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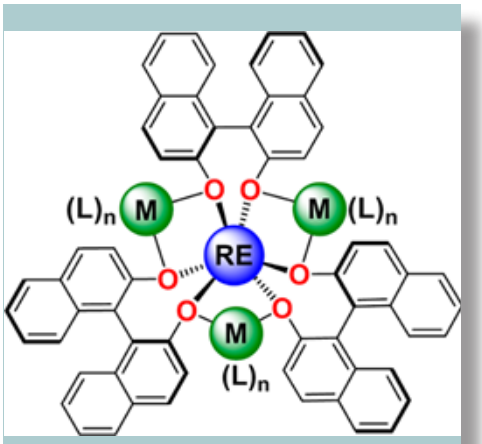

Stable, single precursor for the synthesis of enantioselective rare earth metal catalysts for multi-functional asymmetric catalysis

Brief Description

Air and water tolerant precatalyst for Shibasaki's rare earth metal BINOLate catalysts

Inventor

Patrick J. Walsh, Professor of Chemistry and Alan G. MacDiarmid Term Chair
Eric J. Schelter, Associate Professor of Chemistry

STATE OF DEVELOPMENT

- Proof-of-principle testing

INTELLECTUAL PROPERTY

PCT pending (WO/2014/205437)

REFERENCE MEDIA

Robinson et al. JACS, 2015, 137(22), p. 7135-7144.
Robinson et al. JACS, 2014, 136(22), p. 8034-8041.

DESIRED PARTNERSHIPS

- License
- Co-development

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Problem

Asymmetric catalysis is used for synthesizing optically active or chiral materials, which form the basis for the production of numerous pharmaceuticals, natural products, fine chemicals, and biologically active compounds. Because of the cooperative activation of reaction partners, multi-functional asymmetric catalysts improve reactivity and selectivity compared to traditional catalysts. The Shibasaki rare earth-alkali metal-BINOLate (REMB) framework is one of the most successfully employed heterobimetallic asymmetric catalysts that supports a range of reactions. However, despite the Shibasaki catalyst's synthetic utility, there has not been a straightforward strategy to generate it without the impediment of rigorously anhydrous conditions.

Solution

The Walsh and Schelter labs have designed a novel class of self-assembled hydrogen-bonded rare earth tris(BINOLate) complexes from precatalysts, expanding catalytic functionality for many asymmetric reactions. The precatalysts are from rare earth nitrate hydrates and amine bases as precursors. The precatalyst can be generated under single operational conditions (open air and with wet solvents), and it can be isolated and stored in a stable form after generation. The synthesis of REMB complexes from the precatalyst is via an acid-base cation exchange that can be performed using metal halides or pseudo-halides.

Advantages

- Cost-effective with inexpensive MX salts, amines, and lanthanide nitrates
- Improved operations by avoiding use of moisture-sensitive strong bases
- Improved or comparable stereoselectivity in Michael additions and Aldol reactions
- Stable in solution and solid state
- High-yielding, scalable reaction

Applications

- Precatalysts for Shibasaki REMB frameworks
- Asymmetric catalysis

(Image, top) REMB framework, where RE = Sc, Y, La-Lu; M = Li, Na, K; B = (S)-BINOLate (1,1'-bi-s-naphtholate); RE/M/B = 1/3/3. From Robinson et al, JACS, 2014.