

Computational Design of Strong Organic Hydride Donors



Mario Damjanović and Borislav Kovačević

mario.damjanovic@irb.hr

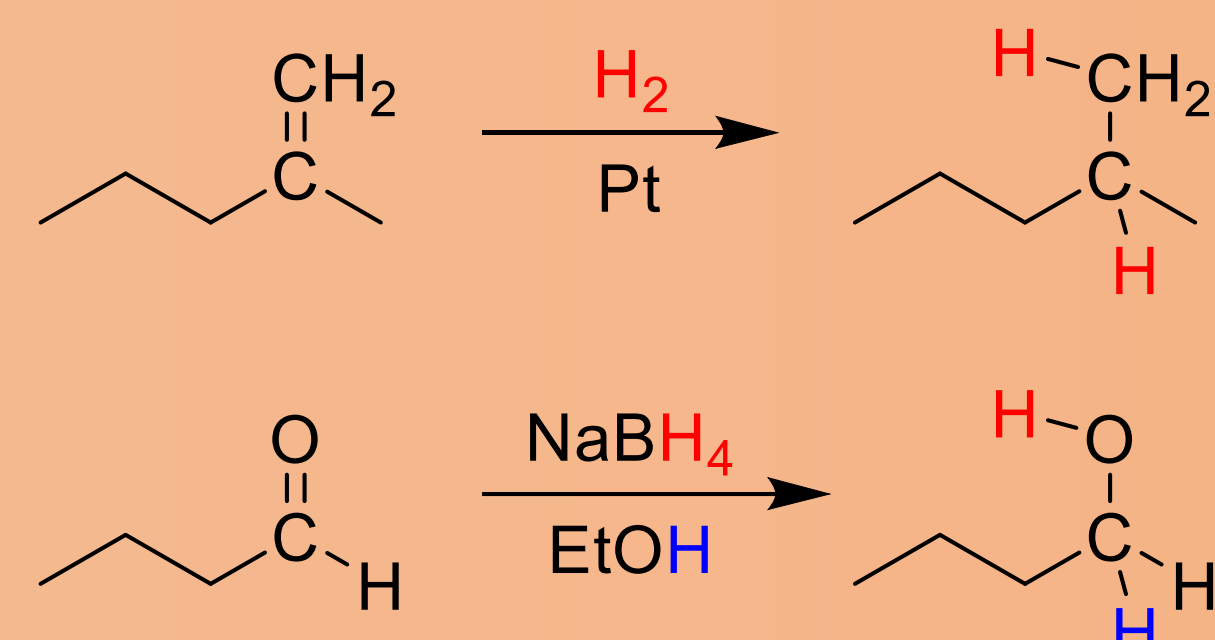
Division of Physical Chemistry, Ruđer Bošković Institute, Zagreb, Croatia



Hydride Donors

Hydride transfer drives:

- Reactions in synthetic chemistry
- Biological redox processes
- Reduction reactions



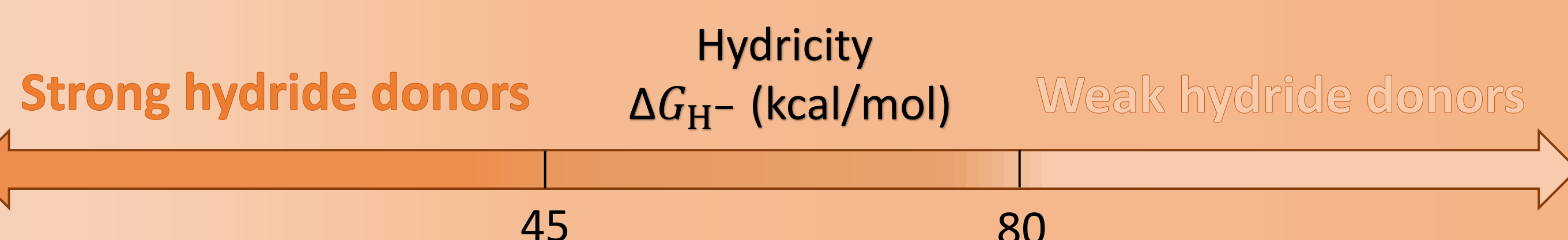
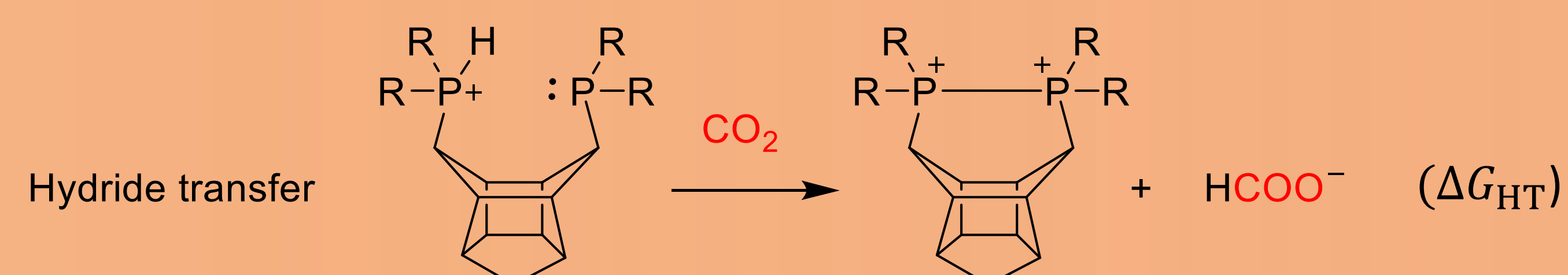
Due to the high cost, scarcity and lack of selectivity of metal hydrides used so far, there is a need for the design of metal-free hydride donors.

Thermodynamic Hydricity

Hydride donor strength is expressed in terms of thermodynamic hydricity, defined as the Gibbs energy change of the reaction:

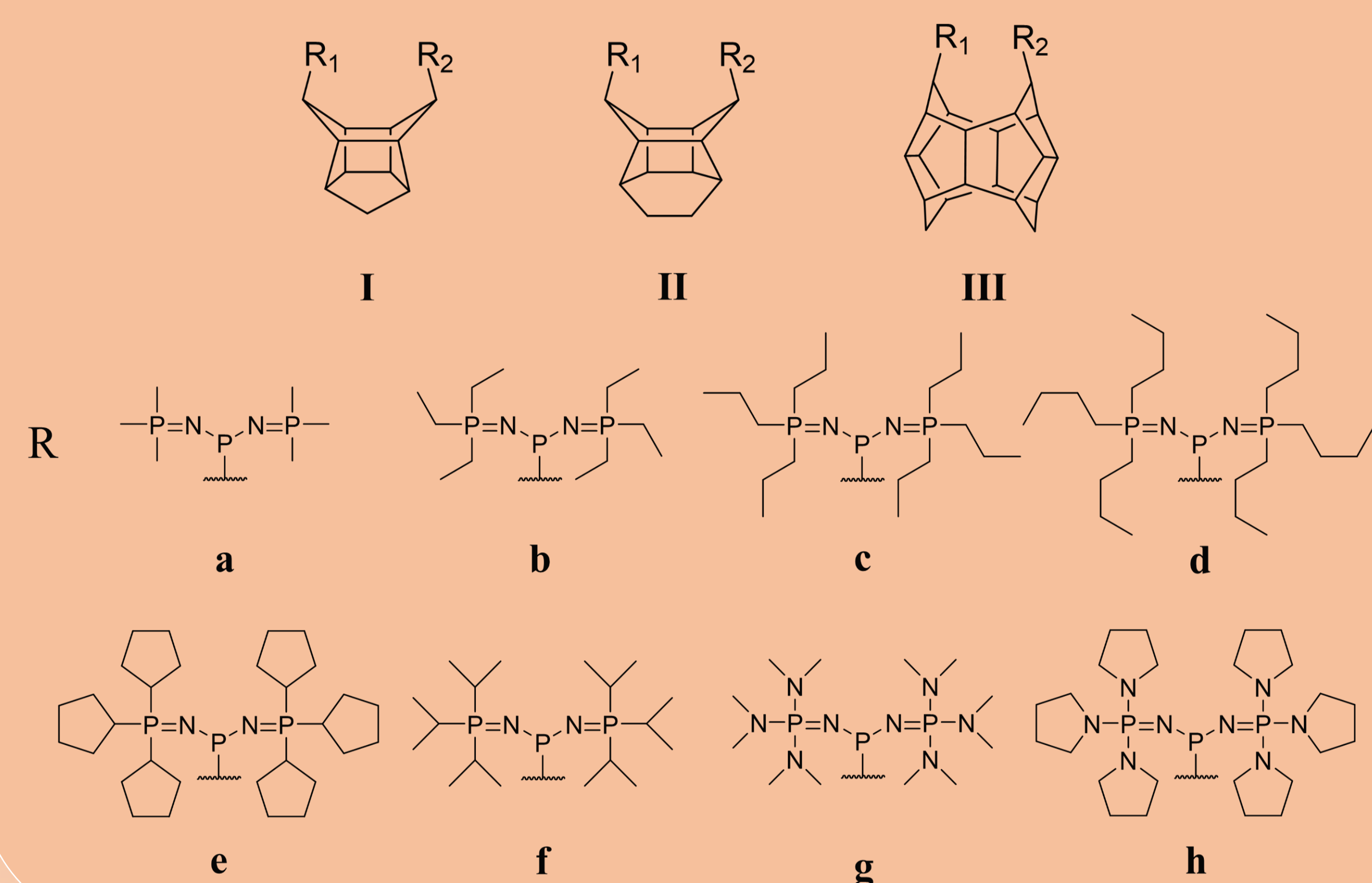


Hydricity, ΔG_{H^-} , was determined using DFT by modeling hydride transfer from the molecule of interest to CO_2 in acetonitrile:

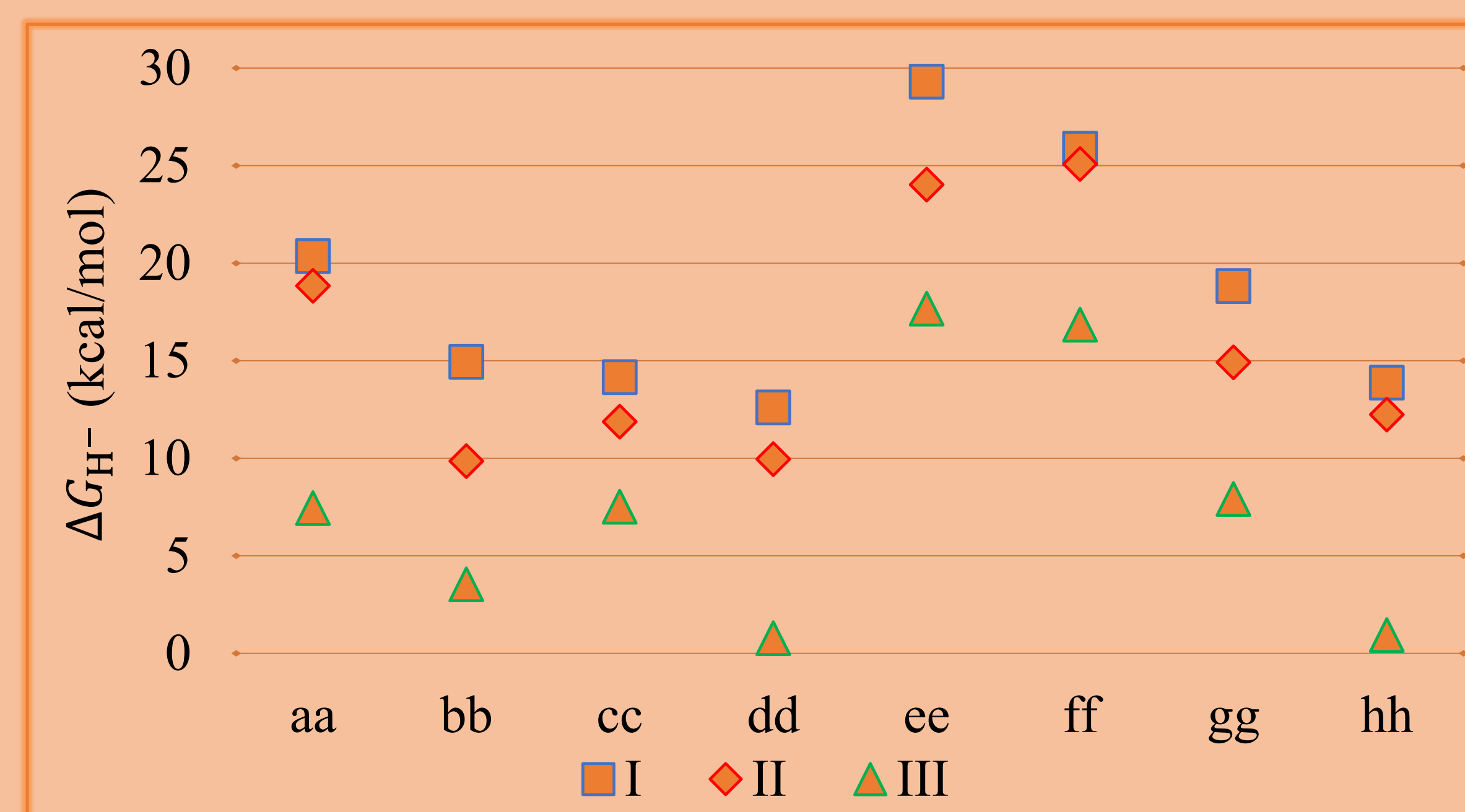


Hydricity of Proton-sponge-like Bisphosphines

By introducing phosphazanyl phosphine groups to an aliphatic scaffold, compounds resembling proton sponges were designed.

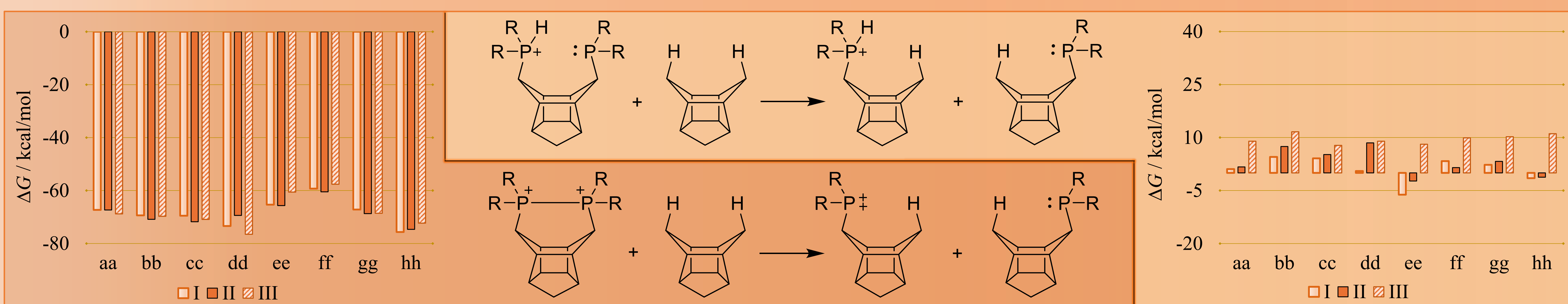


- Most of designed compounds have lower hydricity than superhydride LiEt_3BH ($\Delta G_{\text{H}^-} = 25 \text{ kcal/mol}$).
- They are significantly stronger hydride donors than triphosphazanyl phosphines, whose hydricity values are in the range of 70 to 100 kcal/mol [1,2].



The large difference in hydricity is attributed to the formation of a dative P-P bond, which stabilizes the resulting dication. Based on homodesmic reactions, this stabilization was calculated to be about 70 kcal/mol.

In the protonated form, a P-P bond cannot form to provide stabilization; instead, slight destabilization (0-10 kcal/mol) occurs due to steric hindrance.



Computational Details

- Conformational search was performed using the CREST software
- Best conformers were reoptimized in order to locate the lowest-energy minimum at the DFT level
- Frequency analysis and geometry optimizations were performed at (PCM) ω B97XD/6-311++G(d,p) level of theory in acetonitrile as solvent
- Single-point energies were calculated in acetonitrile at the (PCM) ω B97XD/6-31G(d,p) level of theory.

Conclusion

- Proton-sponge-like bisphosphines are very strong hydride donors
- P-P bond stabilization significantly enhances hydricity
- Strong electron donating groups stabilize dication

References:

- [1] D. Barić, M. Damjanović, Z. Glasovac, I. Despotović, and B. Kovačević, *Chemical Communications*, 62 (2026) 4833–4837
 [2] M. Damjanović, B. Kovačević, *Molecules*, submitted for publication.

This work has been fully supported by the Croatian Science Foundation under the project [IP-2024-05-7730]