

Molecular Transition Metal-Lanthanide Compounds

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Transition metal-lanthanide materials have become invaluable to modern society through their use in powerful yet lightweight permanent magnets, rechargeable batteries, and magnetic films, among other things. Such uses render them applicable in numerous electronic devices, data storage systems, hybrid cars, and even dentures.^{1,2,3,4} Transition metal-lanthanides are also interesting from a fundamental chemical perspective, as they represent an important opportunity to gain greater insight into the nature of chemical bonding, particularly polar metal-metal bonding. For this purpose especially, having access to molecular rather than bulk systems is desirable, in order to simplify computational investigations. Furthermore, successful strategies in the formation of molecular transition metal-lanthanides could prove to be useful alternatives to current techniques in the formation of bulk materials.⁵

Much progress has been made over the past several decades concerning early-late heterobimetallic molecular systems, including fascinating examples of cooperative reactivity with polar or polarizable organic substrates.^{6,7,8} However, until recently, only one example of a crystallographically-characterized molecule containing an unsupported bond between a transition metal (Ru) and a lanthanide (Lu) existed.^{9,10}

In the last few years, Kempe and coworkers have made substantial progress in the synthesis of molecules with unsupported transition metal-lanthanide bonds, successfully obtaining molecules with Re-Yb and Ru-Yb bonds using both salt elimination and alkane elimination strategies.^{10,11} Arnold and coworkers also successfully used salt elimination to form an unsupported Fe-Nd bond (Figure 1).¹²

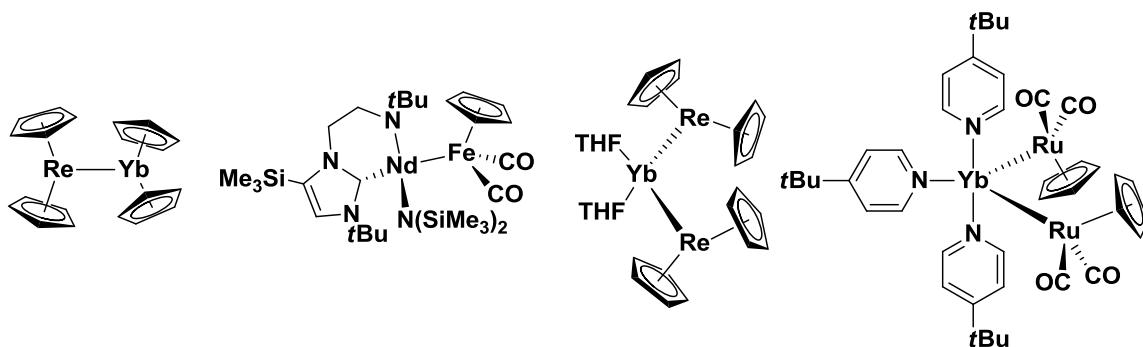
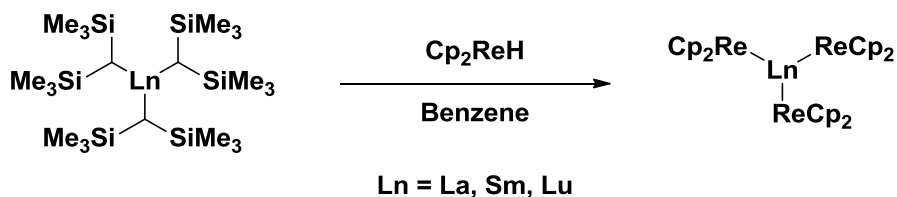


Figure 1. Heteroleptic transition metal-lanthanides with unsupported metal-metal bonds.

The last two molecules in Figure 1 are the first examples of molecular transition metal-lanthanides with two unsupported transition metal-lanthanide bonds.^{10,11} Finally, using Lewis base-free lanthanide starting material and the alkane elimination route, Kempe and coworkers synthesized the first homoleptic molecular transition metal-lanthanides. They established the generality of their synthetic methodology by using the largest (La), smallest (Lu), and mid-sized (Sm) lanthanides (Scheme 1).⁵

All three molecules crystallized from benzene, and are extremely air- and moisture-sensitive. The LnRe₃ cores exhibit nearly perfect trigonal planar geometry, and the rhenocenyl ligands are arranged in a pinwheel fashion to minimize steric repulsions. Apparently due to crystal packing forces associated with the presence of co-crystallized

benzene, the cyclopentadienyl rings of one of the three rhenocenyl ligands are staggered, whereas those of the other two are eclipsed.⁵



Scheme 1. Synthetic route to the formation of homoleptic transition metal-lanthanides.

Computational analysis was performed on $\text{La}(\text{ReCp}_2)_3$. Density functional theory (DFT) calculations at the BLYP level were used to optimize the structure, and the electron localizability indicator ELI-D was used in the context of the Atoms in Molecules (AIM) paradigm to analyze the chemical bonding. For comparison, an intermetalloid with a similar local arrangement of metal atoms, Y_2ReB_6 , was optimized using the local density approximation (LDA) and the chemical bonding was analyzed by ELI-D.⁵ The advantage of using the AIM paradigm is that, due to its defining atoms by one- and two-particle (electron) matrices rather than molecular orbital or valence bond wavefunction approximations, it allows comparison between structures that are of a different nature chemically, but may have similar local bonding situations.^{5,13}

The computational analysis revealed the presence of genuine chemical bonds between La and Re in $\text{La}(\text{ReCp}_2)_3$ (two ELI-D maxima per bond, as shown in Figure 2), and indicated substantial similarity in the bonding situations for both the molecular and intermetalloid species (Figure 2).⁵

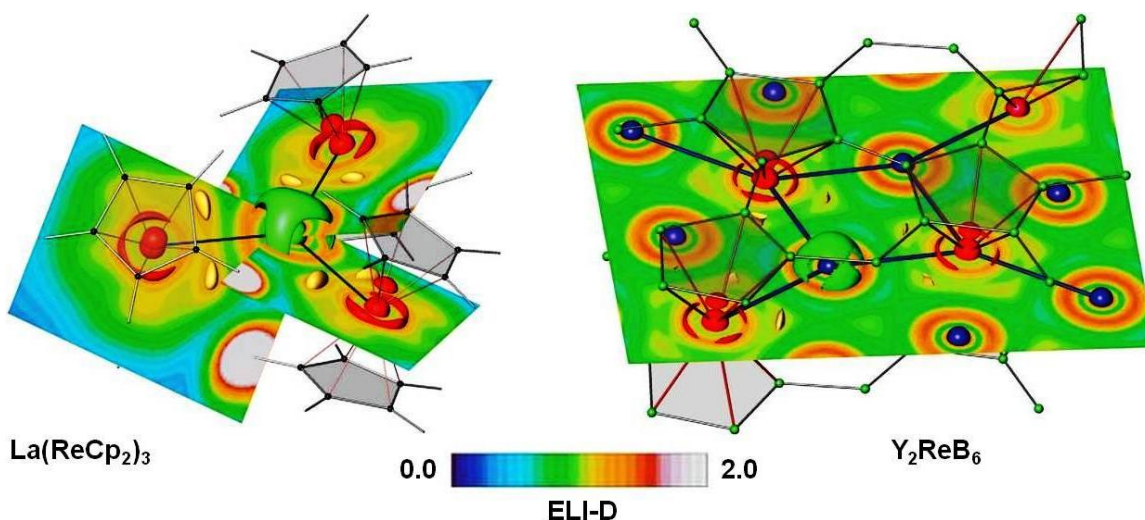


Figure 2. Computational ELI-D comparison between $\text{La}(\text{ReCp}_2)_3$ and Y_2ReB_6

The attainment of molecular homoleptic transition metal-lanthanides represents an exciting opportunity to gain insight into the nature of chemical bonding between

transition metals and lanthanides. It is also conceivable that the alkane strategy employed here could be used to obtain bulk transition metal-lanthanide materials under much milder conditions than are currently used, through the reaction of transition metal polyhydrides with lanthanide polyalkyls.⁵

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