums and Grignard reagents with transition-metal halides. However, these methods inevitably face some problems, such as limitation of kinds of transfer groups, functional-group intolerance and so on. As the booming development of organometallic chemistry of transition-metals, new transmetalation process using transition metal complexes as transfer reagents has been explored and it shows remarkable advantage compared with traditional transmetalation process. Meanwhile, over the past half century, organozirconium chemistry, especially organozirconium complexes with two cyclopentadienyl ligands (zirconocenes), has witnessed continuous development and played important roles in modern organic syntheses [3]. Many of the reactions involving zirconocenes have started out as stoichiometric but have been developed into important catalytic processes. The further transformation of organozirconium compounds greatly rely on transmetalation reaction. Moreover, transmetalation of organozirconium afforded various new types of organometallic complexes. In principle, transmetalation of organozirconium usually involved an organic group transfer from zirconium with another metal halide (usually chloride), which was considered as σ -bond metathesis process (Scheme 1). [4] The transmetalation process was thermodynamically favorable because Zr has the electronegativity of 1.33, which is one of the lowest electronegativities among transition-metals [5]. And also, the stability of Zr–X bond is another driving force of this transmetalation process.

Though a large number of transmetalation reactions between organozirconium compounds and other metals have been reported, there are still a few review articles available. In this review, we would like to summarize the typical examples of transmetalation reactions that originated from organozirconium compounds (Scheme 2). Since most of the organozirconium compounds were zirconocene complexes, we will focus on organic transfer from zirconocene to *p*-block elements and transition-metals. In addition, miscellaneous transmetalation reactions beyond zirconocene system, such as zirconium pincer complexes



Scheme 1. General process for the transmetalation involving organozirconium.

and arylzirconium complexes, will be introduced. In the most of cases, the direct transmetalation of Zr to other metals proceed well at ambient condition. In other cases, a tandem dual transmetalation, which involves transmetalation of Zr to another metal (M') and stepwise transmetalation of M' to the target metal (M), was developed. For example, the transmetalation of Zr to B can be fulfilled by the third element Sn. In particular, some transmetalation reactions can be designed as catalytic processes. For example, the transmetalation from Zr to mid transition metals can be accelerated by using Cu or Pd as catalyst.

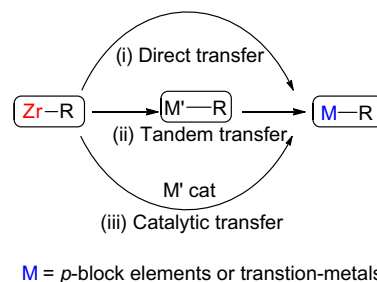
2. Transmetalation with *p*-block elements

2.1. Transmetalation to aluminum

Although zirconocene complexes have a long history of more than sixty years [6], it came into organic synthesis in mid-1970s when Wailes [7] and Schwartz [8] groups discovered hydrozirconation of alkenes and alkynes with Cp_2ZrHCl (Schwartz reagent). This reaction provides versatile and utilized routes for the functionalization of C–C multiple bonds. However, the further derivatization was strictly limited to hydrogenation and halogenation, due to the intrinsically considerably weaker nucleophilicity of Zr–C bond. Only a few examples were reported for direct formation of C–C bond from Zr–C bond [8]. This difficulty was overcome by introducing stoichiometric or catalytic metal salts.

In 1977, Schwartz and coworkers firstly reported transmetalation from zirconium to aluminum. Treatment of alkylzirconocene with $AlCl_3$ yielded the corresponding organoaluminum dichloride, which was converted to ketone *via* reaction with acyl chloride (Scheme 3) [9].

The transmetalation between Zr and Al, in many cases, was in equilibrium, and the bimetallic four-membered intermediate was observed [10]. This unique property was involved in many catalytic systems. In 1978, Negishi and coworkers reported methylalumination of alkynes with Me_3Al by using Cp_2ZrCl_2 as a catalyst, in which Al to Zr transmetalation and Zr to Al transmetalation were proposed as the key steps (Scheme 4) [11]. This reaction shows high regioselectivity and nearly perfect *syn*-stereoselectivity with functional-group compatibility. In 2006, Lipshutz and coworkers found that the regioselectivity was increased to >99% with only



Scheme 2. Transmetalation reactions originated from organozirconium via (i) Direct transfer; (ii) Tandem transfer; (iii) Catalytic process.

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