

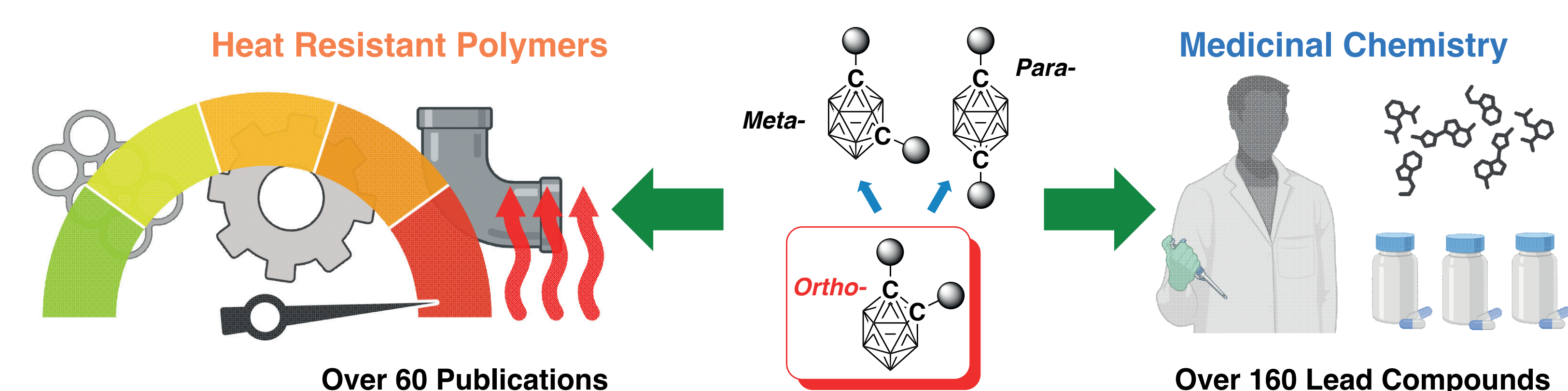
Comparison of synthetic routes to decaborane dianion $[B_{10}H_{10}]^{2-}$ – key precursor for carboranes



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Background of the project

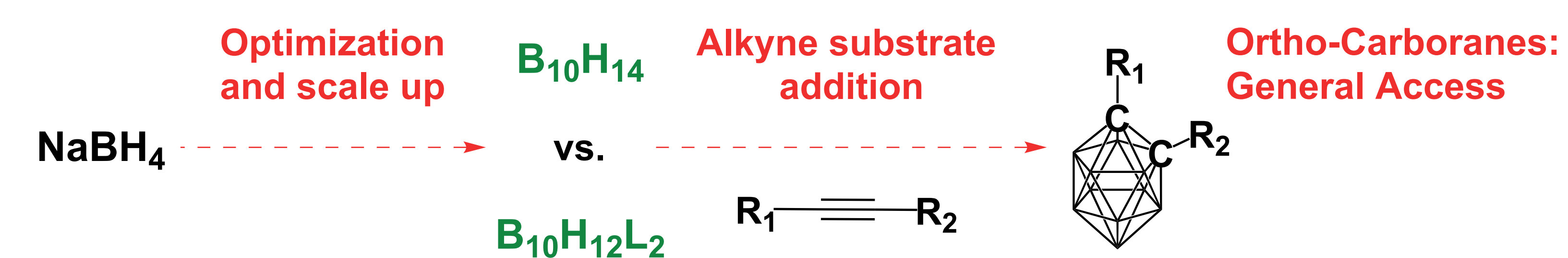
Carboranes ($B_{10}H_{10}C_2RR'$) are valuable for developing **heat-resistant polymers and medicinal chemistry compounds**. The straightforward-accessible “parent” **ortho-carborane core is still not available** both commercially and synthetically on a pilot production scale.



Preliminary Results

We aimed to **find the most reliable precursor to ortho-carboranes** from scalability, preparative potential, and safety perspectives. The traditional approach suggests $B_{10}H_{14}^{[1]}$ (*nido*-decaborane) due to its well-established synthetic pathways and relative availability. However, $B_{10}H_{14}$ presents **challenges such as sensitivity to air and moisture, potential toxicity, and the need for careful handling and storage**. To address these issues, we explored $B_{10}H_{12}L_2^{[2]}$ as an alternative precursor. Our goal was to compare $B_{10}H_{12}L_2$ with $B_{10}H_{14}$ in the formation of *ortho*-carboranes, evaluating its viability and advantages. $B_{10}H_{12}L_2$ was chosen for its **promising stability, lower toxicity, and simpler handling requirements**.

Possible Approaches to Ortho-Carboranes:

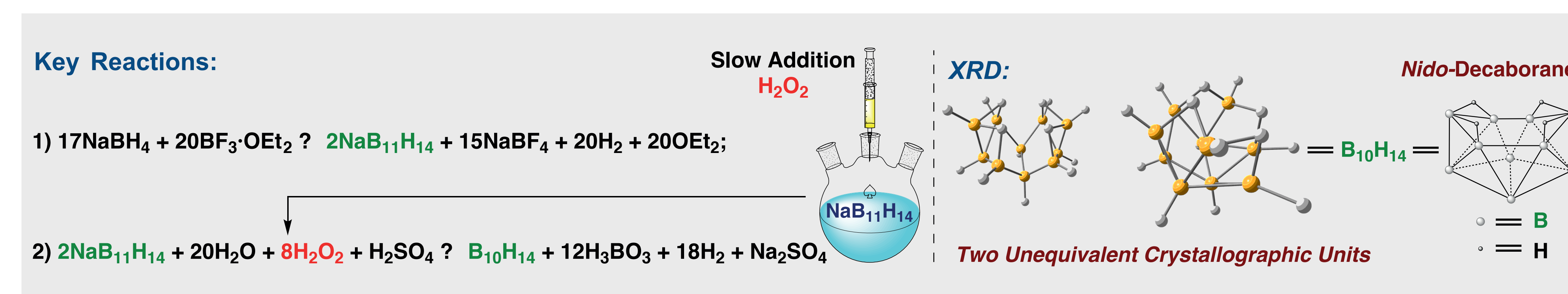


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Preparation and XRD of Key $B_{10}H_{14}$ *Nido*-Decaborane Precursor

We have scaled preparation of $B_{10}H_{14}$ to 20 grams per operation using “slow addition protocol”. The structure was confirmed by XRD.



Synthesis of $B_{10}H_{12}L_2$, - a safe alternative to $B_{10}H_{14}$ via $[B_{10}H_{10}]^{2-}$ intermediate

We focus on the synthesis **decaborane dianion ($[B_{10}H_{10}]^{2-}$)**, a basic precursor to intermediates like $B_{10}H_{12}L_2$. In order to have access to multigram quantities of $B_{10}H_{12}L_2$, we optimized the synthesis of the key $[B_{10}H_{10}]^{2-}$ dianion.

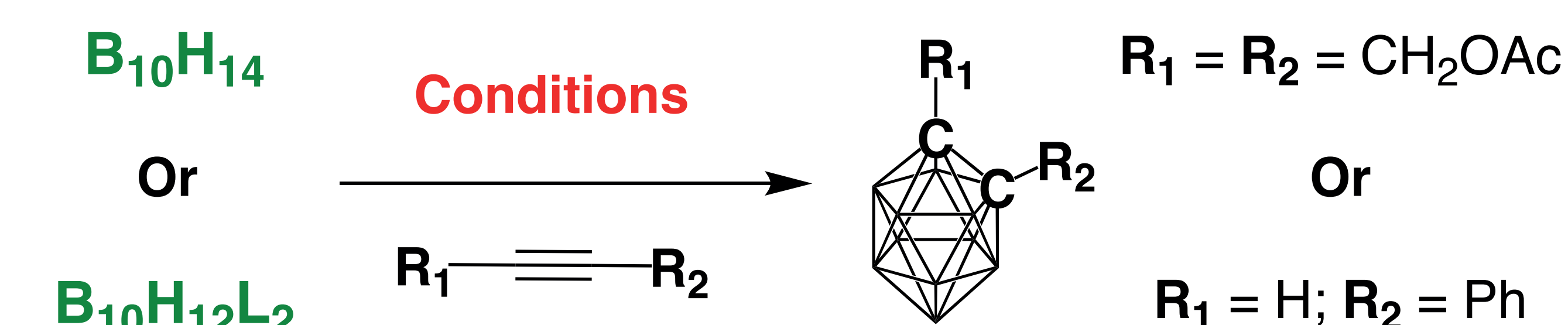
Protocol	Reagents	Et ₄ NBH ₄ (% purity)	Et ₄ NBH ₄ (% yield)
1	Et ₄ NOH + NaBH ₄ (1:2) / NaOH	97,1	66
	Et ₄ NOH + NaBH ₄ (1:2) / KOH	79,0	78
2	Et ₄ NBr + NaBH ₄ (1:1) / NaOH	-	0
	Et ₄ NBr + NaBH ₄ (1:1) / KOH	59,4	61
3	Et ₄ NCl + NaBH ₄ (1:1)	94,7	78

PROTOCOLS:

1. Et₄NOH added with NaBH₄ in NaOH/methanol at r.t. and stirred for 4 h;
2. Et₄NBr added with NaBH₄ in KOH/ethanol at r.t., and stirred for 4 h;
3. Et₄NCl added with NaBH₄ in methanol, at r.t., and stirred for 4 h.

Solvatochromic properties of Imidazo[1,5-a]pyrazin-1-ols

- Both $B_{10}H_{14}$ and $B_{10}H_{12}L_2$ yield desired *ortho*-carboranes;
- **None of the test reactions performed went in accord with literature procedure, further investigation is needed;**
- We were able to isolate analytical quantities of some *ortho*-carboranes of interest.



References:

1. Dunks, G. B., et al., *Inorg. Syntheses* **1984**, 202-207;
2. Muetterties, E. L., et al., *Inorg. Chem.* **2002**, 3 (3), 444-451..