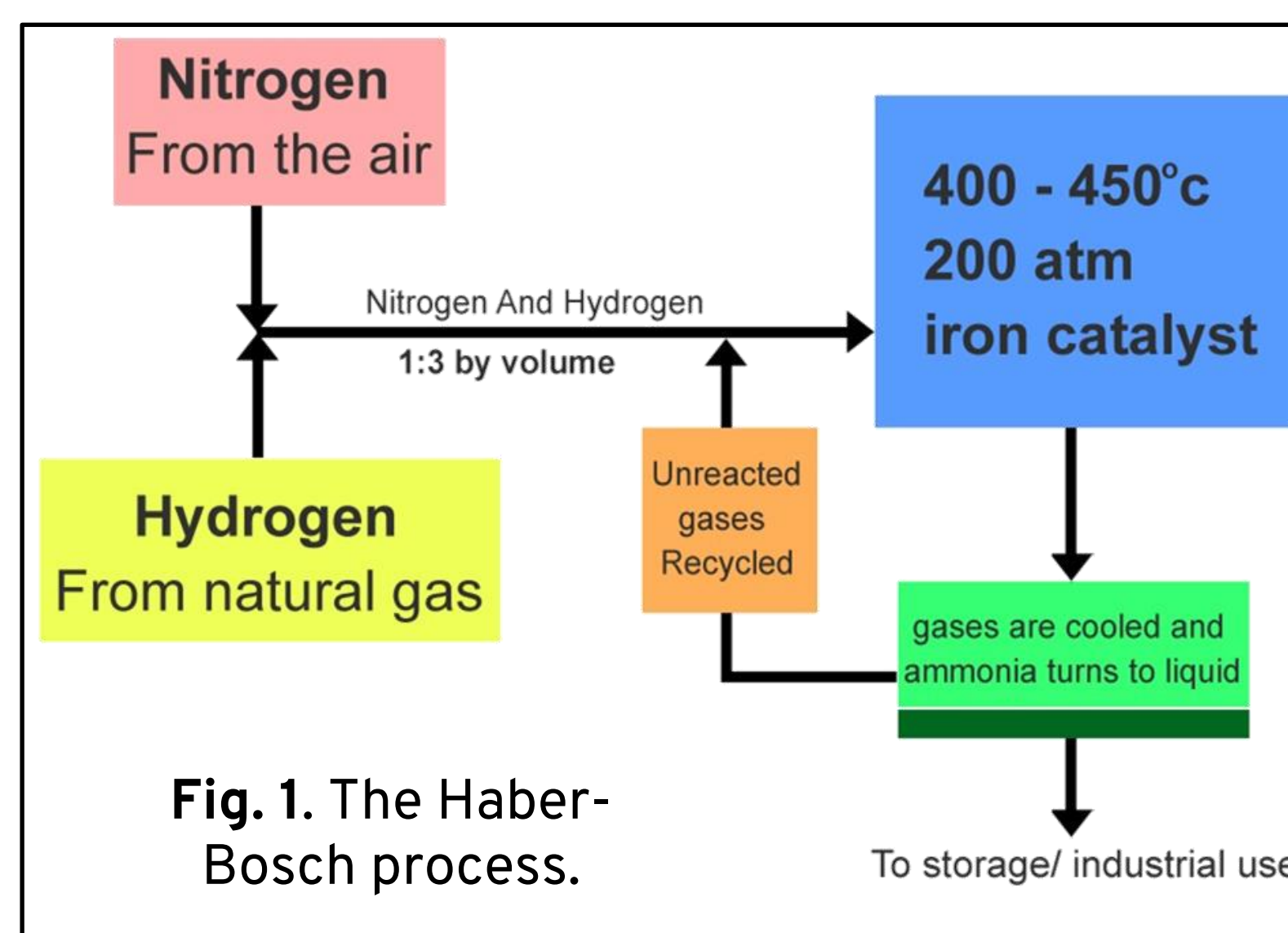


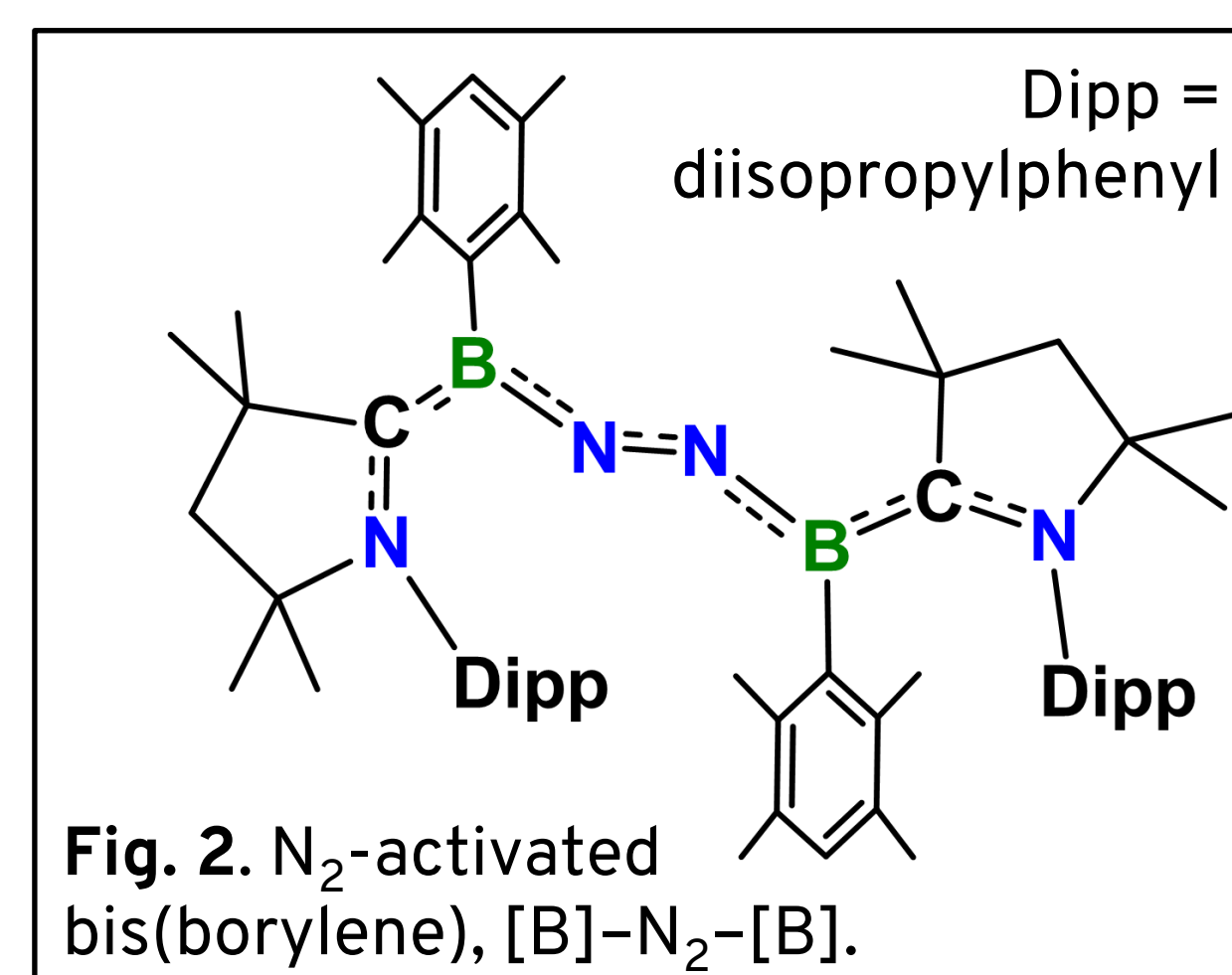
Introduction

- **Haber-Bosch Process:** Vital for NH₃ production from N₂ in agriculture and industry (Fig. 1).
- **Energy-Intensive Process:** High energy consumption and reliance on fossil fuels.
- **Greenhouse Gas Emissions:** Significant contribution to emissions, particularly CO₂.
- **High Temperatures and Pressures:** Further intensify energy use and carbon footprint.
- **Call for Sustainable Alternatives:** Urgent need to find greener methods for N₂ capture and NH₃ production.



Goals and Methods

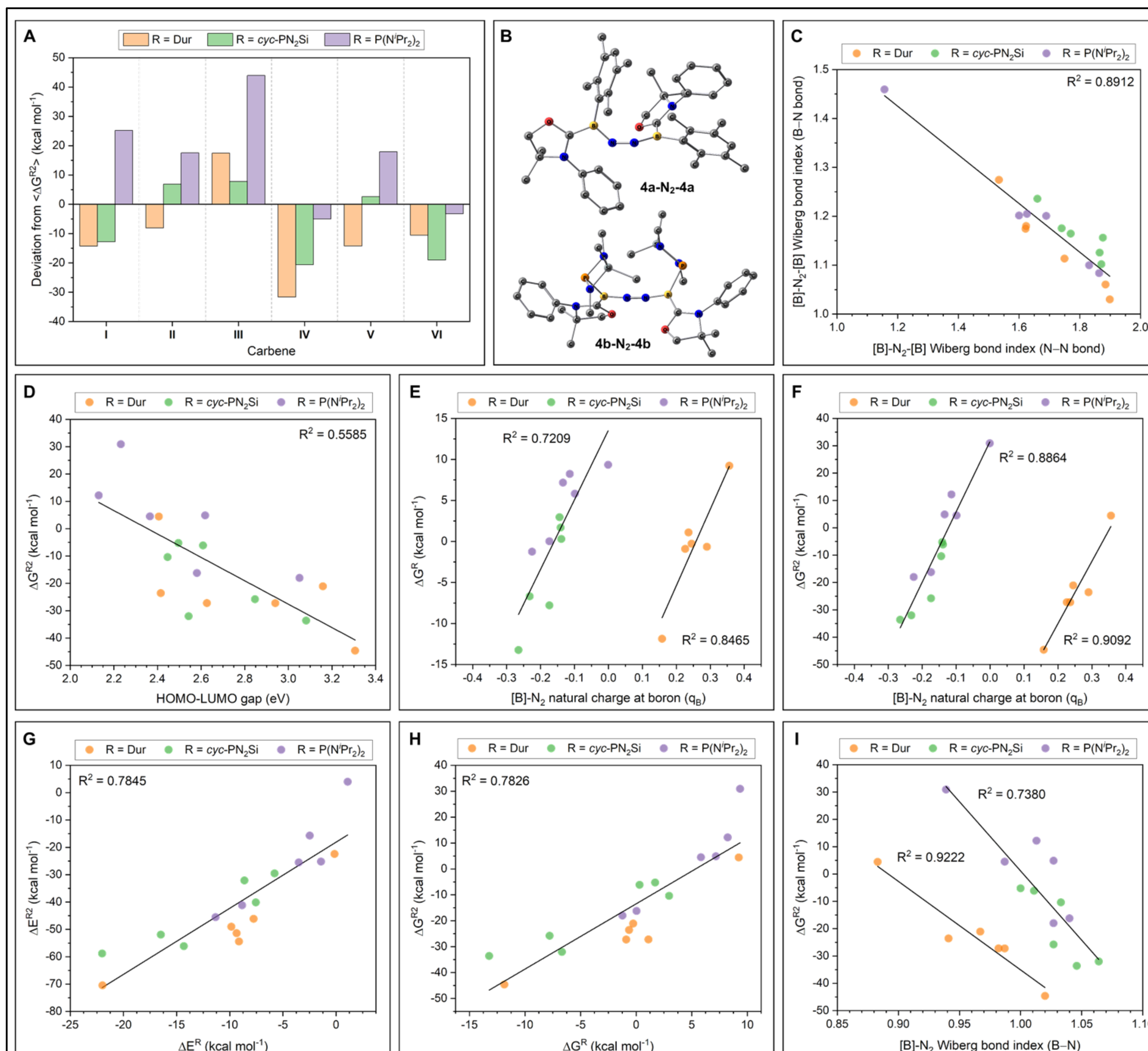
- **Goal:** Use computational chemistry to craft boron-based systems capable of potentially activating N₂ at room temperature and catalysing its reduction to NH₃.
- **Reasons for Boron:** Widely distributed main group element in both Earth's crust and in the ocean. Entry to Group 13 chemistry and transition-metal-free chemistry. Borylenes of the form [LBR] (Fig. 2) have demonstrated reactivity toward N₂.
- **Computational Methods:** Geometries + frequencies: M06-D3/def2-SVP. Single-point energies: ωB97XD/def2-TZVP. Implicit solvents (benzene) with PCM. Concentration correction included for ΔG. Natural population analyses with NBO. [B]–N₂ bonding situation with EDA-NOCV.
- **EDA-NOCV decomposition scheme:** $\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp}$



Results and Discussion (Chem. Eur. J. 2022, 28, e2021041 – HOT PAPER)

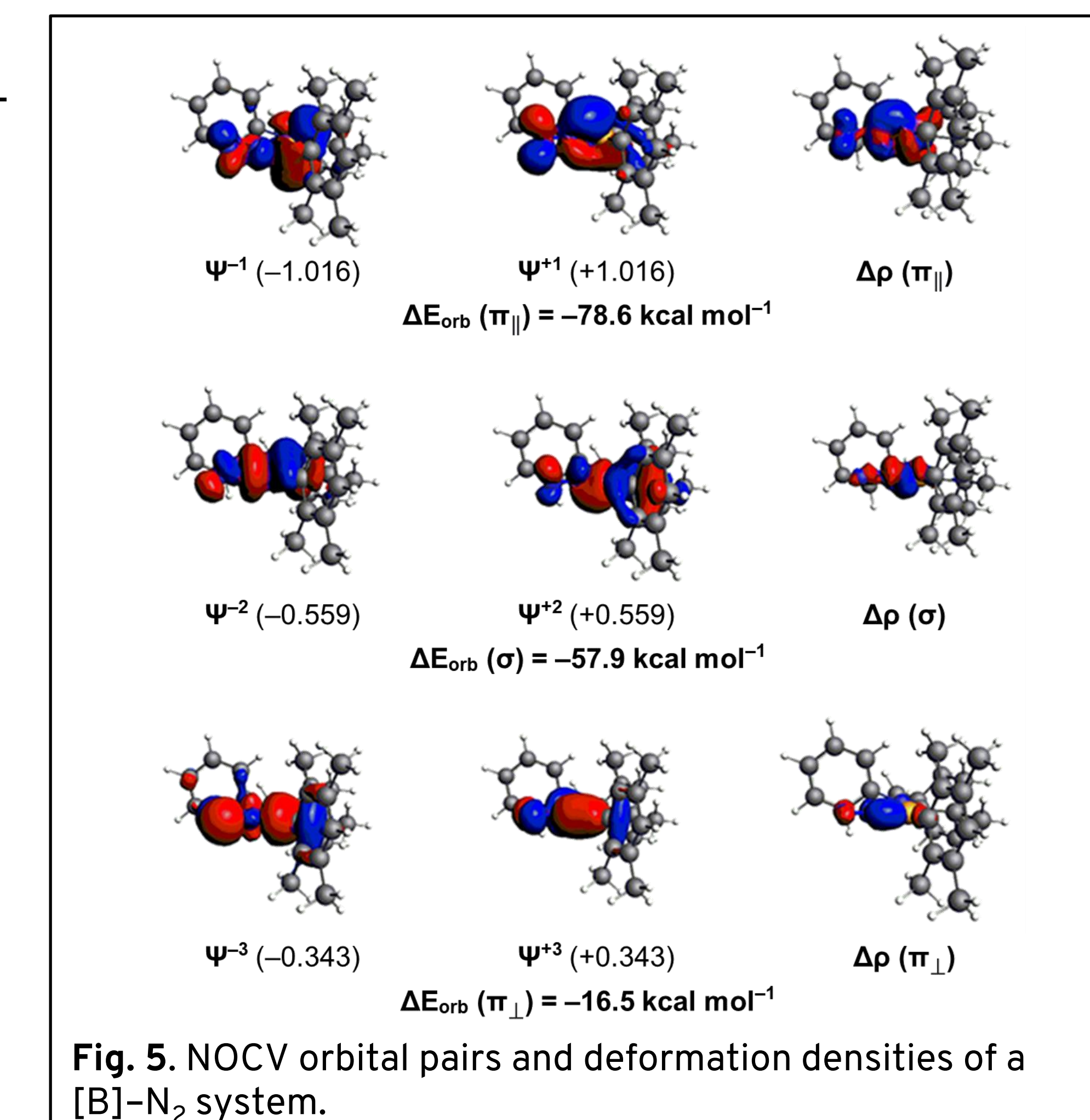
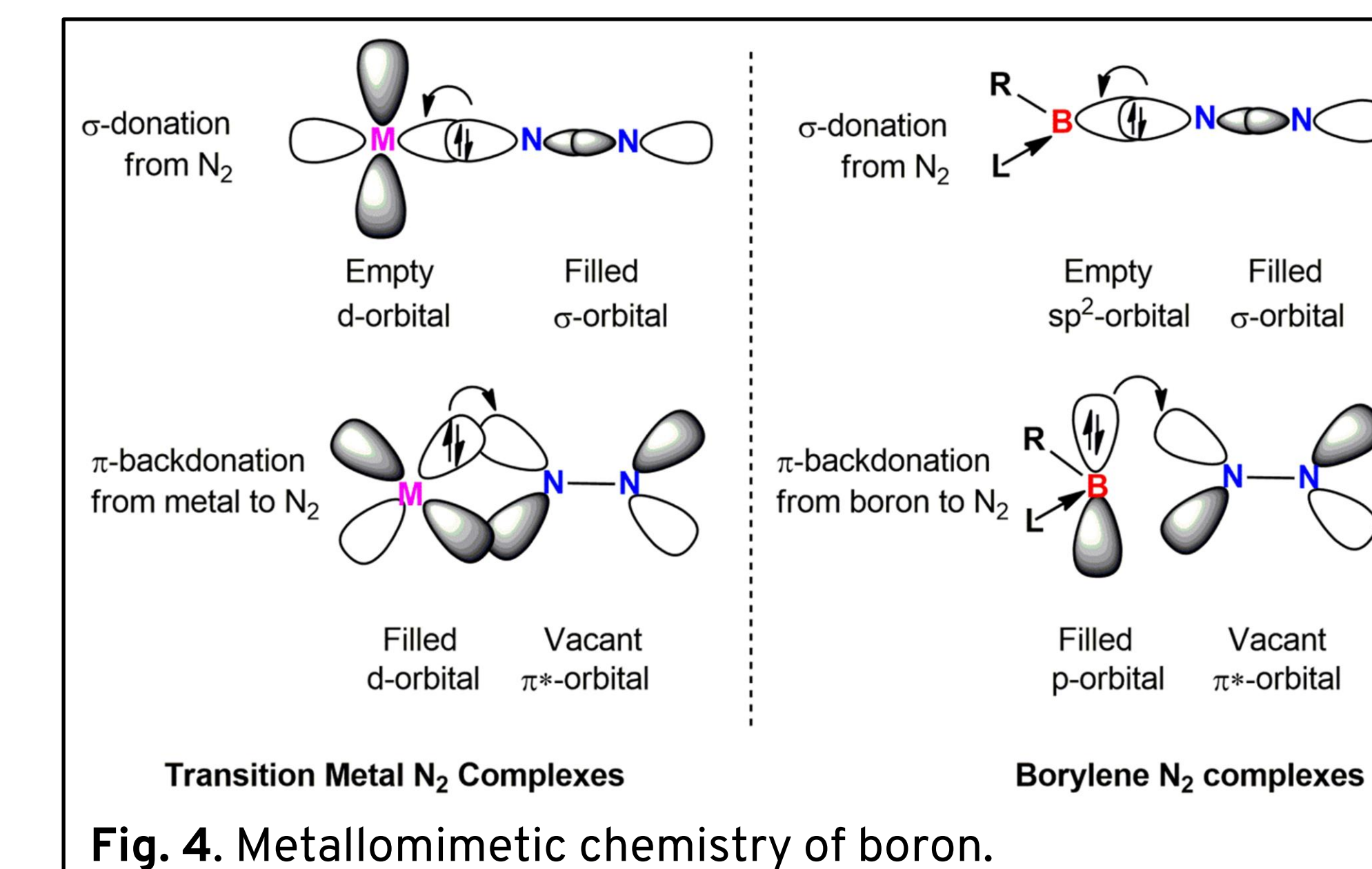
A – Energy and geometrical correlations

- **No single geometrical property** can account for the energy profile of the distinct [B]–N₂ systems.
- **Strong linear correlations** are found between ΔG and the [B]–N₂ natural charge at boron, indicating the more negative the natural charge, the larger the exergonicity.



B – EDA-NOCV bonding situation

- The interaction between a dicoordinate borylene fragment of the form [LBR] and N₂ in a hypothetical complex of the form [LRB(N₂)], or [B]–N₂, can be envisioned to be similar to that in transition metal dinitrogen complexes (i.e., [L_nM–N₂], Fig. 4).
- EDA-NOCV analysis explored bonding in B–N₂ complexes (Fig. 5).
- All complexes exhibited substantial ΔE_{int} values.
- ΔE_{elstat} contributed 35%-43%, while ΔE_{orb} was the major contributor (57%-64%).
- ΔE_{orb} revealed [B]→N₂ π-backdonation dominance, with in-plane π component (π_{||}) being the major contributor (32%-54%).
- σ-donation played a minor role (17.8%-50%).
- Phosphorus-substituted borylenes had higher Pauli repulsion, balanced by electrostatic and orbital interactions, with added benefit from dispersion interactions.
- The studied [B]–N₂ complexes further benefit from a non-negligible contribution from dispersion interactions (ΔE_{disp}).



Acknowledgements

Conclusion

The strategic **tuning** of the **natural charge at boron** opens up possibilities for the **design** of novel borylenes capable of **dinitrogen activation** and fixation, representing a critical initial step towards **catalytic ammonia production** involving main group elements.