



# Синтез прекурсоров к металлоорганическим соединениям РЗЭ

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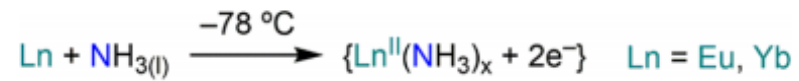
Москва, 2026 г.

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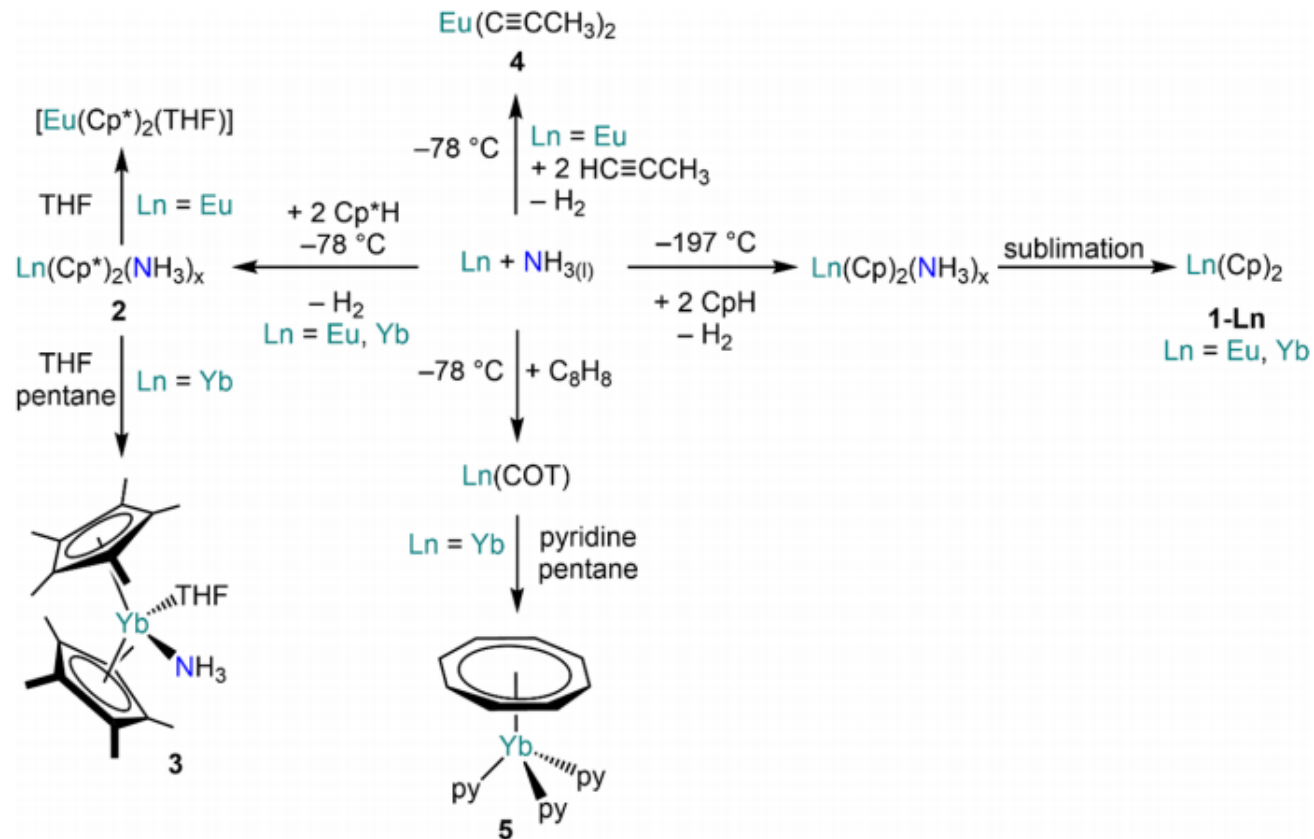
# Синтез в жидком аммиаке

Scheme 1. Synthesis of Ammonia Solution of Divalent Lns



Warf, J. C., & Korst, W. L. (1956). *The Journal of Physical Chemistry*, 60(11), 1590-1591.

Scheme 4. Synthesis of Divalent Ln Organometallic Complexes in Liquid NH<sub>3</sub> <sup>83-87</sup>

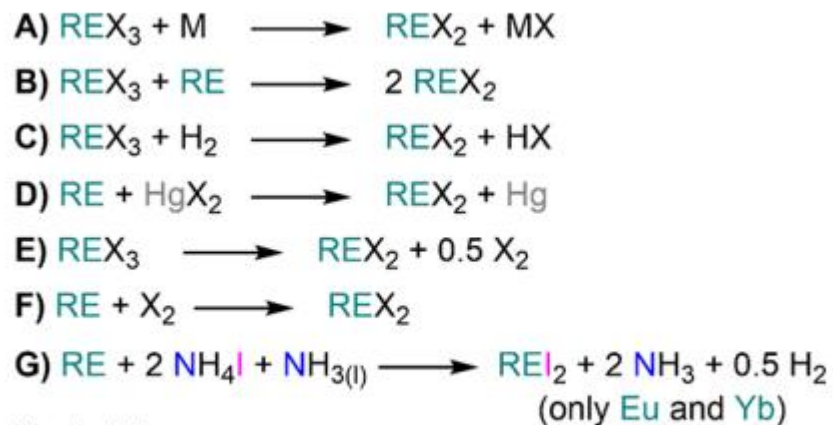


$$\mathrm{RE}(X)_n + m\mathrm{M}(\mathrm{L}) \rightarrow \mathrm{RE}(\mathrm{L})_m(X)_{n-m} + m\mathrm{M}(X)$$

# Галогениды РЗЭ

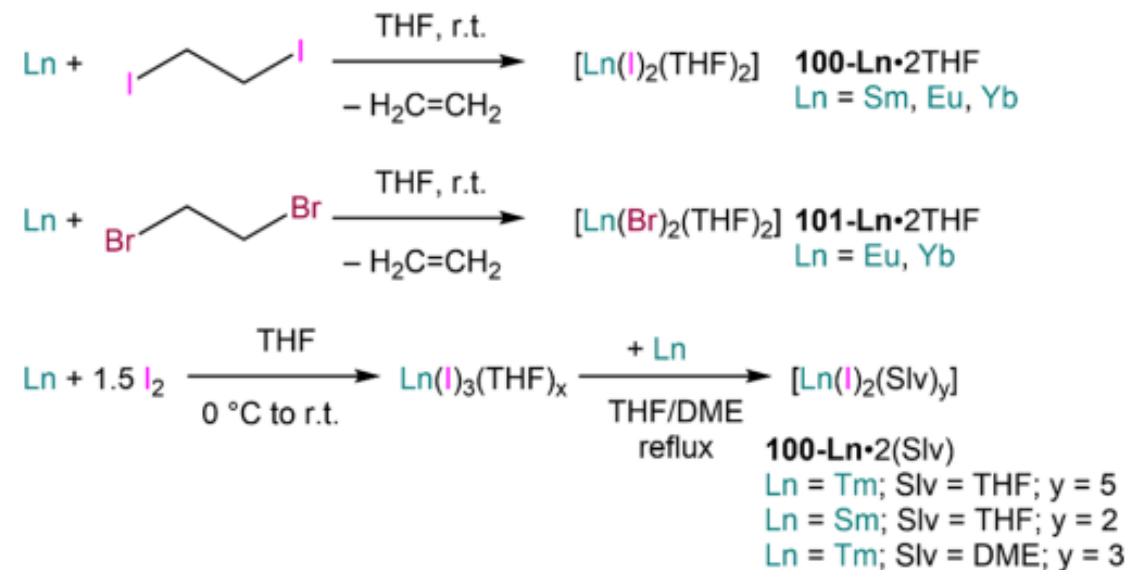
## Двухвалентные РЗЭ

Scheme 35. Preparation of Solvent-free RE Dihalides



X = halide  
 M = alkali metal, AE  
 Group 13 metal, Ln

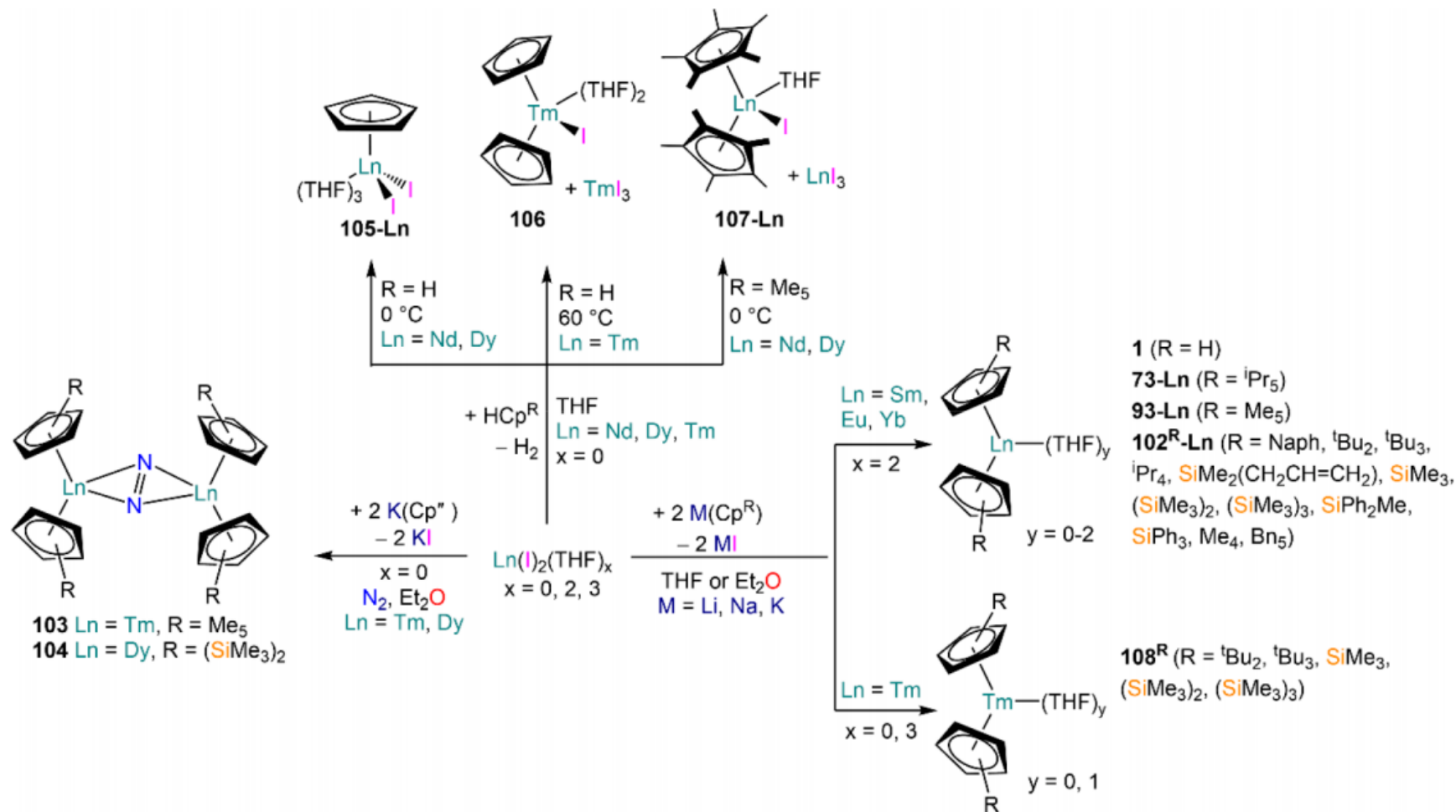
Scheme 36. Synthesis of Solvated  $LnX_2$  Salts  $100-Ln \cdot 2THF$  ( $Ln = Sm, Eu, Yb$ ),<sup>246-248</sup>  $101-Ln \cdot 2THF$  ( $Ln = Eu, Yb$ ),<sup>247</sup>  $100-Tm \cdot 5THF$  and  $100-Tm \cdot 3DME$ <sup>252,253</sup>



# Галогениды РЗЭ

## Двухвалентные РЗЭ

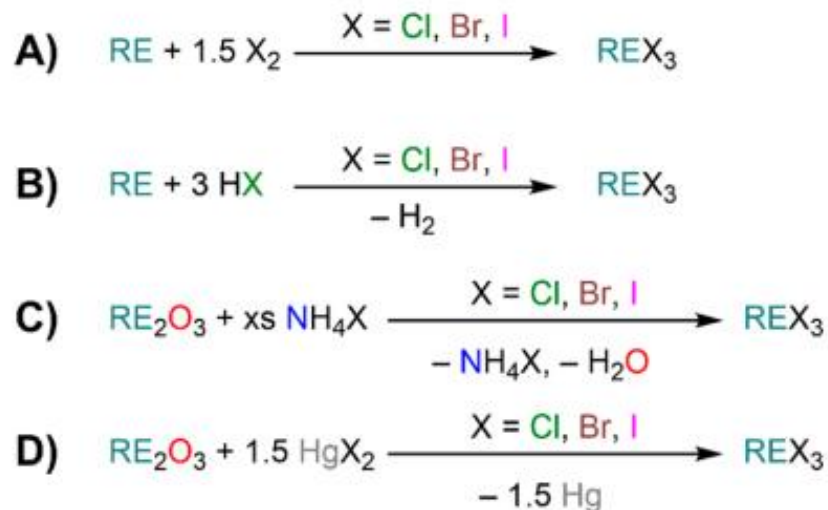
Scheme 37. Reactivity of  $\text{LnI}_2$  ( $\text{Ln} = \text{Nd, Sm, Eu, Dy, Tm, Yb}$ ) with Cyclopentadienes and Cyclopentadienyl Metal Salts<sup>247,271,273–279,282,283</sup>



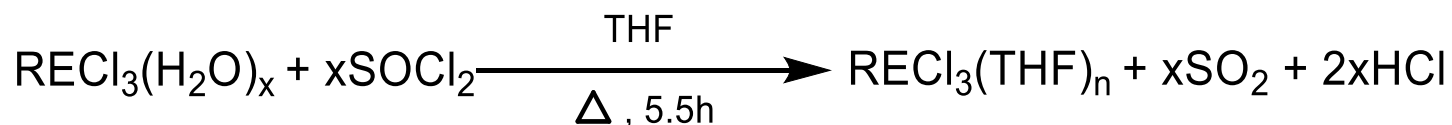
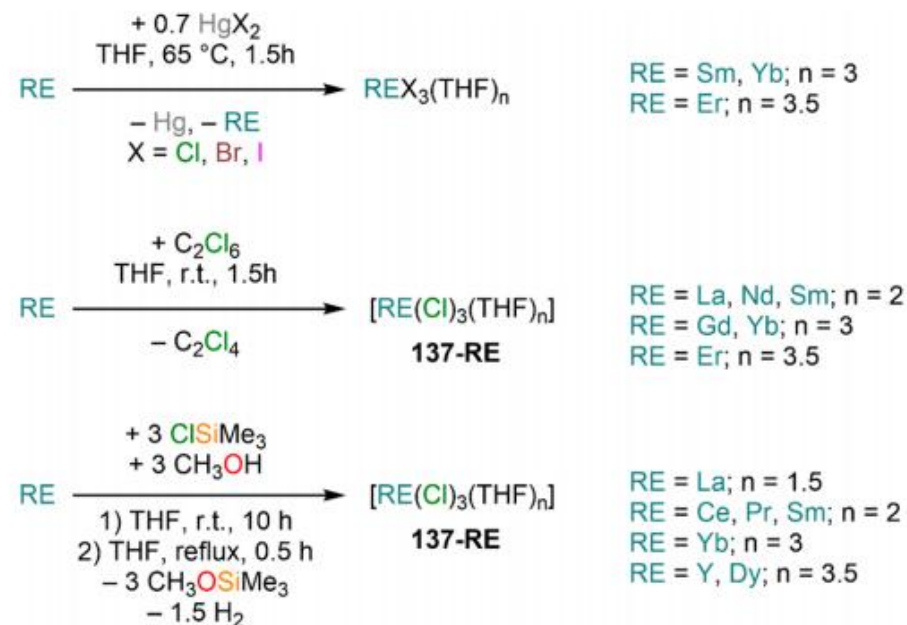
# Галогениды РЗЭ

## Трехвалентные РЗЭ

Scheme 41. Main Synthetic Strategies for the Preparation of Trivalent RE Halides



Scheme 43. Synthesis of Solvated Trivalent RE Halides via RT Reactions with  $HgX_2$ <sup>126,345</sup> or Direct Reaction with Hexachloroethane<sup>171</sup> or Trimethylsilylchloride<sup>353</sup>

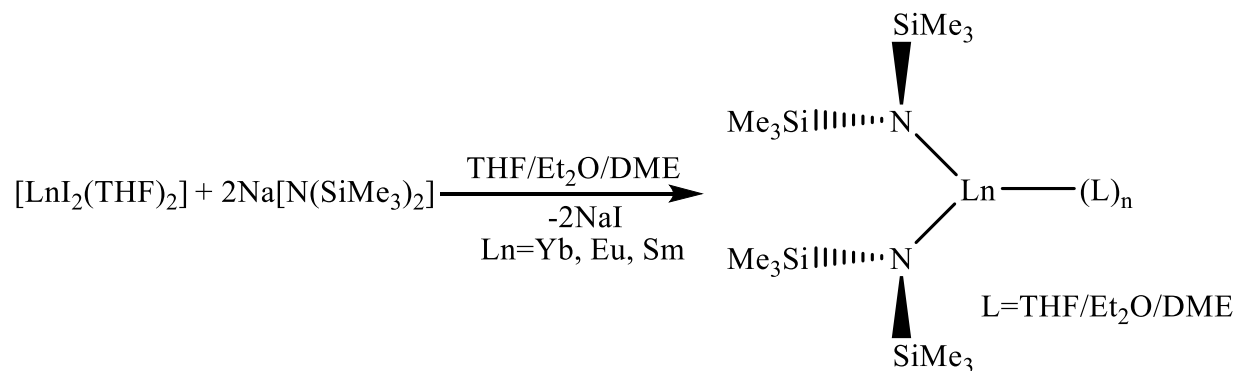


Brauer, G. (Ed.). (2012). *Handbook of Preparative Inorganic Chemistry V2* (Vol. 2). Elsevier.

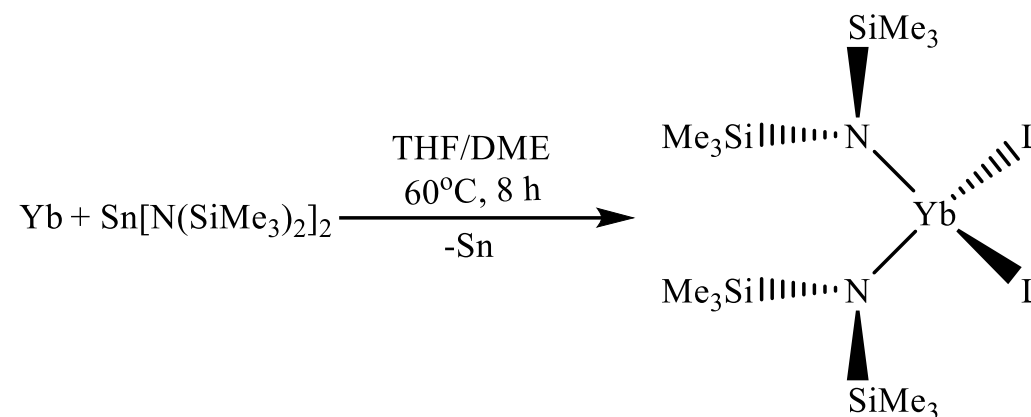


# Бис-триметилсилиламидные комплексы РЗЭ

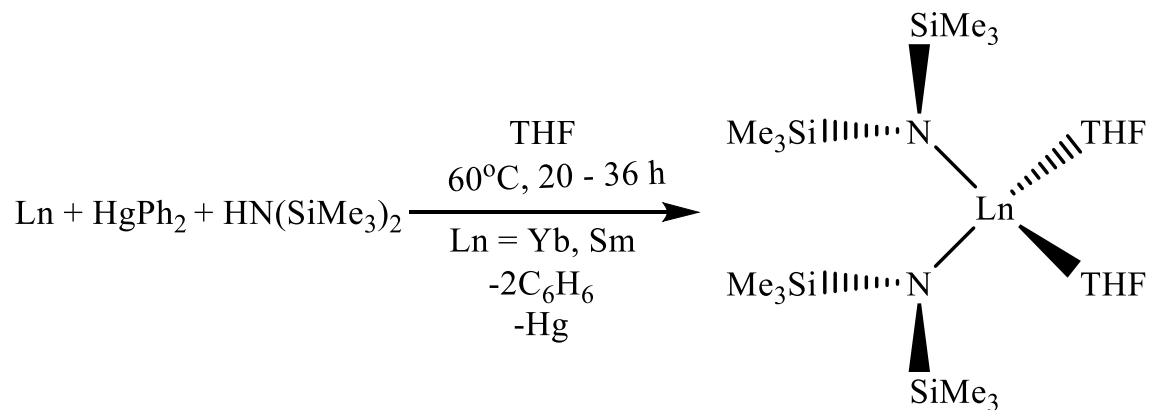
## Двухвалентные РЗЭ



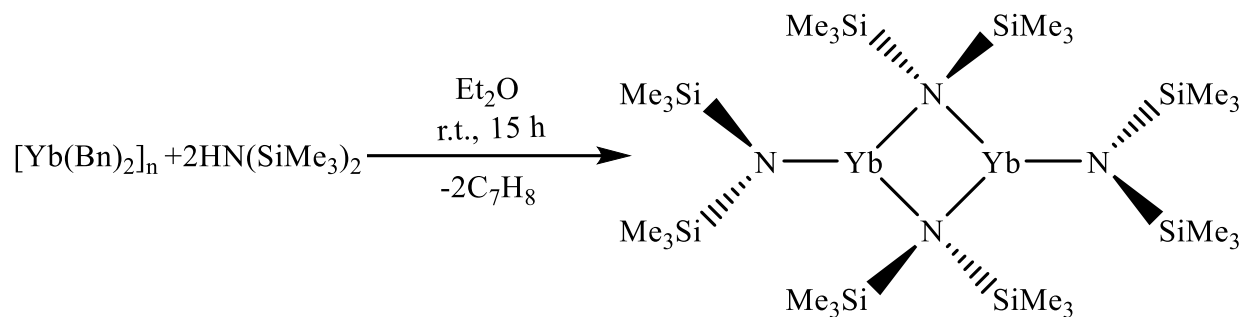
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Bekir, C., Hitchcock, P. B., Lappert, M. F., & Smith, R. G. (1992). *Journal of the Chemical Society, Chemical Communications*, (13), 932-934.



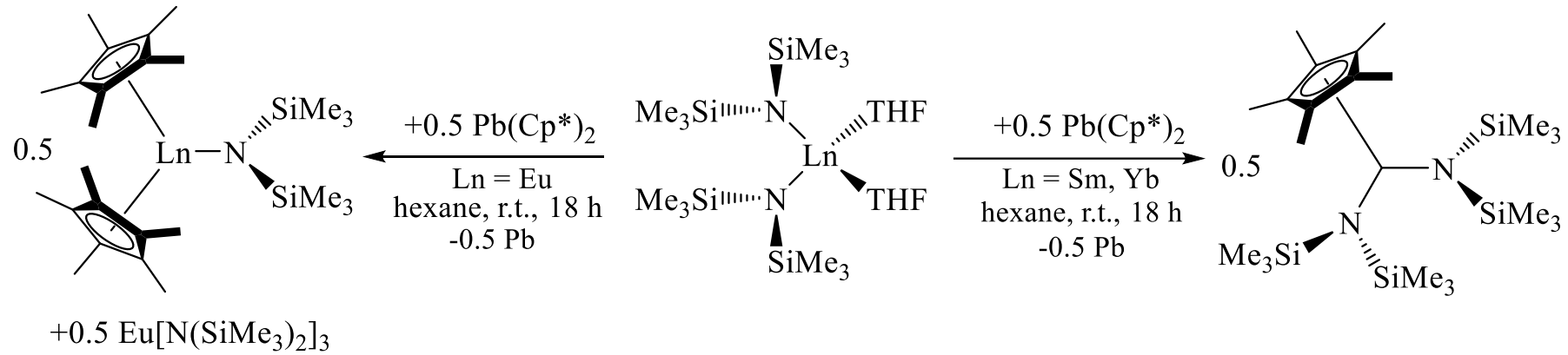
Deacon, G. B., Raverty, W. D., & Vince, D. G. (1977). *Journal of Organometallic Chemistry*, 135(1), 103-114.



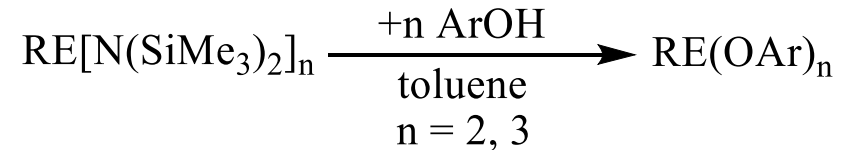
Katzenmayer, M. M., Wolf, B. M., Mortis, A., Maichle-Mössmer, C., & Anwander, R. (2021). *Chemical Communications*, 57(2), 243-246.

# Бис-триметилсилиламидные комплексы РЗЭ

## Двухвалентные РЗЭ



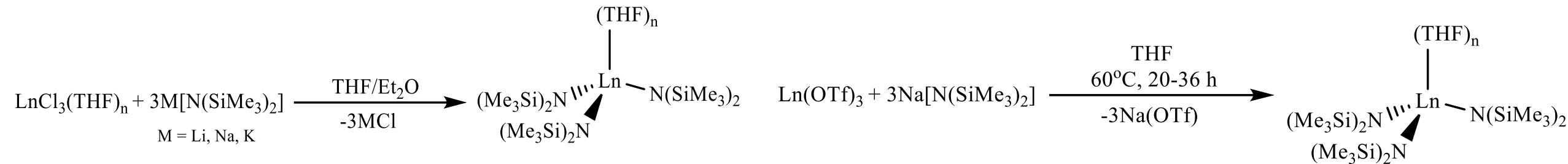
Bienfait, A. M., Wolf, B. M., Tornroos, K. W., & Anwander, R. (2015). *Organometallics*, 34(24), 5734-5744.



ávan den Hende, J. R. (1994). *Journal of the Chemical Society, Chemical Communications*, (12), 1413-1414.

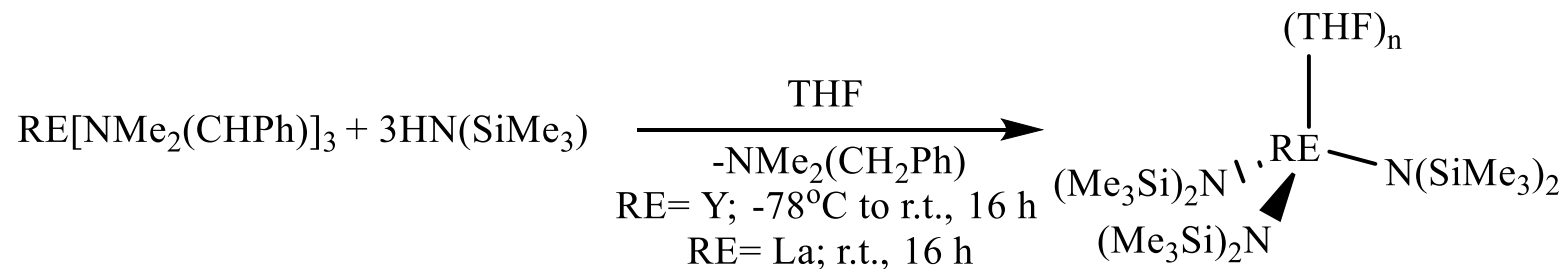
# Бис-триметилсилиламидные комплексы РЗЭ

## Трехвалентные РЗЭ



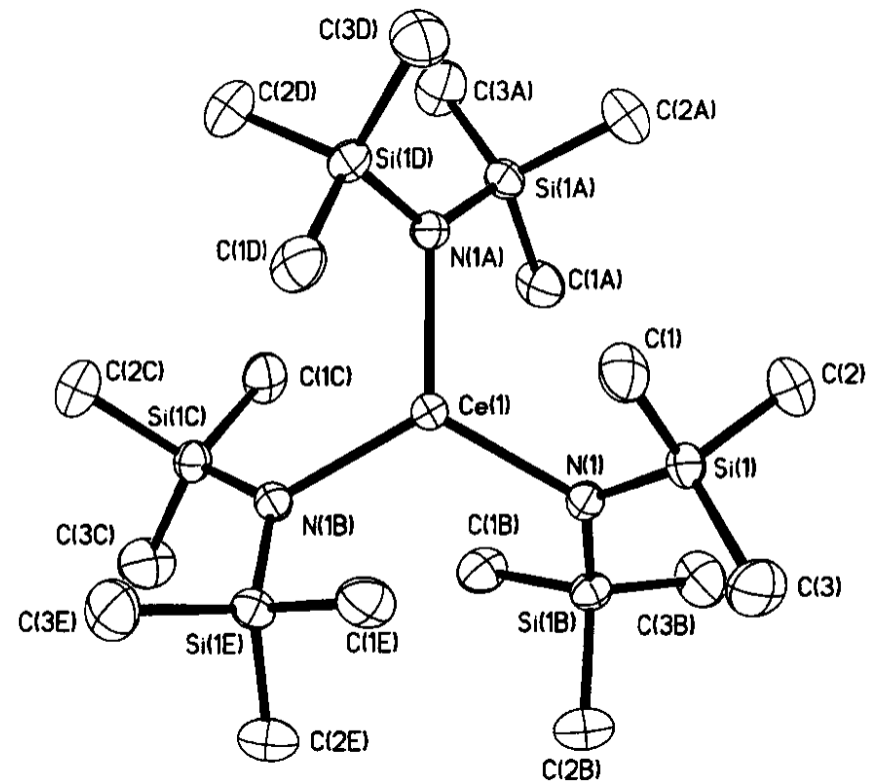
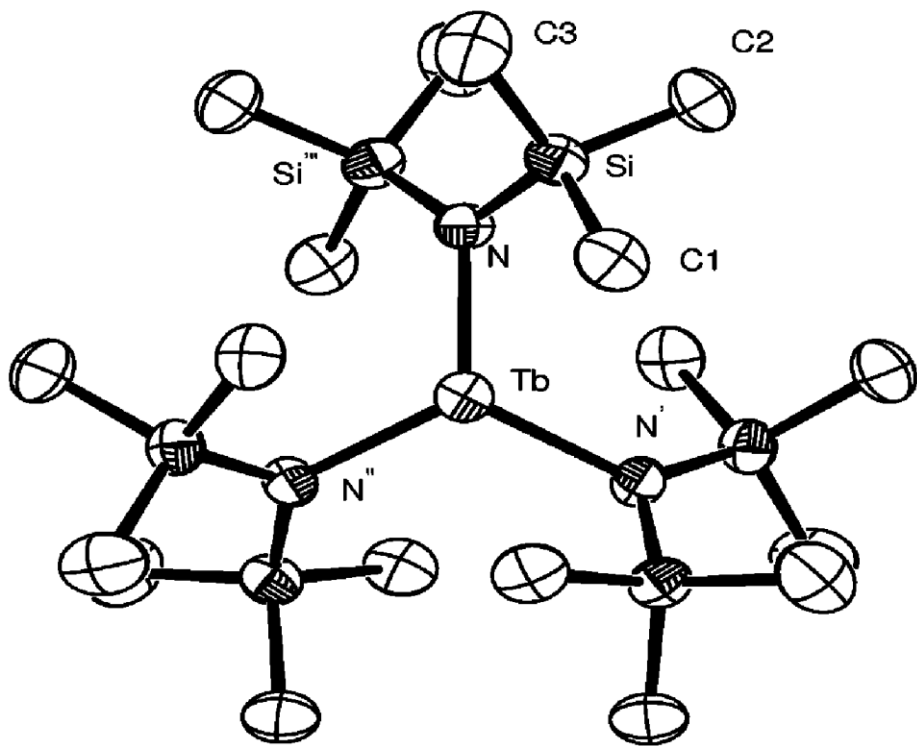
Bradley, D. C., Ghotra, J. S., & Hart, F. A. (1973). *Journal of the Chemical Society, Dalton Transactions*, (10), 1021-1023.

Schuetz, S. A., Day, V. W., Sommer, R. D., Rheingold, A. L., & Belot, J. A. (2001). *Inorganic Chemistry*, 40(20), 5292-5295.



Behrle, A. C., & Schmidt, J. A. (2011). *Organometallics*, 30(15), 3915-3918.

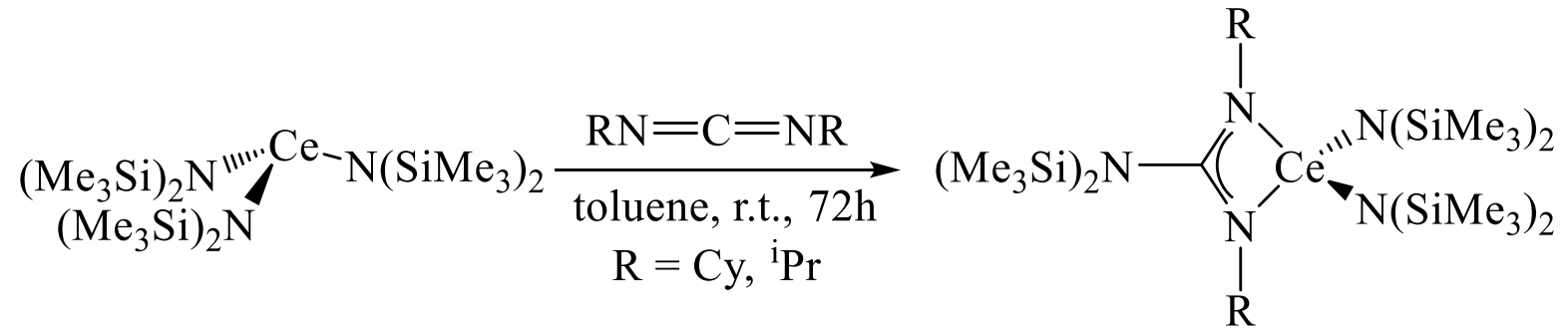
# Кристаллические структуры бис-триметилсилиламидных комплексов



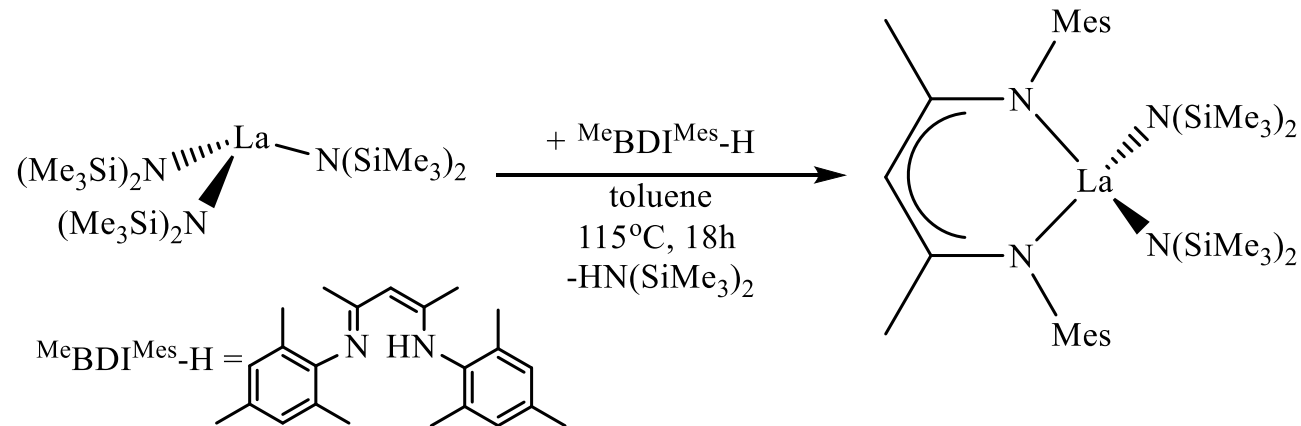
Аналогичную структуру имеют производные Nd, Yb, Eu, Sc, Dy, Er и Pr

# Бис-триметилсилиламидные комплексы РЗЭ

## Трехвалентные РЗЭ

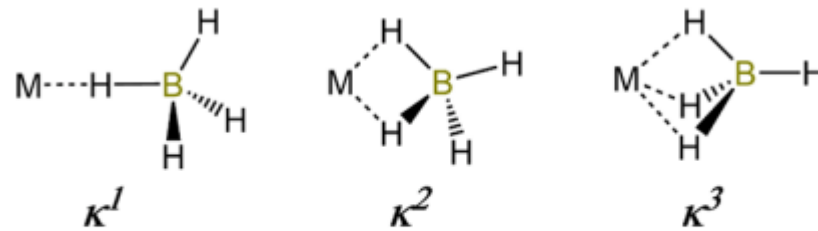


Yin, H., Carroll, P. J., Manor, B. C., Anna, J. M., & Schelter, E. J. (2016). *Journal of the American Chemical Society*, 138(18), 5984-5993.



Vitanova, D. V., Hampel, F., & Hultsch, K. C. (2005). *Journal of organometallic chemistry*, 690(23), 5182-5197.

# Боргидриды РЗЭ

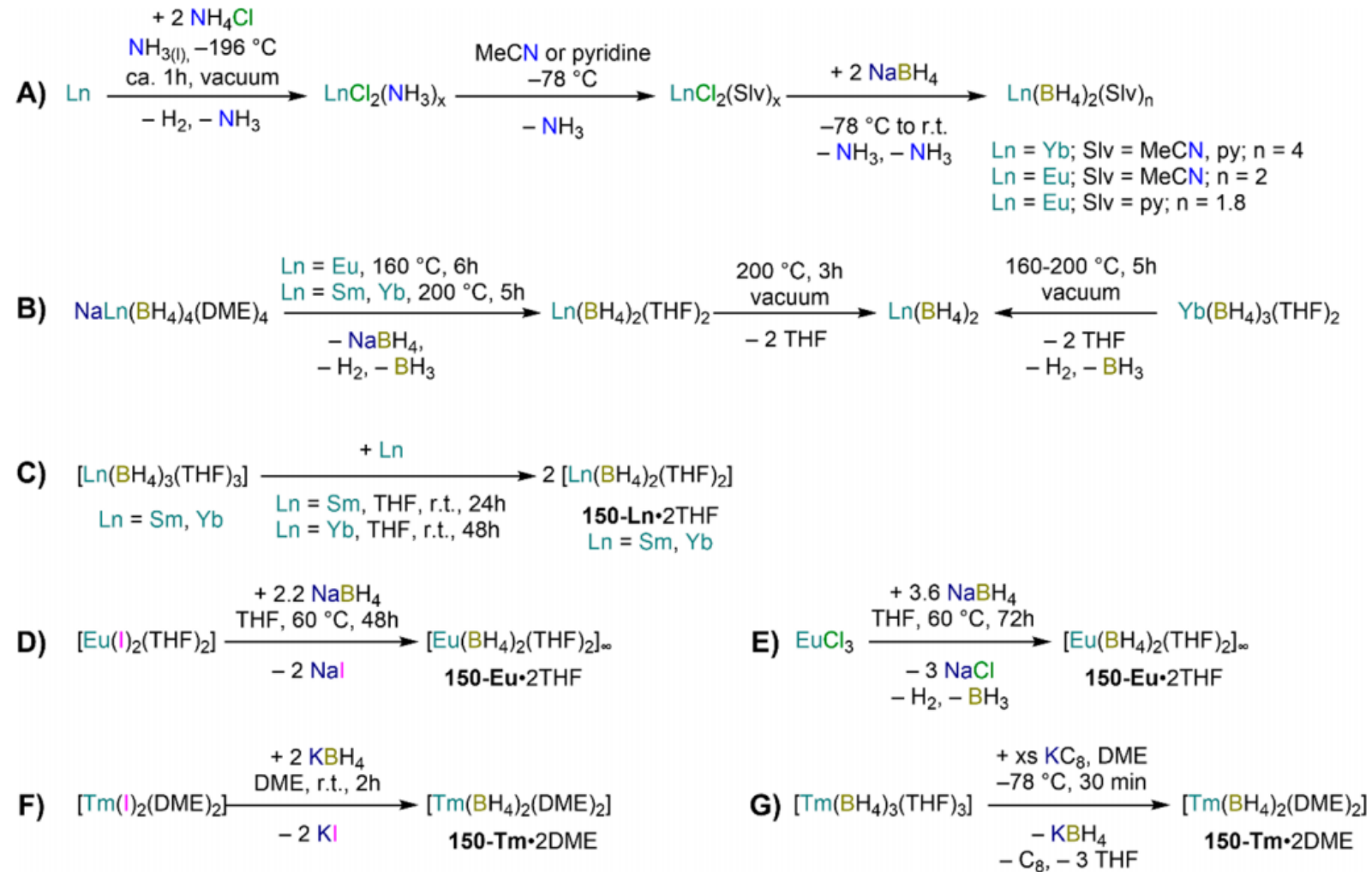


**Figure 8.** Typical binding modes of the borohydride ligand in metal complexes.

# Боргидриды РЗЭ

## Двухвалентные РЗЭ

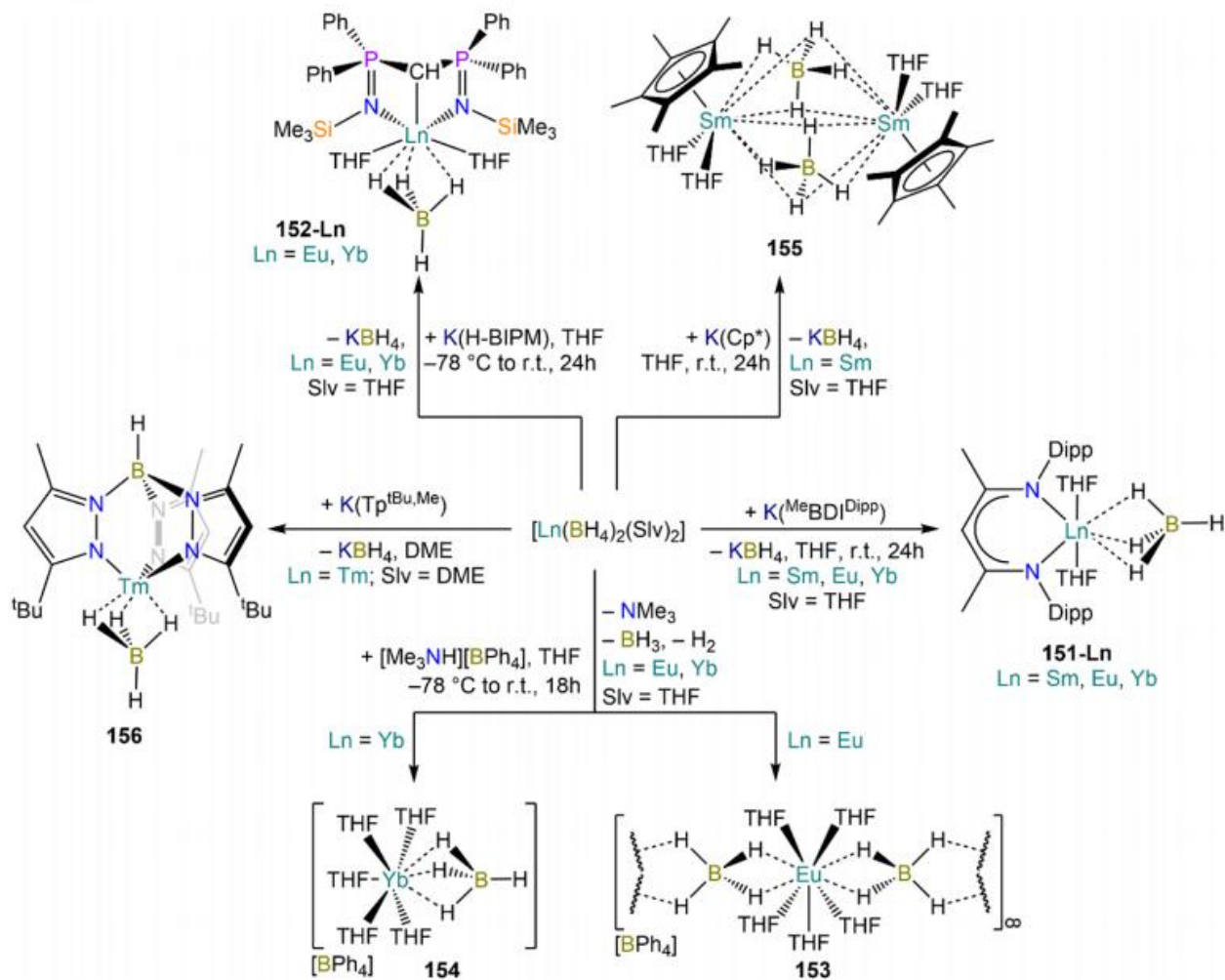
Scheme 47. Synthesis of Divalent Ln(BH<sub>4</sub>)<sub>2</sub> Complexes<sup>19,439–442</sup>



# Боргидриды РЗЭ

## Двухвалентные РЗЭ

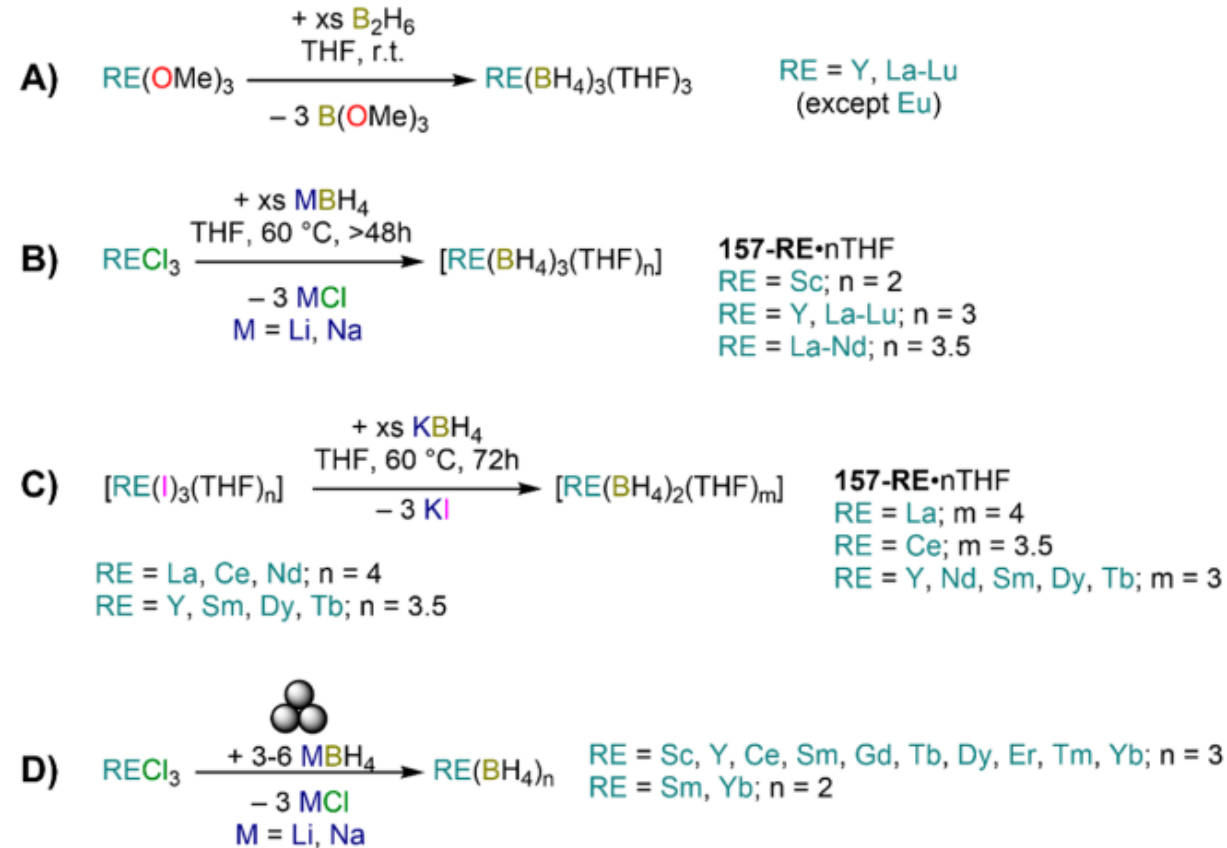
Scheme 48. Selected Applications of  $\text{Ln}(\text{BH}_4)_2$  Starting Materials<sup>441-443,446</sup>



# Боргидриды РЗЭ

## Трехвалентные РЗЭ

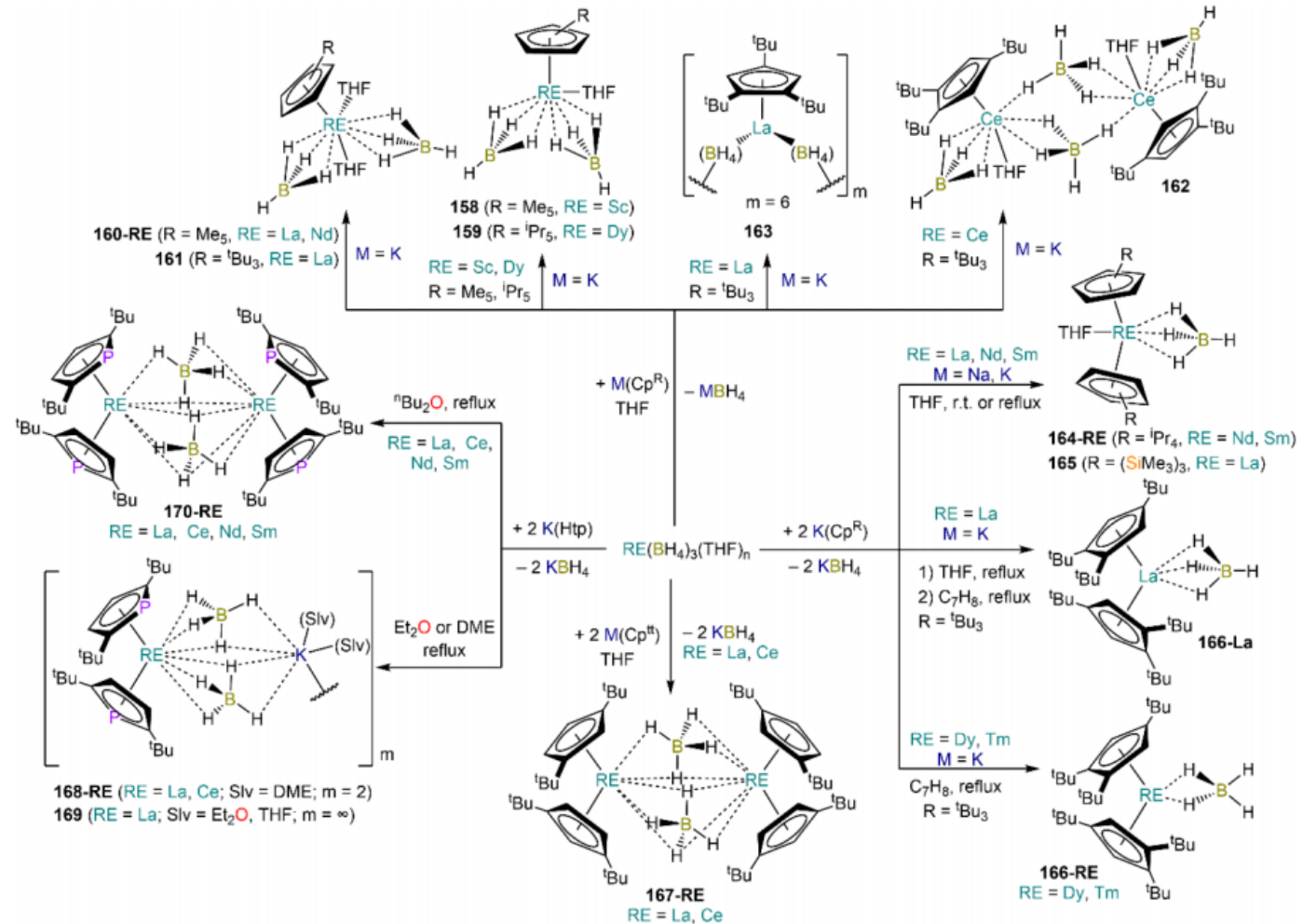
Scheme 49. Synthesis of  $\text{RE}(\text{BH}_4)_3(\text{THF})_n$  Complexes *via* Solution Methods and Synthesis of Solvent-free  $\text{Ln}(\text{BH}_4)_2$  and  $\text{RE}(\text{BH}_4)_3$  *via* Ball-Milling<sup>435–437,443,447,448,451–461</sup>



# Боргидриды РЗЭ

## Трехвалентные РЗЭ

Scheme 50. Selected Examples of Salt Elimination Reactions between  $RE(BH_4)_3$  Reagents and Cyclopentadienyl<sup>435,438,452,465-4</sup> and Phospholyl<sup>437</sup> Ligand Transfer Reagents



# Литература

Информация для доклада была взята из обзора:

Ortu, F. (2022). Rare earth starting materials and methodologies for synthetic chemistry. *Chemical Reviews*, 122(6), 6040-6116.

<https://doi.org/10.1021/acs.chemrev.1c00842>

## CHEMICAL REVIEWS

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Review


### Rare Earth Starting Materials and Methodologies for Synthetic Chemistry

Fabrizio Ortu\*

 Cite This: *Chem. Rev.* 2022, 122, 6040–6116

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**ABSTRACT:** The number of rare earth (RE) starting materials used in synthesis is staggering, ranging from simple binary metal-halide salts to borohydrides and “designer reagents” such as alkyl and organoaluminate complexes. This review collates the most important starting materials used in RE synthetic chemistry, including essential information on their preparations and uses in modern synthetic methodologies. The review is divided by starting material category and supporting ligands (*i.e.*, metals as synthetic precursors, halides, borohydrides, nitrogen donors, oxygen donors, triflates, and organometallic reagents), and in each section relevant synthetic methodologies and applications are discussed.

