

Eppur si muove! And yet it moves! Study of the intermolecular dynamic behaviour of multidentate ferrocenyl phosphines and their corresponding d^{10} metal complexes in solution

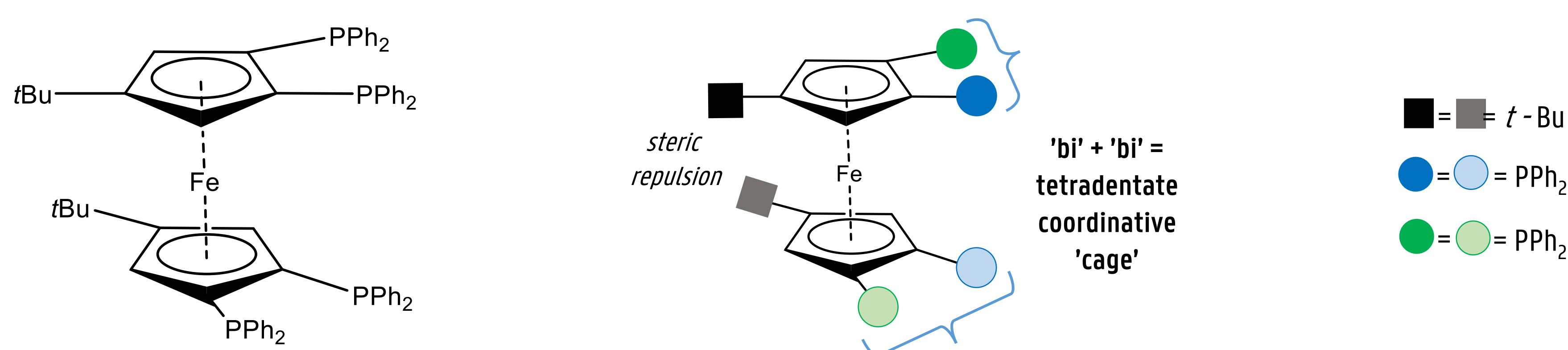
César A. Urbina Blanco¹, Andrés R. León Garzón¹, Benjamin Kovács², José Martins², Jean-Cyrille Hierso³, Mark Saeys¹, Titus van Erp⁴ and Sander Roet⁴

CesarAlejandro.UrbinaBlanco@UGent.be, Mark.Saeys@UGent.be

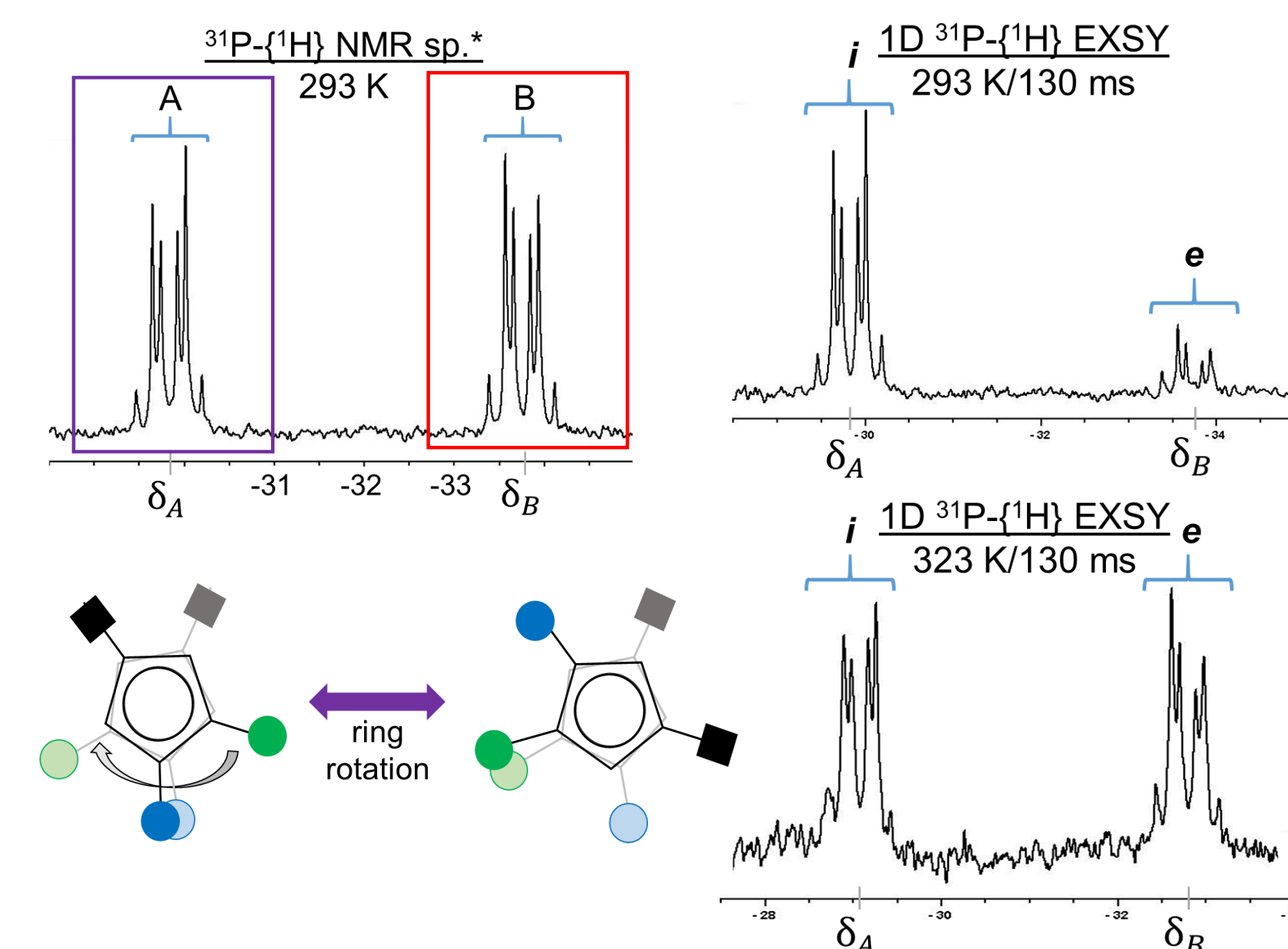
¹ Laboratory For Chemical Technology, Ghent University, Ghent, Belgium; ² NMR and Structure Analysis Research unit, Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium; ³ Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Université de Bourgogne, Dijon, France; ⁴ Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway.

Introduction: multidentate ferrocenyl phosphines

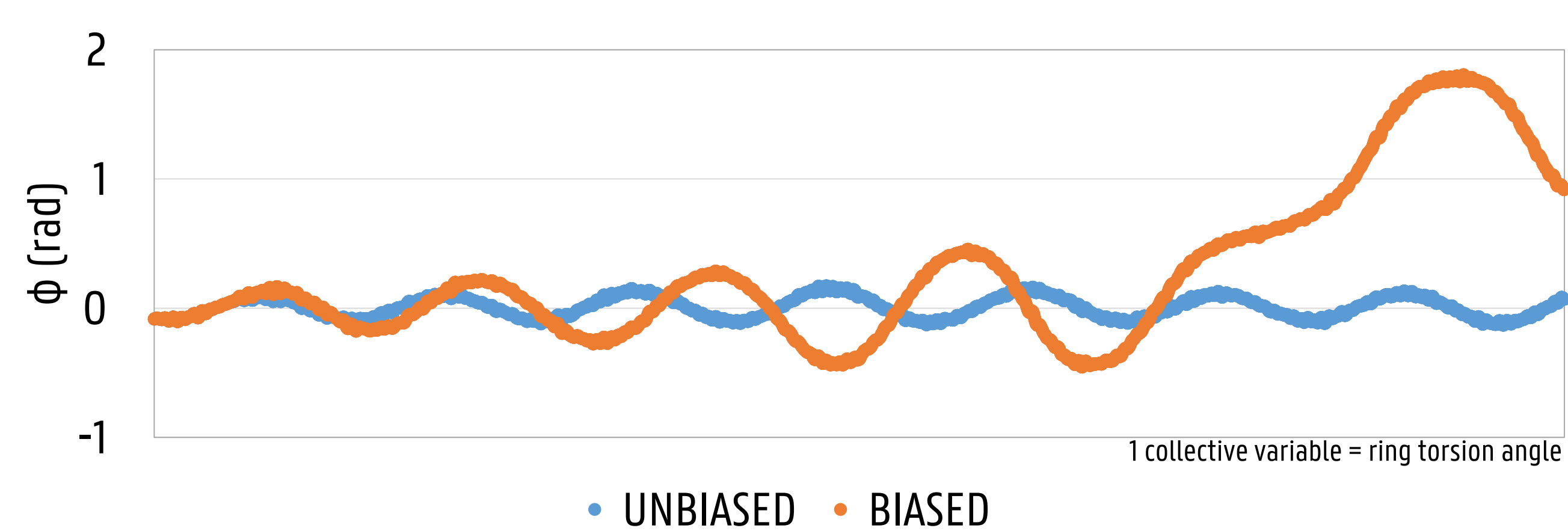
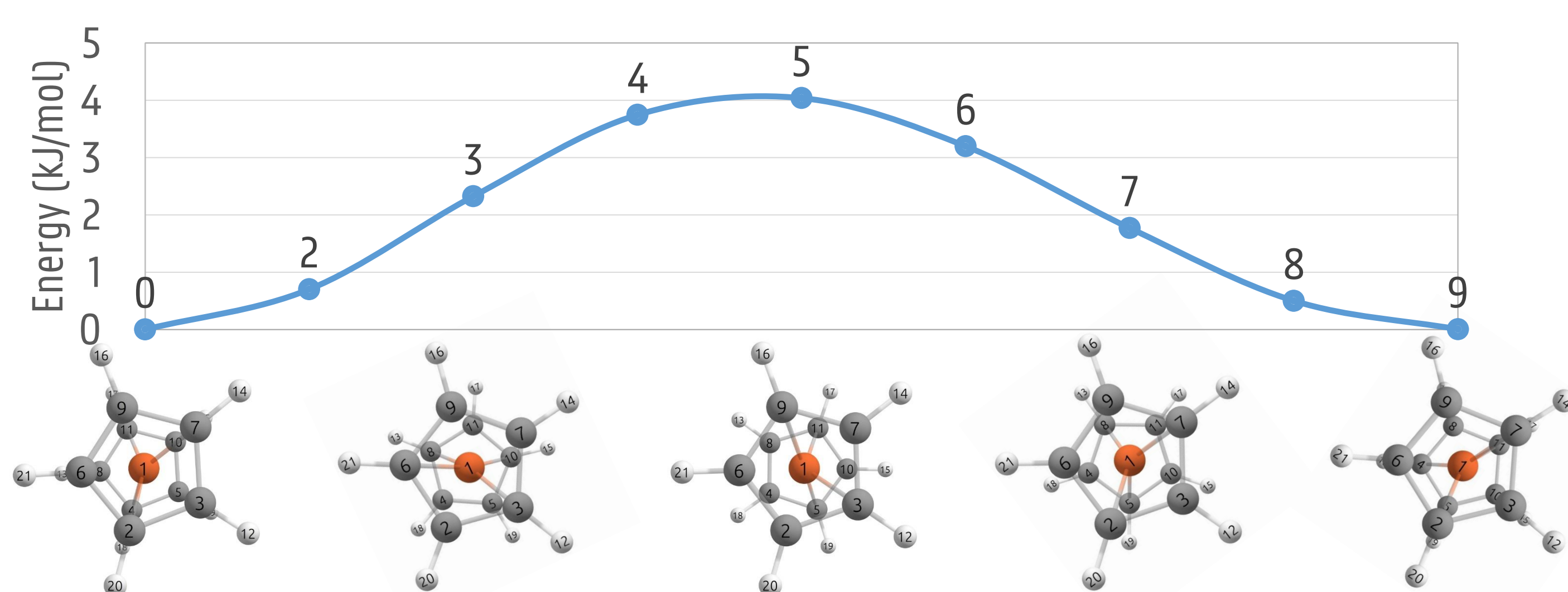
- Multidentate ferrocenyl phosphines offers multiple coordinative sites for a $\equiv P$: lone electron pair acceptor.
- The Cp rings are typically equipped with bulky substituents \rightarrow the antiparallel ring rotation (twisting) is hindered \rightarrow a permanent coordinative 'cage' is formed consisted of multiple coordinative sites
- Application:** molecular cluster, nanoparticle, surface stabilizers/activators [1], and common ligands in transition metal catalyzed Suzuki cross-coupling reactions [2]



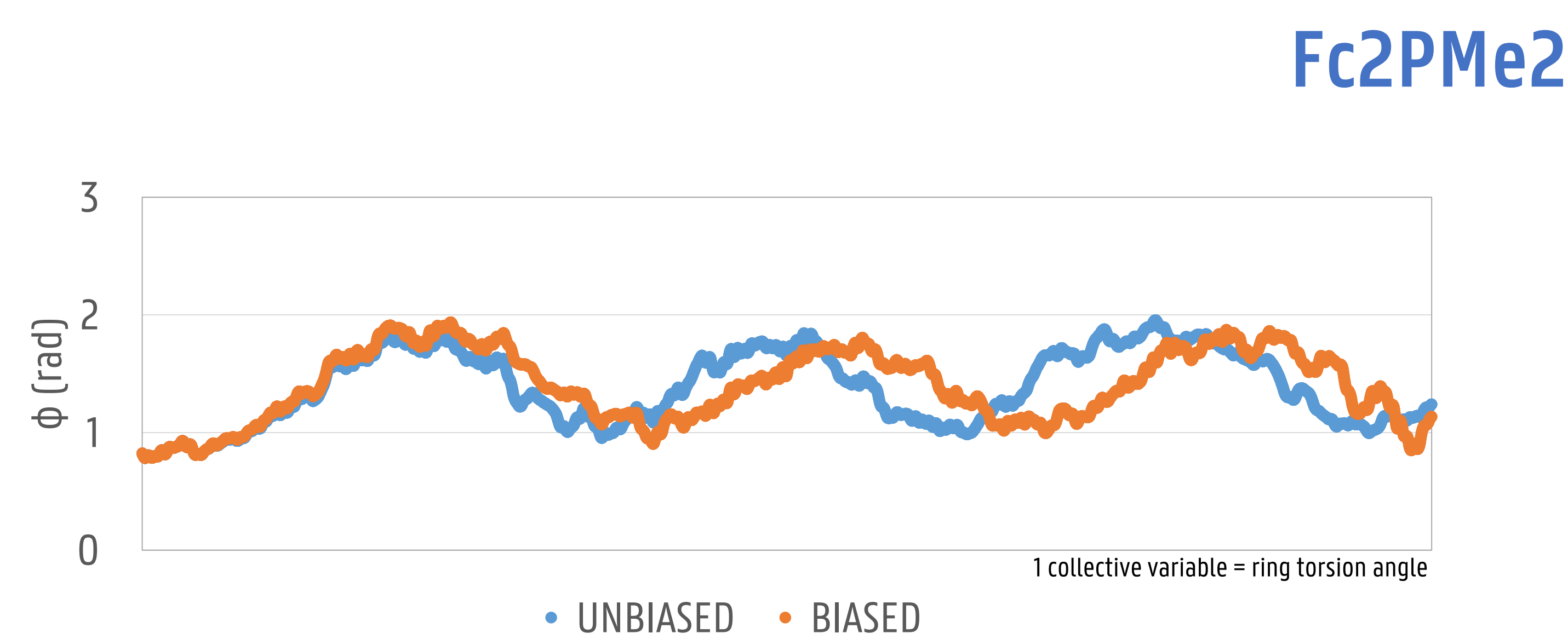
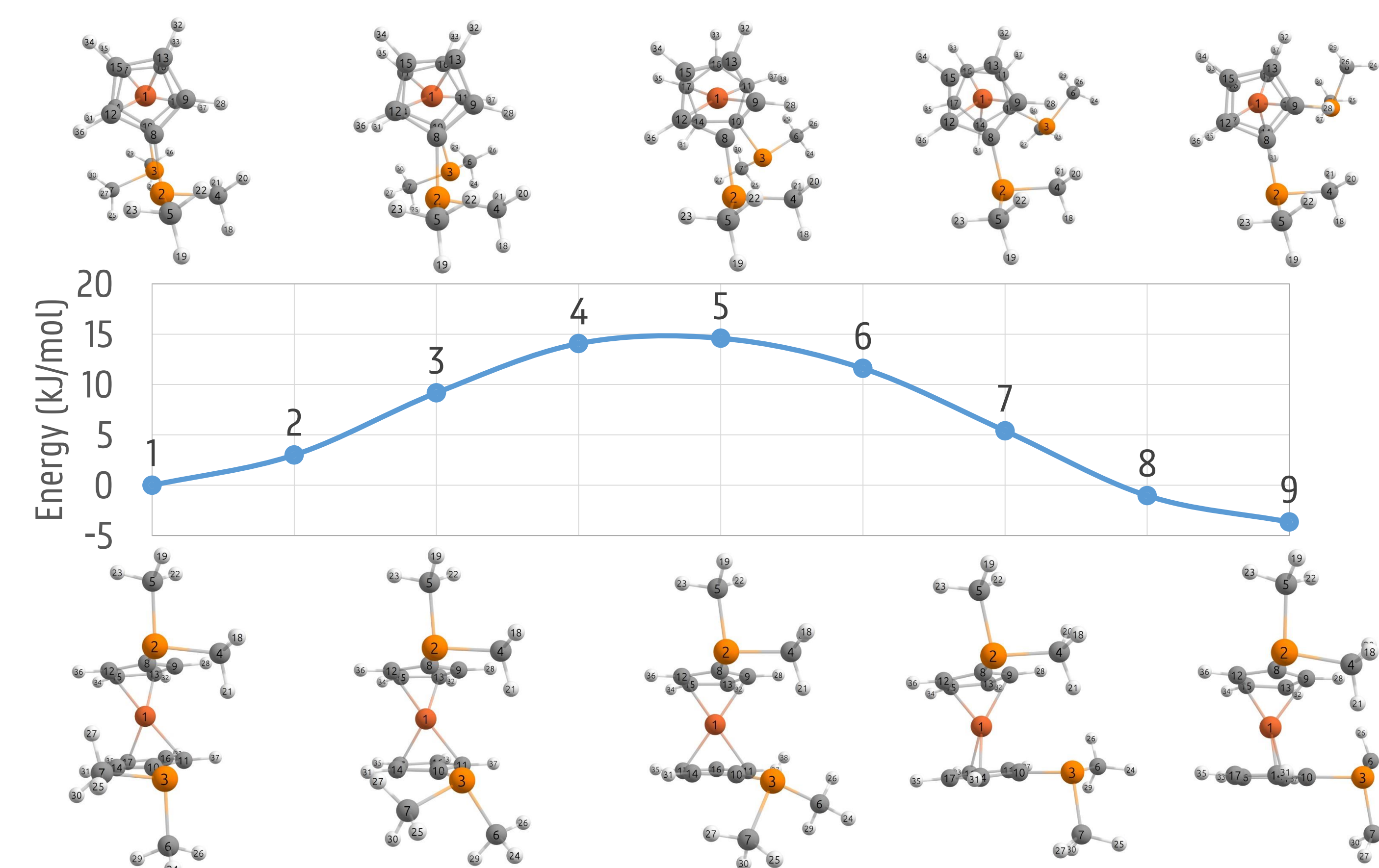
Experimental Evidence: Understanding the NMR



Our Modelling Approach (Ongoing): Statics (NEB) & Dynamics (Metadynamics)



The rotational barrier (≈ 4 kJ/mol) agrees quite well with literature [3]. The low barrier allows the molecule to rotate freely at room temperatures. The present bias allows the rotation of the ring in dynamic simulations.



The barrier is almost fourfold higher in the presence of 2-methylphosphine ligands according to static calculations. One of the phosphines rotates in the NEB simulation. The small bias is not able to make a rotation in the metadynamics simulation.

NEB

- CP2K
- PBE + Grimme's DFT-D3
- DZVP basis set

MD

- CP2K + Plumed
- PBE + Grimme's DFT-D3
- DZVP basis set
- Nosé-Hoover Thermostat @ 300 K
- dt = 0.5 fs
- Bias: Height 0.25 kJ/mol; Width = 0.035 rad

References

[1] Zhang, S., Leem, G. *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 113-120 [2] Hierso, J.-C., Fihri, A. *et al.*, *Organometallics*, 2003, **22**, 4490-4499 [3] House, J. E. (2012). *Inorganic Chemistry*, Elsevier Science.

Future Work

- Systematic inclusion of further ligand substitutes to the ferrocene structure for both static and dynamic simulations.
- Tweaking of the metadynamic simulation parameters to enhance the rotation of the ferrocene structures with ligand substitutes.
- Inclusion of additional collective variables to account for the rotation of the phosphine ligands in the dynamic simulations.