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Review

Paramagnetic organometallic Cr(II)/Cr(III) redox-active catalysts

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Contents

Abstract

The synthesis and reactivity of well-defined paramagnetic organometallic complexes of the first-row transition metals is an area of increasing research, as new applications of these species are discovered. While most inorganic chemists studying paramagnetic organochromium compounds have been investigating their application for olefin polymerization, redox-active chromium catalysts have been developed for C–C bond forming reactions for organic synthetic applications. In particular, a variety of chiral ligands have been introduced for the coupling of organic halides and aldehydes by chromium reagents, the Nozaki–Hiyama–Kishi (NHK) reaction. This article describes some of the coordination chemistry of Cr(II) and Cr(III) that led to these asymmetric NHK catalysts and that continues to underpin the unique reactivity profile of these reagents, as well as reviewing recent progress in the development of these and other paramagnetic organometallic catalysts based on more than one oxidation state of chromium.

Keywords: Paramagnetic complexes; Asymmetric catalysts; Chromium; Reduction-oxidation reactions

1. Introduction

In the past decade, several important advancements have been made in catalysts involving paramagnetic, redox-active organometallic chromium complexes. In keeping with the theme of this issue of *Coordination Chemistry Reviews*, this review will focus on organometallic compounds, and specifically paramagnetic Cr complexes that alternate between two oxidation states as part of their catalytic cycle. Particular attention will be paid to the most well-developed application in this area, the Nozaki–Hiyama–Kishi (NHK) reaction, which couples organic halides and aldehydes and is based on the Cr(II)/Cr(III) redox pair. The scope of this article precludes coverage of the many examples of paramagnetic catalysts that involve only a single oxidation state of chromium, such as Cr(III) catalysts for olefin polymerization [1], asymmetric ring-opening of epoxides [2], or asymmetric hetero-Diels–Alder reactions [3].

Despite the relatively exotic nature of paramagnetic organometallic species, the asymmetric applications featured in this review are undeniably at the forefront of current catalysis

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research. As new catalytic applications involving paramagnetic first-row transition metal complexes are developed, there has been an increasing interest in the synthesis of well-defined compounds with tunable ancillary ligands to help understand the relevant structure–activity relationships [4]. This review is intended as a guide to those interested in the rational design of catalysts for these as-yet understudied systems. For each of the types of applications involving redox-active paramagnetic organochromium catalysts, emphasis is placed on well-defined complexes that have been isolated and characterized. While ligand design considerations are always critical for organometallic catalysis, the reactivity of paramagnetic first-row transition metal complexes in particular is dictated on a large number of interdependent factors. The ligand σ- and π-bonding properties, the metal's oxidation and spin state(s), coordination number, and ligand geometry can all play a role in influencing the reactivity of the complex. However, many of these factors can be understood using relatively simple Ligand Field Theory (LFT) considerations. Indeed, inorganic chemists have been striving to understand transition metal reactivity for many decades now, and this review will attempt drawing parallels to earlier work by chromium chemists that may help illuminate some recurring structural motifs and reactivity trends of relevance to current catalytic applications.

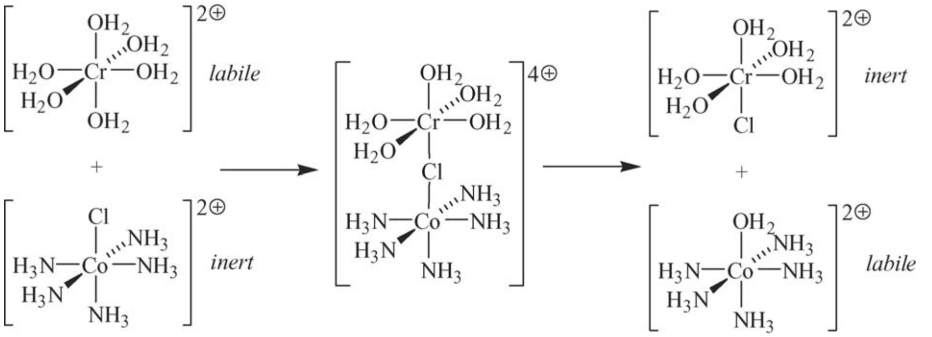
2. C–C bond formation with Cr(II)/Cr(III)

2.1. Activation of organic halides with $Cr^{2+}_{(aq)}$

Considering that they differ only by a single electron, the discrepancy in the rate constants for water exchange between $[Cr(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ of over 10 orders of magnitude is astounding [5]. The incredible differences in reactivity between $Cr^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$ and related transition metal complexes was the focus of much research after World War II [6], leading to the development of Ligand Field Theory. By successfully accounting for a wide variety of spectroscopic and reactivity trends based on straightforward arguments of the occupancy and relative energies of the valence d-orbitals, the impact of LFT on the study of transition metal complexes can be compared to the influence of Valence Bond Theory in organic chemistry. Both LFT and VBT gave experimental chemists a convenient back-of-the-envelope conceptual framework to explain their results and predict new reactivity.

The explanation of why high spin octahedral d^4 complexes with $t_{2g}^3e_g^1$ electronic configurations are labile while octahedral d^3 complexes ($t_{2g}^3e_g^0$) are inert is an integral part of most undergraduate inorganic chemistry courses dealing with transition metal reactivity. While these principles remain central to many coordination chemists (including presumably most of the readers of this journal), it is worth pointing out that LFT considerations are not typically employed even by inorganic chemists when discussing reactivity in current organometallic chemistry. To those interested primarily in catalysis or the synthetic organic application of transition metal reagents, the central ideas of LFT may be even more foreign. And yet these principles are especially critical for those wishing to harness the reactivity of paramagnetic first-row transition metal complexes.

A famous example of the use of the enormous variation in ligand exchange rates observed for $Cr^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$ is shown in Eq. (1), which was used to provide critical evidence for the inner-sphere mechanism of electron transfer [7]. When the labile high spin d^4 Cr(II) complex $[Cr(H_2O)_6]^{2+}$ and the inert low spin d^6 Co(III) compound $[Co(NH_3)_5Cl]^{2+}$ react in aqueous solution, the chloro ligand on cobalt can displace one of the aqua ligands to form the illustrated bridging complex. Following transfer of an electron from Cr(II) to Co(III) through the bridging chloro group, the relative rates of ligand exchange of the two metals are reversed. As a result, the labile d^7 Co(II) complex surrenders the chloro ligand to the inert d^3 Cr(III) center. While the Co(II) rapidly dissociates its ammine ligands to form $[Co(OH_2)_6]^{2+}$, the Cr(III) $[Cr(H_2O)_5Cl]^{2+}$ complex retains all of its ligands, including the chloro group. Lack of incorporation onto Cr of added radioactively labeled chloride ions in solution provided additional proof for the proposed inner-sphere electron transfer mechanism [7].



(1)

LFT and inner-sphere electron transfer are the backdrop for Eq. (2), the activation of benzyl chloride with $Cr^{2+}_{(aq)}$ to give two Cr(III) species, $[Cr(Cl)(H_2O)_5]^{2+}$ and $[Cr(CH_2Ph)(H_2O)_5]^{2+}$, performed by Anet and Leblanc in 1954 [8]. From the perspective of organometallic chemistry, almost every characteristic of the Cr(III) benzyl species runs contrary to the expected requirements of a stable transition metal alkyl complex. During this period, the research groups of Wilkinson and Fischer were using the 18 electron rule as a guide to prepare stable diamagnetic complexes in low formal oxidation states, with