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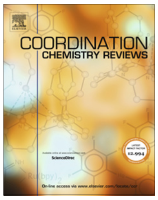

Review

Input of P, N-(phosphanyl, amino)-ferrocene hybrid derivatives in late transition metals catalysis

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ABSTRACT

Unequally functionalized ferrocenes give access to valuable hemilabile reactivity in catalytic reaction. We address the synthesis of hybrid (P, N)-ferrocenyl compounds for which recent catalytic breakthrough applications have been reported, transversely in late transition metals chemistry. Palladium, nickel, rhodium, iridium, and emerging iron and gold catalysis are illustrated from selected examples, which include C—C bond formation from cross-coupling and polymerization, allylic substitution, cyanation, hydroformylation, C—H arylation and silylation and hydrogenation reactions.

Contents

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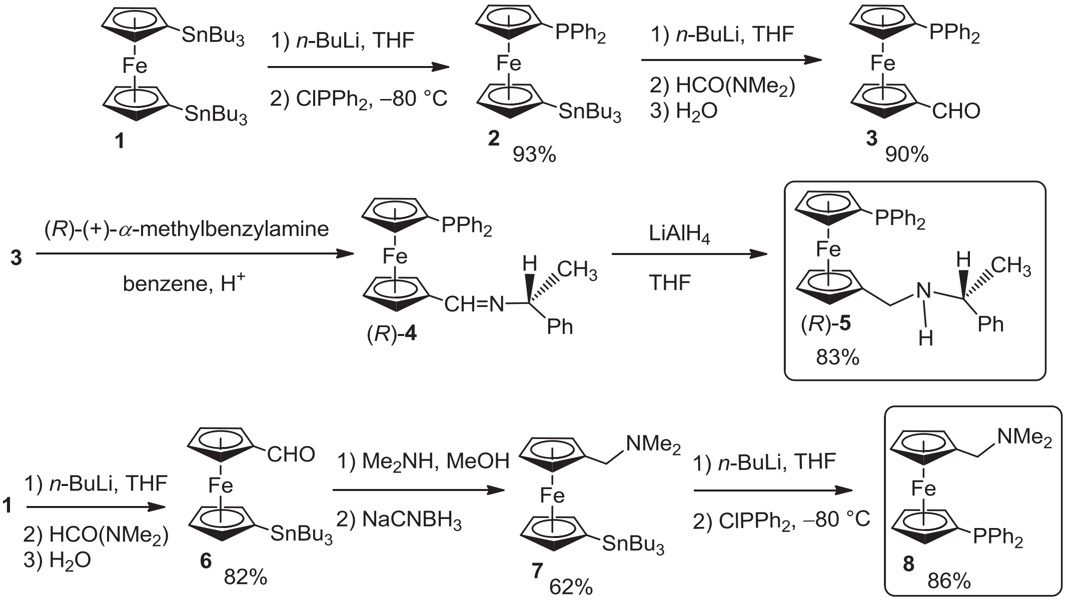
1. Introduction

Ferrocene derivatives bearing donor atoms (P, N, O, S, *etc.*) combined with transition metals are widely applied in modern transition metal-catalyzed organic reactions [1]. Among such compounds unequally polyfunctionalized ferrocenes give access to valuable hemilabile reactivity. Hemilabile ligands provide to coordination complexes open coordination sites due to reversible coordination, which can be decisive in the course of catalytic reactions. Braunstein and co-workers early on reviewed the concepts and interests attached to hemilabile ligands [2], including valuable (P, N)-hybrids which incorporate both soft phosphorus and hard nitrogen Pearson's donors. Hybrid ligands may also induce push–pull properties or *trans*-effects at coordination metal, which contributes to enlarge their reactivity scope. Accordingly: «*...metal complexes containing hemilabile ligands have been found to be catalytically active in a range of reactions, including hydrogenation, carbonylation or its reverse, hydroformylation of olefins and epoxides, allylation, epoxidation...*» [2,3].

The varied platforms used as spacers to support donor atoms provide decisive properties to bifunctional hybrid ligands. We focused the present review on the synthesis of hybrid (P, N)-ferrocenyl compounds and their recent catalytic applications, across late transition metals chemistry. To give a clear, yet concise, perspective we quoted reports from the period 2005 to 2017, with a focus after 2014. Palladium, nickel, rhodium, iridium, and even uncommon iron and gold catalysis are illustrated from selected examples. In this survey, bifunctional, trifunctional and tetrafunctional (P, N)-hybrid ferrocene derivatives are discussed. The complexes which incorporate ferrocene ligands achieved efficient catalysis in connection with unique features combining rigidity, steric hindrance and rotational flexibility. These properties, which includes *inter alia* coordination bite angle to metals, ferrocene backbone conformation, planar chirality, or functionalization at cyclopentadienyl (Cp) rings and at donor atoms have been previously discussed and a detailed discussion fall out of the scope of this review [4]. However, ferrocene appeared to be a suitable backbone in (P, N)-ligands because of a number of valuable characteristics already well-identified in the complexes they form [4c]: (1) The ferrocene platform accommodates changes in the electronic density at the metal center by varying the geometry around iron (essential along a catalytic cycle), (2) The ligand backbone is redox active [4d], this feature remains to be better exploited in relation to the reactivity of the resulting transition metal complexes -(for instance as noninnocent ligands); (3) In common complexes of 1,1′-disubstituted ferrocenes a *cis*-coordination of the two donors is adopted, thus, one side of the metal center is blocked, leaving the other side open to attack by various substrates; (4) Finally, in complexes weak interaction of donor–acceptor type may occur between iron and the complexed transition metal, potentially influencing a modified reactivity of the complex compared to other (P, N)-bidentate ligands. In addition, desirable features of ferrocene for use as a scaffold for chiral ligands have also been exploited for (P, N)-ferrocene ligands [4e]: (1) the backbone of a chiral ligand should not be too flexible (so as to provide an appropriate chiral environment) in this sense ferrocene generates unique "ring compounds" with adequate rigidity with the formation of six-membered [—C—P—metal—N—C—Fe—] metallacycles; (2). Derivatization is possible from cyclopentadienyl electrophilic substitution reactions to introduce various donor groups to the ferrocene skeleton; (3) When two functions are introduced at the same cyclopentadienyl ring, the ferrocene platform offers additional very attractive planar chirality; (4) The innate steric environment is often a crucial feature in controlling stereo- and enantioselectivities, and the framework of ferrocene is clearly sterically bulky.



Scheme 1.

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