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Review

Hydroxide complexes of the late transition metals: Organometallic chemistry and catalysis

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ABSTRACT

Transition metal hydroxides of the late transition metals are now relatively common, and play a special role in both the synthesis of new complexes and in important catalytic reactions. The basic nature of this ligand lends these complexes to transmetallation and deprotonation reactions, while small molecules such as CO_2 can insert into the metal–oxygen bond. This review analyses and discusses the progress of this field over approximately the past decade.

Contents

1. Introduction

Transition metal complexes of groups 8–11 have a variety of interesting and useful roles in organometallic chemistry and catalysis. Amongst these species, transition metal hydroxide complexes have found application in catalysis and small molecule activation. Spectroscopic studies of pincer-supported nickel and palladium complexes have allowed the quantification of the electron donating properties of a range of anionic ligands, including hydroxide [1], showing that hydroxide is somewhat similar to bromide and chloride in this respect, but less electron donating than iodide or amide. However, the range of reactivity that is observed from this simple anionic ligand is varied and exciting. In addition, late transition metal hydroxide complexes have been implicated in

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reactions such as Suzuki-Miyaura cross-coupling reactions, where a palladium or nickel hydroxide complex is formed *in situ* and transmetalates more rapidly with a boronic acid than a metal halide complex transmetalates with a boronate [2,3].

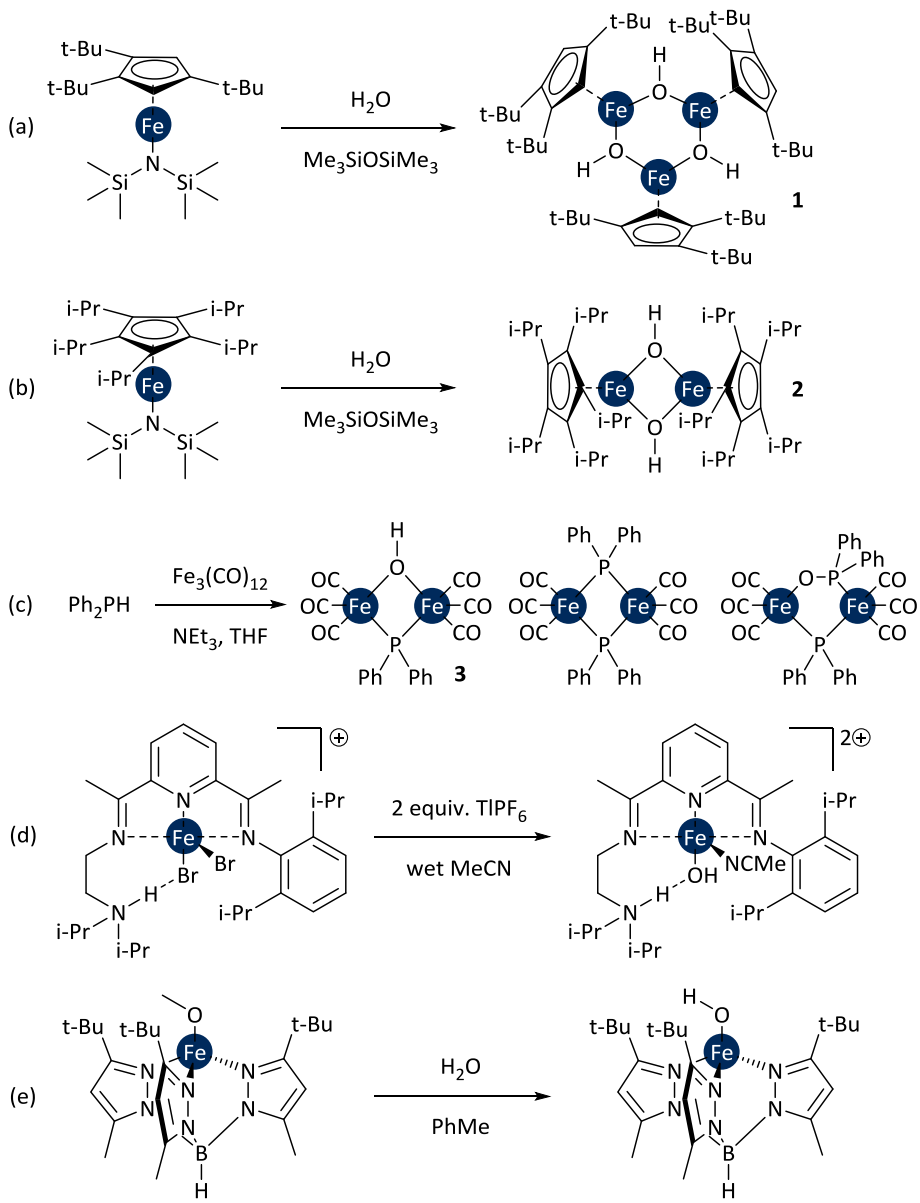
The most common methods by which these species are prepared are (i) halide replacement using a metal hydroxide salt and (ii) the reaction of a complex with a highly basic ligand, such as $N(SiMe_3)_2$ (HMDS), with water. Late transition metal hydroxide complexes tend to exhibit several common reactivity patterns. Firstly, the relatively basic hydroxide ligand (pK_a of H_2O in DMSO = 33) [4] can deprotonate many reagents with relatively acidic C—H bonds, such as alcohols, acetylenes, fluoroarenes, and so forth. Metal hydroxide complexes are often used as starting materials for the preparation of silyloxide complexes [5]. Secondly, it is often possible to achieve insertion of molecules such as CO_2 into the metal–oxygen bond. Thirdly, transmetallation from, for example, boronic acids is often a robust and general way to use hydroxide complexes for the generation of new organometallic complexes.

This review covers much of the progress in this field over the past decade or so; Roesky and co-workers published a detailed review in 2006 [6], and so this manuscript considers the primary literature since then. We will consider the synthesis, properties, and reactions of each transition metal hydroxide complex, with a particular focus on their relevance to or promise in homogenous catalysis.

2. Group 8: iron, ruthenium, and osmium

2.1. Iron

There are relatively few known well-defined iron hydroxide complexes, and all are prepared using methods that involve the presence of water. The complexes are most often polynuclear species with bridging hydroxyl ligands, and are typically prepared by the reaction of iron complexes with water. $[Fe(Cp')(N(SiMe_3)_2)]$ reacts with degassed water, in $(Me_3Si)_2O$, to form the trinuclear complex $[Fe(Cp')(\mu\text{-}OH)]_3$ (**1**) (Cp′ = 1,2,4-tri(*tert*-butyl) cyclopentadienyl) (Scheme 1(a)) [7]. The product is a high spin Fe^{II} complex ($S = 2$) that shows antiferromagnetic coupling between the metal centres. **1** is thermally unstable and decomposes by



Scheme 1. Synthesis of iron hydroxide complexes.