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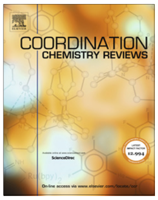

Review

Open-shell iron hydrocarbyls

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Dedicated to Professor Pierre Braunstein on the occasion of his 70th birthday.

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ABSTRACT

Open-shell iron hydrocarbyl species attract great interests in the recent years for their relevance to the key intermediates of many iron-catalyzed organic transformations, and also their rich electronic structures that might lead to unique physical properties. While a plenty of studies on open-shell iron hydrocarbyls are scattered in literature, pertinent review on the chemistry of this type of intriguing complexes is lacking. In this article, we summarize the synthetic methods, structure and spectroscopic features, as well as the established reactivity of open-shell iron hydrocarbyl complexes, particularly those with the coordination numbers less than five. As we shall see, while the preparation methods of open-shell iron hydrocarbyls parallel with those of their closed-shell analogs, the open-shell nature of this type of organo-iron species could endow them unique spectroscopic features and also reactivity.

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1. Introduction

The processes of metal–carbon bond-forming and -breaking are the central events of many transition-metal-mediated organic transformations. The synthesis, structure, and reactivity of organometallic compounds, particularly those featuring σ-type alkyl, aryl, alkenyl, and alkynyl ligands, namely metal hydrocarbyls, thus, have been the hardcore of modern organometallic chemistry [1]. Iron hydrocarbyls are among the transition-metal species subjected to extensive study [2]. In the last century, great efforts had been exercised on iron hydrocarbyl compounds featuring cyclopentadienyl and carbonyl ligands. With the strong ligand field provided by these ligands, these iron hydrocarbyl compounds are usually coordinatively saturated and have low-spin states as their ground states. While cumulated knowledge on low-spin iron hydrocarbyls forms the basis on which many iron-mediated transformations operate, there are systems obviating the use of these classical strong field ligands [3]. For example, bulky amines, imines, phosphines, and *N*-heterocyclic carbenes (NHCs) are commonly used in iron-catalyzed olefin polymerization, carbon–carbon bond-forming cross-couplings, carbometallation reactions, and hydrosilylation reactions [3]. The reaction mixtures employing these ligands usually are paramagnetic, and NMR spectroscopic methods are not as informative as for traditional diamagnetic systems in providing mechanistic clues. Consequently, mechanisms of these reactions have remained poorly understood. The status aroused great research interests to disclose the structure, spectroscopy, and reactivity of the palpable intermediates, among which are open-shell iron hydrocarbyls.

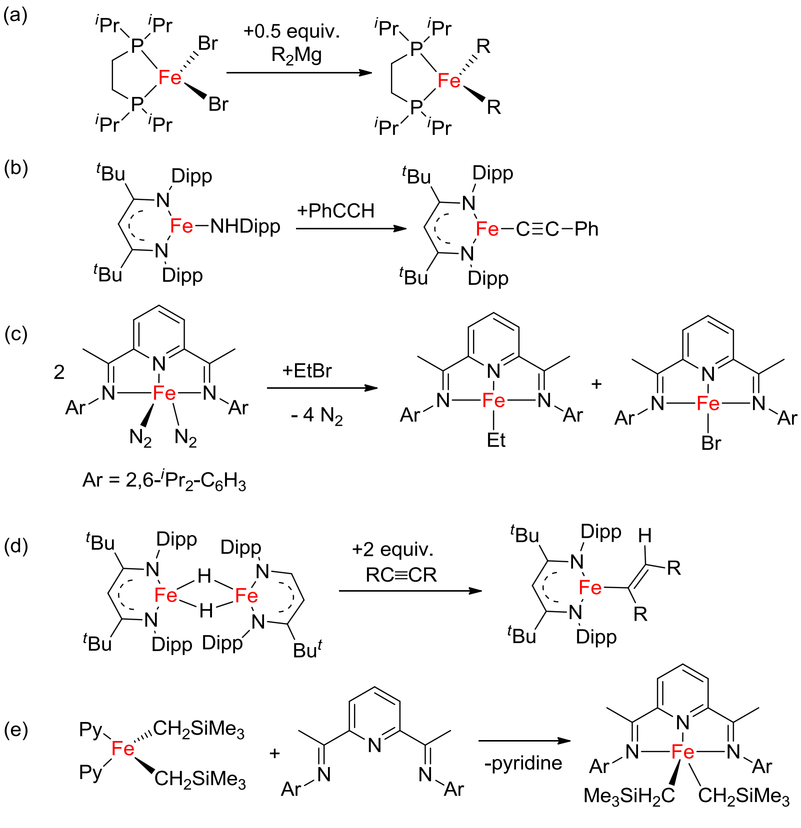
As a late 3*d* transition-metal, iron under weak-field ligand environment can readily form complexes with high-spin or intermediate-spin electronic configurations. This type of complexes has singly occupied molecular orbitals, and represents an important class of open-shell complexes. It is recognized that transition-metal species with different spin states could have distinct structure features, magnetic properties, and also chemical reactivity [4]. The influence on reactivity was well-demonstrated by the different outcome of the interaction between the low-valent metal species CpM(CO) (M = Co, Rh, Ir) at its $S = 1$ and $S = 0$ states with C—H bonds [5], and also the differentiated hydrogen-atom-abstraction reactivity of late transition-metal oxo and imido complexes [6]. As for transition-metal hydrocarbyls, the effects of spin-states on the reactivity of metal–carbon bonds are expected, but have not been clearly identified. Considering the emergence of a large body of studies on open-shell iron hydrocarbyls in the recent years, a review on the chemistry of open-shell iron hydrocarbyls might throw some light on the myth, and should also be helpful for aiding further development of iron catalysis.

The present review aims to provide an overview on the chemistry of open-shell iron hydrocarbyl compounds, particularly those with the coordination numbers less than five. There are also examples of five-coordinate open-shell iron hydrocarbyls in literature. Due to limitation of space, their chemistry is not included, and readers are encouraged to read related reviews and original papers [7]. Considering the large numbers of the reported open-shell iron hydrocarbyls with coordination numbers less than five, we do not intend to present a detailed comprehensive review on them, but wish to summarize their chemistry in terms of their preparation methods, major categories, characterization data, and disclosed reactivity. After these sections, a summary and perspective is made at the end of the article.

2. Preparation

2.1. Preparation methods

Synthetic methods for open-shell iron hydrocarbyl complexes parallel with those used for their closed-shell analogs, including



Scheme 1. Synthetic methods for open-shell iron hydrocarbyls.

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