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Synthesis of novel copper-rare earth BINOLate frameworks from a hydrogen bonding DBU-H rare earth BINOLate complex†

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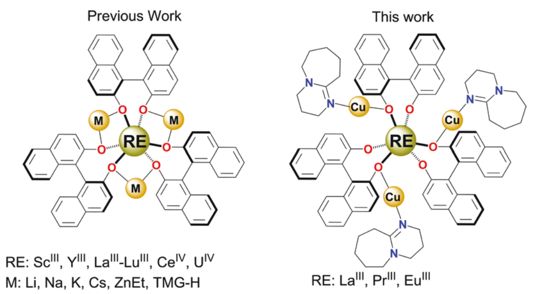
The preparation of a novel H-bonding DBU-H$^+$ BINOLate Rare Earth Metal complex enabled the synthesis of the first copper-Rare Earth Metal BINOLate complex (CuDBU-REMB). CuDBU-REMB was compared to the analogous Li complex using X-ray crystallography and Exchange NMR spectroscopy (EXSY). The results provide insight into the role of the secondary metal cation in the framework's stabilization.

Asymmetric catalysis is the most important method for the preparation of optically active compounds, which are crucial in pharmaceutical and organic materials applications.[1–3] Specifically, chiral Rare Earth metal (RE) complexes continue to be advantageous for a number of Lewis-acid catalysed reactions.[4–6] The REMB framework $[M_3(THF)_n][(BINOLate)_3RE]$ (REMB; RE = Sc, Y, La–Lu; M = Li, Na, K; B = 1,1′-bi-2-naphtholate; RE/M/B/ = 1/3/3; Scheme 1), pioneered by Shibasaki, is among the most enantioselective heterobimetallic catalysts, where changing of M, RE, or substitution of BINOL enables diverse reactivity.[5,7] We have shown that this framework is not only robust, but variable beyond Shibasaki's original concept. While the central cation is typically a trivalent rare earth cation, this site can also be occupied by a tetravalent cerium or tetravalent uranium ion.[8–11] The cation in the secondary coordination sphere can also be replaced with alternatives to alkali metals to include ethyl zinc ($ZnEt^+$), and 1,1,3,3-tetramethyl guanidinium (TMG-H$^+$), where the latter functions as a hydrogen-bond donor.[10,12,13] By substituting the secondary coordination metal with zinc, we were able to increase the reactions capable by the REMB framework to include enantioselective ethylation of aldehydes.[12] In light of this variability, we expected that copper(I) could also occupy the secondary coordination sphere, due to its chemical similarities to Zn(II). We were also interested in copper because copper complexes are known to catalyse a host of organic reactions.[14–18] Thus, we envisioned that the introduction of copper into the secondary coordination sphere would increase the library of reactions available to the REMB framework.

The preparation of previously reported REMB complexes with Li, Na, K, or Cs can be accomplished using protonolysis or transmetallation reactions.[10,19] However, $[(ZnEt)_3(THF)_3][(BINOLate)_3RE]$ can only be prepared cleanly from protonolysis of a $[(BINOLateH)_3RE]$ species generated *in situ* (Scheme 2A).[12] Despite this observation, for the current work, application of protonylsis to copper *tert*-butoxide $(CuOtBu)_4$, or mesitylcopper $(CuMes)_n$ resulted in complex mixtures of products. Inspired by our previous demonstration that $[TMG\text{-}H]_3[(BINOLate)_3RE]$ acts as an air-stable precursor to many alkali metal-containing REMB complexes, we hypothesized that the copper analogue could be synthesized from a similar hydrogen-bonded framework with 1,8-diazabicyclo(5.4.0) undec-7-ene (DBU). Herein we disclose the synthesis of $[Cu_3(DBU)_3][(BINOLate)_3RE]$ (**2-RE**) from the analogous $[DBU\text{-}H]_3[(BINOLate)_3RE]$ (**1-RE**) hydrogen-bonded precursor.

Complexes **1-RE** were prepared by treatment of THF solutions of (*S*)-BINOL and (DBU) with a THF solution of the corresponding $RE[N(SiMe_3)_2]_3$ (Scheme 2B). The complexes



Scheme 1 Left: Previously synthesized REMB frameworks, which all adopt the same basic structure; right: this work introducing copper from the corresponding H-bonding framework.

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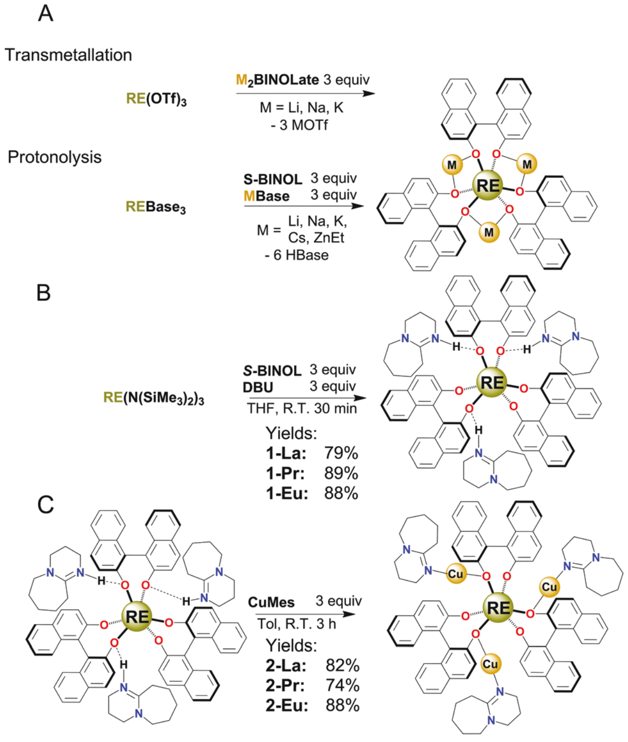
† Electronic supplementary information (ESI) available: X-ray structures of **1-La**, **1-Pr**, **2-La**, **2-Pr**; NMR data for all compounds; and additional EXSY-NMR data. CCDC 1850918-1850923. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt03335h



Scheme 2 A) Previous methods of synthesis of REMB frameworks (B) synthesis of complexes **1-RE** from the corresponding RE amide bases. (C) Synthesis of complexes **2-RE** from **1-RE**.

were isolated by crystallization in good yields (79–88%). X-ray diffraction quality crystals of **1-RE** were grown from THF solutions layered with pentane, revealing a 6-coordinate lanthanide cation. In the cases of **1-Pr** and **1-Eu**, three $HDBU^+$ cations engage in hydrogen bonding, while in **1-La** only one $HDBU^+$ cation engages in this interaction (Fig. 1; Fig. S1†). The ^1H NMR spectra of **1-RE** exhibited 6 signals attributed to BINOLate resonances and 16 broad resonances attributed to diastereotopic DBU resonances indicating a pseudo-D_3 symmetric complex on the NMR timescale.

Treatment of complexes **1-RE** with three equivalents of $(CuMes)_n$ in toluene resulted in a new set of BINOLate resonances that were assigned as complexes **2-RE**. Crystallization of this species from hot toluene layered with pentane led to the isolation of **2-RE** in 74–88% yields (Scheme 2C). The NMR spectra indicated a pseudo-D_3 symmetric complex, consistent with previously described REMB complexes (Scheme 2C). However, the X-ray structure revealed a complex with pseudo-C_3 symmetry, in which the copper atoms coordinate to one of the two BINOLate oxygen atoms (Fig. 2). This bridging coordination mode resulted in a lengthening of the Ln–O bond by an average of 0.16 Å, compared to oxygen atoms bound only to the lanthanide ion.

In previous REMB frameworks, the secondary-coordination sphere metal was at least 3-coordinate, bound to two BINOLate oxygen atoms. However, in complexes **2-RE**, the copper atom was only 2-coordinate (∠N–Cu–O > 164°, closest non-bonding atom-Cu > 2.8 Å). Additionally, despite the wide use of DBU as a base in catalysis, there is only one other example of a Cu-DBU coordination characterized by X-ray diffraction.[20] The previously described Cu-DBU complex is a 3-coordinate Cu atom with two equivalents of DBU coordinated and one iodide anion.

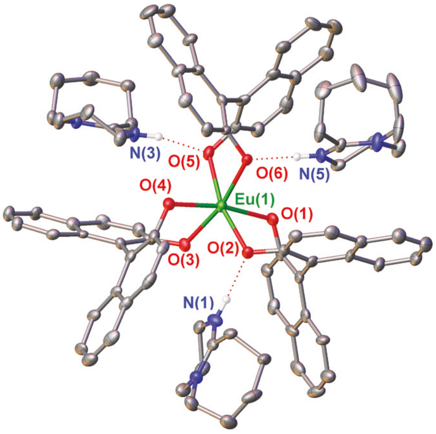


Fig. 1 Thermal ellipsoids of $[DBU\text{-}H]_3[(BINOLate)_3Eu]$ **1-Eu** at the 30% probability level, representative of **1-RE**. C–H hydrogen atoms and disorder removed for clarity. Selected bond lengths (Å): Eu(1)–O(1) 2.275(5), Eu(1)–O(2) 2.331(5), Eu(1)–O(3) 2.247(5), Eu(1)–O(4) 2.261(6), Eu(1)–O(5) 2.317(5), Eu(1)–O(6) 2.334(5), O(2)–N(1) 2.753(8), O(5)–N(3) 2.792(9), O(6)–N(5) 2.701(10). Selected angles (°) N(1)–H(1)–O(1) 175.33, N(3)–H(3a)–O(5) 166.32, N(5)–H(5a)–O(6) 170.72.

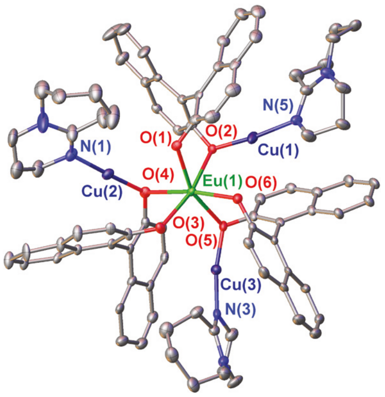


Fig. 2 Thermal ellipsoids of $[Cu(DBU)]_3[(BINOLate)_3Eu]$ **2-Eu** at the 30% probability level, representative of **2-RE**. Disorder, hydrogen atoms, and interstitial solvent removed for clarity. Selected bond lengths (Å): Eu(1)–O(1) 2.256(8), Eu(1)–O(2) 2.410(8), Eu(1)–O(3) 2.202(9), Eu(1)–O(4) 2.400(8), Eu(1)–O(5) 2.362(8), Eu(1)–O(6) 2.284(7), Cu(1)–O(2) 1.820(8), Cu(1)–N(5) 1.868(10), Cu(2)–O(4) 1.885(9), Cu(2)–N(1) 1.859(14), Cu(3)–O(5) 1.825(9), Cu(3)–N(3) 1.820(12). Selected angles (deg) N(1)–Cu(2)–O(4) 177.6(6), N(3)–Cu(3)–O(5) 169.2(4), N(5)–Cu(1)–O(2) 164.6(5).

To investigate the lability of the ligands in solution, an important feature of RE catalysis, we turned to EXSY-NMR to determine the ligand exchange rates, as previously demonstrated by our group.[11,21] The technique has found use for determining the exchange rates of ligands in a multitude of different catalytic systems.[22] For EXSY-NMR to be applicable

Table 1 Associated EXSY rate data and activation parameters for **2-Pr**/**2-Eu**

	Cu-REMB[a]		Li-REMB[b]	
	2-Pr → 2-Eu	**2-Eu → 2-Pr**	**Pr → Eu**	**Eu → Pr**
$k'(s^{-1})$[c]	2.63 ± 0.10[d]	2.63 ± 1.02[d]	0.759	0.806
$\Delta H^{\ddagger}$ (kcal mol^{-1})[e]	11.1 ± 2.3	9.0 ± 1.1	15.1	14.6
$\Delta S^{\ddagger}$ (eu)[e]	−19.8 ± 7.8	−26.4 ± 2.7	−35.6	−41.3
$\Delta G^{\ddagger}$ (kcal mol^{-1})[e]	11.7 ± 2.3	9.7 ± 1.1	17.7	17.6

[a] Values are reported as an average of 3 independently prepared samples. [b] Previously reported values.[21] [c] At 300 K, [2-Pr]/[2-Eu] = 15.0/14.6 mM. k' values determined using EXSYCALC. [d] Values obtained from H_7 at t_{mix} = 170 ms. [e] At 298 K. Additional data can be found in the ESI.

the two species in exchange must have sufficient spectral resolution.[22,23] Therefore, we chose to use a mixture of **2-Pr** and **2-Eu**, due to their solid state structures being isostructural, relatively short relaxation times, and the rare earth cations' anisotropic *g*-tensors having opposite signs.[3,24] In THF-d_8, the rate of transfer of BINOL ligands between **2-Pr** and **2-Eu** was 2.63 s^{-1} (300 K) (Table 1). Using variable temperature EXSY experiments, we also determined the activation parameters (Table 1).

Compared to the previously measured Li-REMB (0.759 s^{-1} for Li-REMB), we found that the BINOLate ligands of **2-RE** were more labile in solution.[21] Likewise, the free energy, enthalpic barriers, and entropic barriers we measured for the exchange between **2-Pr** and **2-Eu** were lower than the analogous Li-REMB (Table 1). We postulate that the increased exchange rate of the BINOLate ligands was due to fewer metal–ligand interactions, in the secondary coordination sphere, increasing the lability of BINOLate ligands. In the case of Li-REMB, the rate of ligand exchange is already faster than the rate of catalysis in the Michael and Henry reactions.[21]

In summary, we have demonstrated that the isolation of a hydrogen-bonding REMB scaffold enabled the synthesis of a Cu-REMB compound using simple ligands. The copper-containing complex was found to adopt an uncommon 2-coordinate geometry in the secondary coordination sphere. EXSY-NMR studies show that the BINOLate ligands exchanged faster than the previously studied Li-REMB complex. We expect that these results will inspire use of hydrogen-bonding networks to build multi-metallic complexes. Future work will explore the utility of these complexes as catalysts.

Conflicts of interest

The authors declare no conflict of interests.

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