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Authors

Huang, Wenliang
Diaconescu, Paula L

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Rare-Earth Metal π -Complexes of Reduced Arenes, Alkenes, and Alkynes: Bonding, Electronic Structure, and Comparison with Actinides and Other Electropositive Metals

Wenliang Huang,^{a,b} and Paula L. Diaconescu^{a,c}

Rare-earth metal complexes of reduced π ligands are reviewed with an emphasis on their electronic structure and bonding interactions. This perspective discusses reduced carbocyclic and acyclic π ligands; in certain categories, when no example of a rare-earth metal complex is available, a closely related actinide analogue is discussed. In general, rare-earth metals have a lower tendency to form covalent interactions with π ligands compared to actinides, mainly uranium. Despite predominant ionic interactions in rare-earth chemistry, covalent bonds can be formed with reduced carbocyclic ligands,

- ^a Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E Young Drive East, Los Angeles, CA 90095
^b Current address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
^c Corresponding author: pld@chem.ucla.edu

especially multiply reduced arenes.

Introduction

The development of the organometallic chemistry of f elements has paralleled that of transition metal organometallic chemistry with early milestones including the isolation of mono-, bis-, or tris-cyclopentadienyl metal complexes¹⁻³ and the famous uranocene molecule.^{4,5} In the last decade, a renaissance featuring compounds containing metal-element multiple bonds, metal arene complexes, molecular complexes with the metal in a low oxidation state, and the display of an unprecedented reactivity for small molecule activation has been observed. In addition to a showcase of beautiful synthetic methods, theoretical studies have contributed to the understanding of the electronic structure of these new molecules. New concepts, such as inverse trans influence⁶ and sterically induced reduction⁷ have been introduced. Recently, following a long debate against the preponderance of ionic interactions, covalent bonding has been accepted in actinide chemistry,⁸⁻¹⁰ especially for uranium, featuring the contribution of both 5f and 6d orbitals. Several excellent reviews and articles have covered some of the latest advancements in the field.¹¹⁻¹⁷ Herein, we present a critical review of rare-earth metal complexes supported by reduced carbocyclic and acyclic π ligands, including cyclopropenyl, cyclobutadienyl, arenes, cycloheptatrienyl, cyclooctatetraenyl, fused arenes, alkenes, dienes, and alkynes. Besides briefly summarizing examples from the literature, the main purpose of this perspective is to highlight the bonding and electronic structure of these rare-earth metal π -complexes; in addition, we will discuss the similarities and differences in bonding and electronic structure between rare-earth metal complexes and those of closely related actinides and, in some cases, other electropositive metals, such as alkali, alkali earth, or early transition metals.

The present perspective includes not only reduced six-membered rings but also three-, four-, seven-, and eight-membered carbon rings, alkenes, and alkynes (Chart 1a). For reduced carbocyclic rings, negatively charged arenes, except for the cyclopentadienyl anion (Cp⁻) or its fused analogues such as indenyl, are surveyed. Neutral π ligands are also omitted. Albeit the assignment of the negative charge on π -ligands is somewhat arbitrary, we will use the following qualitative criterion: the formal charge of the π ligands in a complex is calculated taken into account that rare-earth metals have a +3 oxidation state, except for ytterbium and europium, which are usually more stable in the +2 oxidation state in their organometallic chemistry. For instance,

(Cp⁺₂Sm)₂(η⁵-C₅Me₅)₂(E)-stilbene) (Cp⁺ = η⁵-C₅Me₅)¹⁸ qualifies to be included in our discussion, while Sm(AlCl₄)₃(C₆Me₆)¹⁹ does not. Another important criterion is that the metal ion should coordinate to the η⁵ face of the η⁵ ligand, i.e., metallocycles of butadiene will not be included. Typical coordination modes include side-on, inverse sandwich, and sandwich (Chart 1b). This perspective focuses on rare-earth metal (scandium, yttrium, and lanthanides) complexes; however, when such complexes are absent and structurally similar complexes of actinides are available and relevant, they will be included in the corresponding section. In order to discuss electronic structures comparatively, we only selected compounds that have been characterized by X-ray crystallography. However, the purpose of this perspective is not to summarize all existing literature examples, but rather to extract useful information from isolated examples in order to discuss the bonding and electronic structure of rare-earth metal complexes.

The review is organized as follows: first, carbocyclic η⁵ ligands except arenes will be discussed in the order of their ring size from the smallest, three-membered ring, to the largest, eight-membered ring; then, arenes and aryl substituted arene complexes of rare-earth metals will be surveyed; after that, fused arenes, alkenes, and alkynes will be included.