

Review

Aluminum and gallium complexes as homogeneous catalysts for reduction/oxidation reactions [☆]

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ABSTRACT

The roles of Al(III) and Ga(III) complexes in the homogeneous catalysis of oxidation/reduction reactions is reviewed. Free metal salts and discrete complexes have primarily been used to catalyze hydride transfer between organic molecules, the epoxidation of alkenes, and the activation of allylic and aliphatic C–H bonds. The complexation of more highly coordinating ligands can improve the chemo-, regio-, and/or stereoselectivity of the reactions catalyzed by the free Al(III) and Ga(III) salts. The Al(III) and Ga(III) metal centers can accelerate the reactions by activating one or both of the redox-active starting materials and/or bringing the reagents together to orient them in a closer approximation of the reaction's transition state. Complexation of a redox-active ligand can enable Al(III) and Ga(III) complexes to gain or lose electrons directly. The reactivities of complexes with non-innocent ligands can approximate those of transition metal complexes in that they can be converted into metal-based oxidants and reductants.

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1. Introduction

The two lightest Group 13 elements, aluminum and gallium, are earth abundant, inexpensive, and non-toxic relative to most other metals. Aluminum is the most common metallic element in the earth's crust, accounting for over 8% of its mass. Due its ready accessibility, aluminum and its alloys feature in a huge array of

applications. Aluminum isn't thought of as being particularly toxic. At one point, the metal was thought to possibly play a role in the pathology of Alzheimer's disease [1], but extensive research on this topic hasn't borne this out [2]. Gallium is admittedly far less common than aluminum but is about as abundant as lead and a variety of first-row transition metals, such as cobalt, nickel, copper, and zinc. Like aluminum, gallium is not thought of as being particularly toxic, to the extent where complexes with its radioactive isotopes have been used to improve *in vivo* positron emission tomography images [3–5].

[☆] This is a contribution to the special issue in honor of Prof. Armando Pombeiro.
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Many industrial catalytic processes use expensive and rare transition metals, and alternatives using less expensive and more highly abundant metals are urgently sought to lower the costs and increase the sustainabilities of these reactions. Complexes or salts of aluminum and gallium have been used as catalysts, but most of the catalyzed reactions are between acids and bases; prominent examples include Friedel-Crafts acylation and alkylation [6–17].

Aluminum and gallium complexes have had much more limited roles in the catalysis of oxidation/reduction reactions, largely due to the fact that these metals exist almost exclusively in the +3 oxidation state outside of their elemental forms. Transition metal ions, conversely, often change oxidation state as they catalyze redox reactions. In hydrocarbon oxidation reactions, for example, transition metal complexes can react with a terminal oxidant to form a higher-valent metal species that then reacts with the substrate (Eq. (1)) [18–23]. Alternatively, they can convert the terminal oxidant to a more active form, as is proposed in Fenton chemistry (Eq. (2)) [24–27].



There are two fundamental strategies for how non-redox active metals can influence redox reactions. First, they can interact with and enhance the activity of inorganic or organic oxidants and/or reductants. The mere coordination of a redox-inactive metal ion to an oxidant or reductant can impact its redox potentials [28–30]. This strategy has been used to accelerate hydride transfer reactions and the oxidation of hydrocarbons by a variety of two-electron oxidants. Simple Al(III) or Ga(III) salts are often sufficient to elicit the fundamental reaction of interest, but substituting the salt with a coordination complex with a bidentate or polydentate ligand can often eliminate side reactions or endow the catalyzed reaction with regio- or stereoselectivity and a narrower distribution of products. Second, Al(III) or Ga(III) can be coordinated to a redox-active ligand which acts as the relevant redox partner in the reaction. The resultant main group coordination complexes

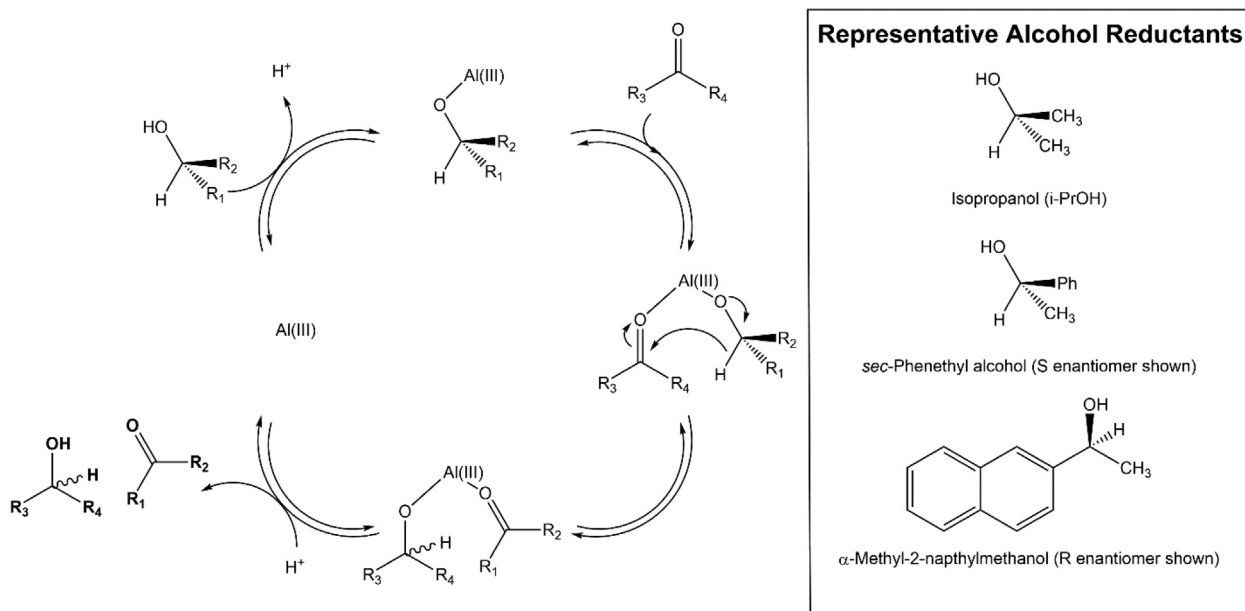
can display transition metal-like reactivity in that metal-based intermediates, rather than a starting material, can serve as the relevant oxidants or reductants in the catalytic cycle.

Although there are heterogeneous materials containing either Al(III) or Ga(III) that have been documented to catalyze redox reactions [31,32], the current review will focus exclusively on homogeneous catalysts.

2. Reactions with simple metal salts

2.1. Ketone reduction/alcohol oxidation

The best-known early example of Al(III)-catalyzed redox reactivity is the Meerwein-Schmidt-Ponndorf-Verley (MSPV) reduction of aldehydes and ketones by primary or secondary alcohols (Scheme 1) [33–35]. The reaction can also be thought of as the oxidation of an alcohol by a carbonyl compound and has been alternatively referred to as Oppenauer oxidation [36]. Aluminum alkoxide salts served as the original catalysts. Al(III) complexes with bidentate organic ligands were later explored as catalysts, and these will be discussed in a later section of this review. No successful MSPV catalysis with simple Ga(III) salts has thus far been reported to the best of my knowledge. MSPV reactions are attractive in that they A) can be run under mild conditions, B) are highly selective for carbonyls over other potentially reducible groups, such as alkenes, and C) can use inexpensive alcohols, such as isopropanol (i-PrOH), as the hydride source. The hydride transfer reaction is reversible but can be driven forward by removing the ketone byproduct, which is most frequently acetone. During the MSPV reaction, Al(III) is proposed to bind to both the carbonyl and the alcohol (Scheme 1). The coordination of the redox partners hastens the reaction in three ways. First, the C=O bond is rendered more susceptible to nucleophilic attack due to the coordination of the positively charged Al(III) to its O atom. Second, the Al(III)-bound alcohol readily deprotonates to an alkoxide, which is a more capable hydride donor. Third, the two redox partners are oriented in a six-membered ring that allows a H⁻ to be transferred more readily from the alkoxide to the carbonyl. In 2004, a combined density functional theory (DFT) and experimental analysis of the MSPV



Scheme 1. General mechanism of MSPV reduction/Oppenauer oxidation.

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