

THE INTRAMOLECULAR DYNAMICS OF A 'RIGID YET TWISTY' FERROCENYL

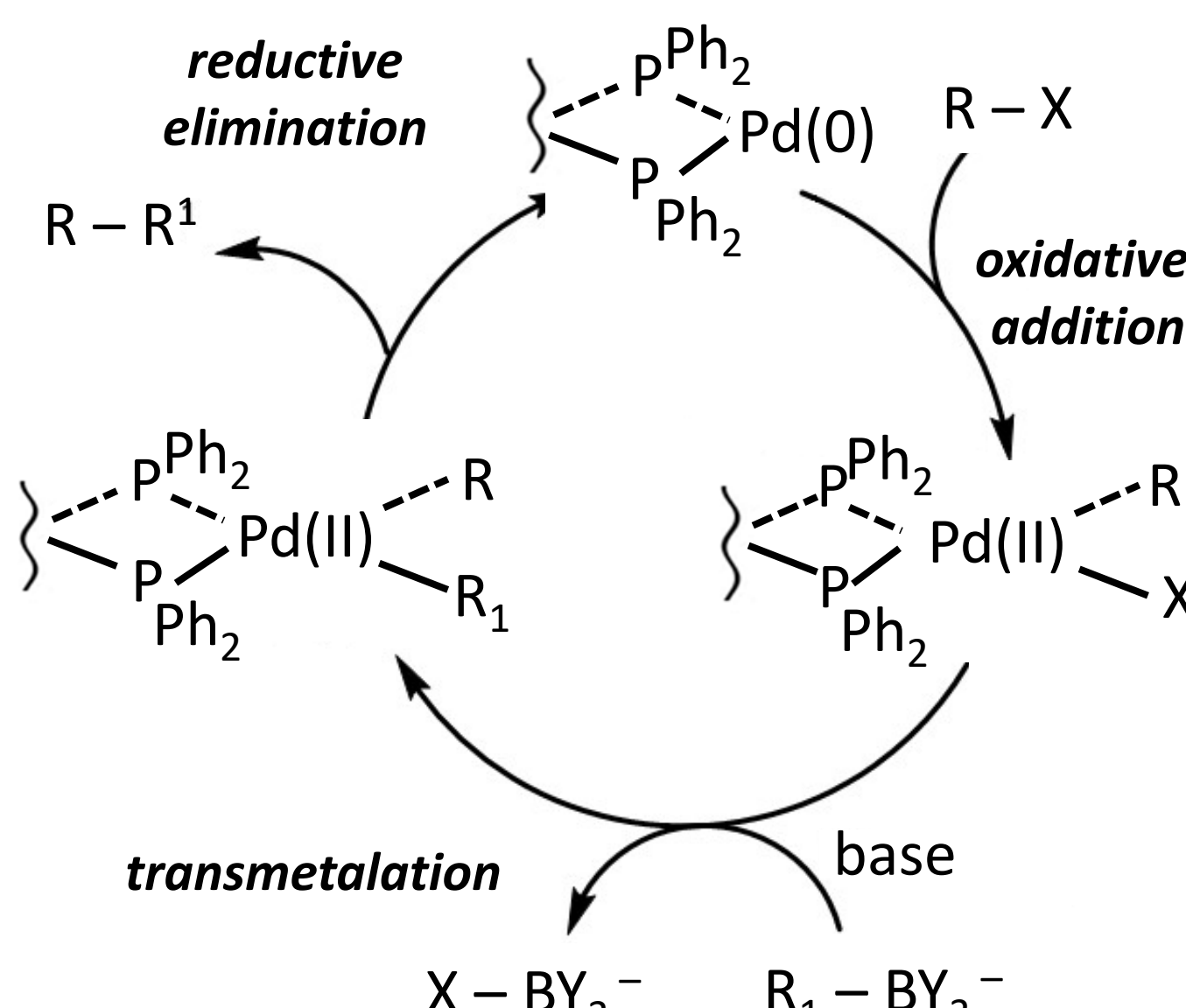
TETRAPHOSPHINE – SERVED WITH SOME ³¹P-NMR DELICACY

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Introduction: multidentate ferrocenyl phosphines

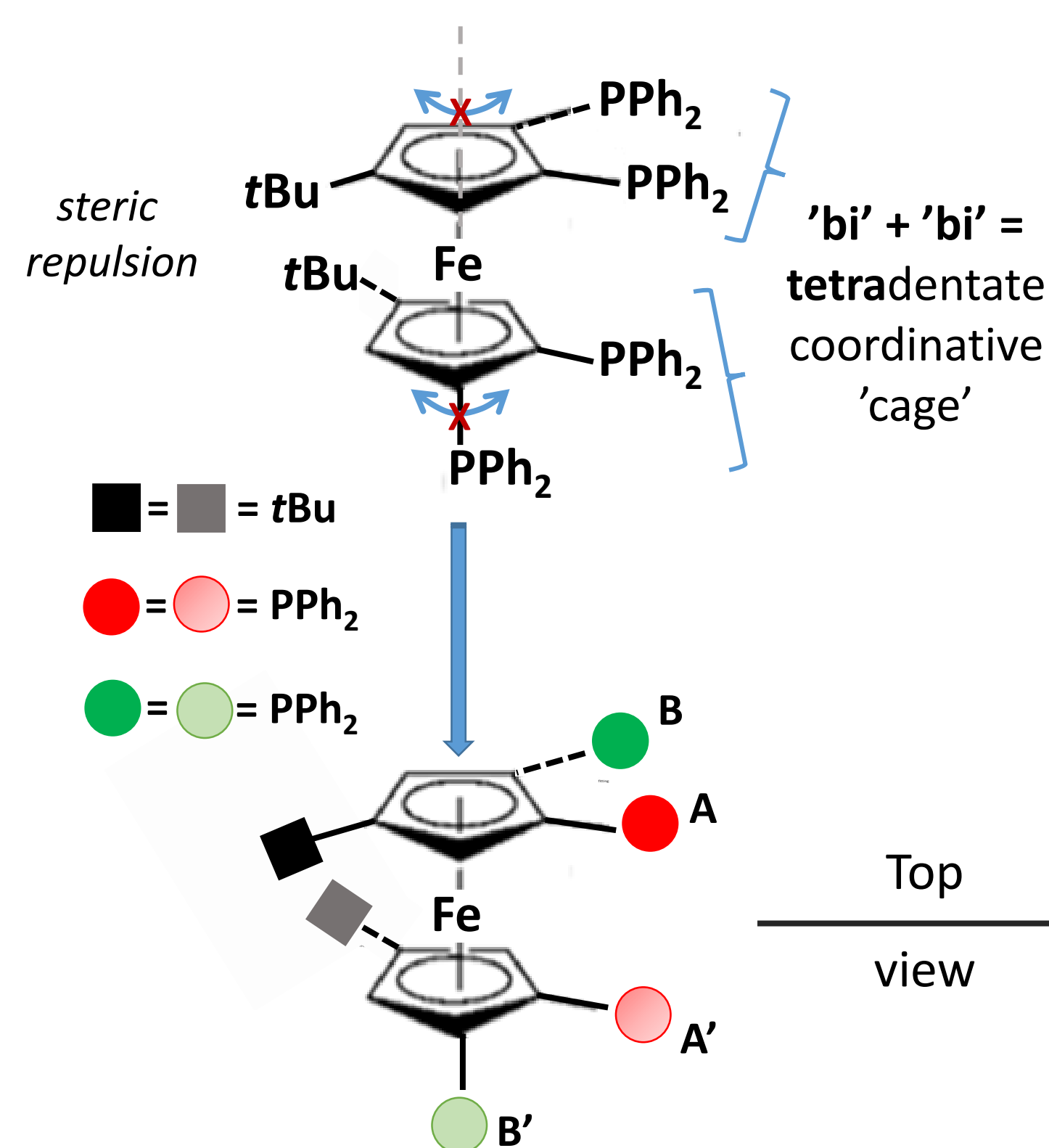
- Multidentate ferrocenyl phosphines offers multiple coordinative sites for a $\equiv P$: lone electron pair acceptor
- The Cp rings are typically equipped with bulky substituents \rightarrow the antiparallel ring rotation (twisting) is hindered \rightarrow a permanent coordinative 'cage' is formed consisted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



Reminder on Suzuki cross-couplings

- Metal center is solubilized before *oxidative addition* by the phosphine
- Bulkiness of the ligand facilitates the *reductive elimination* step
- Multiple coordinative sites provide longer catalytic lifetime and higher efficiency

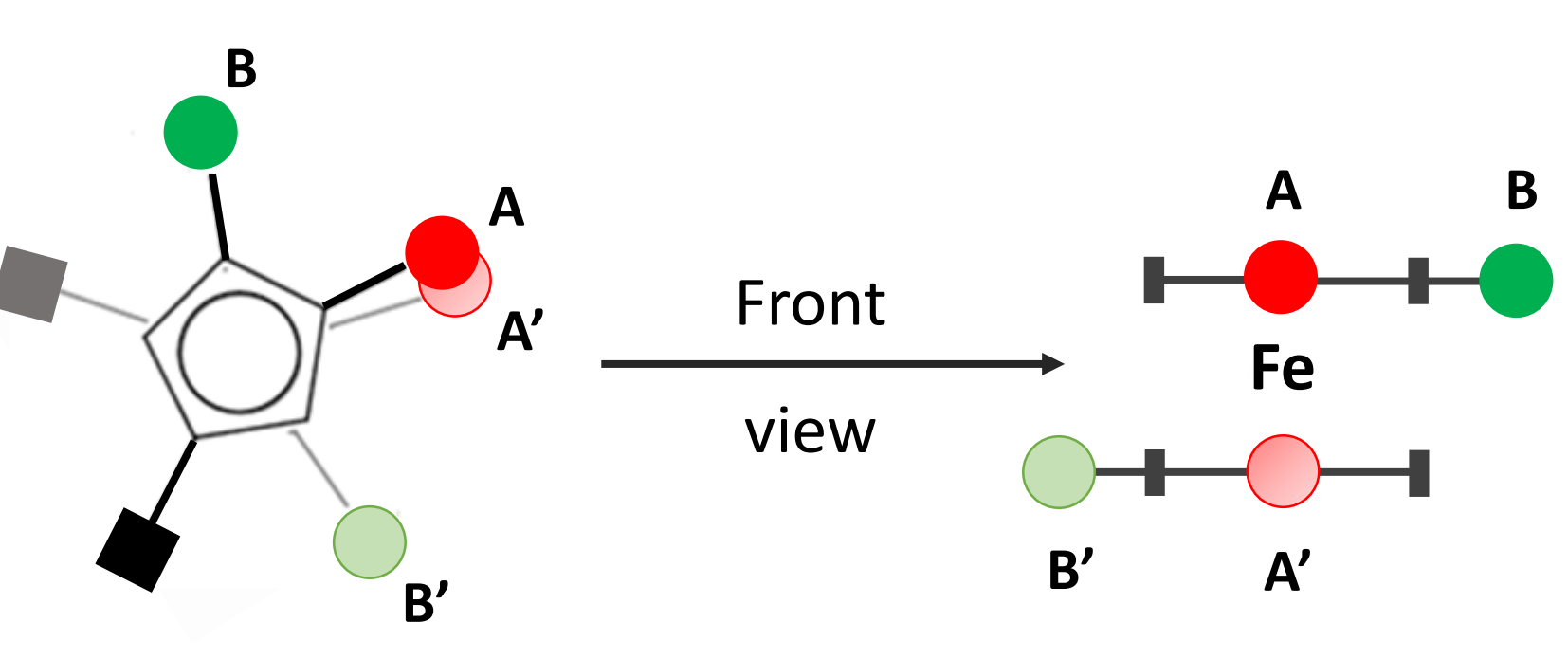
Investigated molecule: Fc(P)₄tBu



Objectives: hindered motions to reveal

- Conception of 'static, rigid' conformation (see left) to be refined
- Hindered antiparallel Cp rotations to characterize – both in a qualitative and quantitative fashion
- Sufficiently long time scale is needed ... \rightarrow

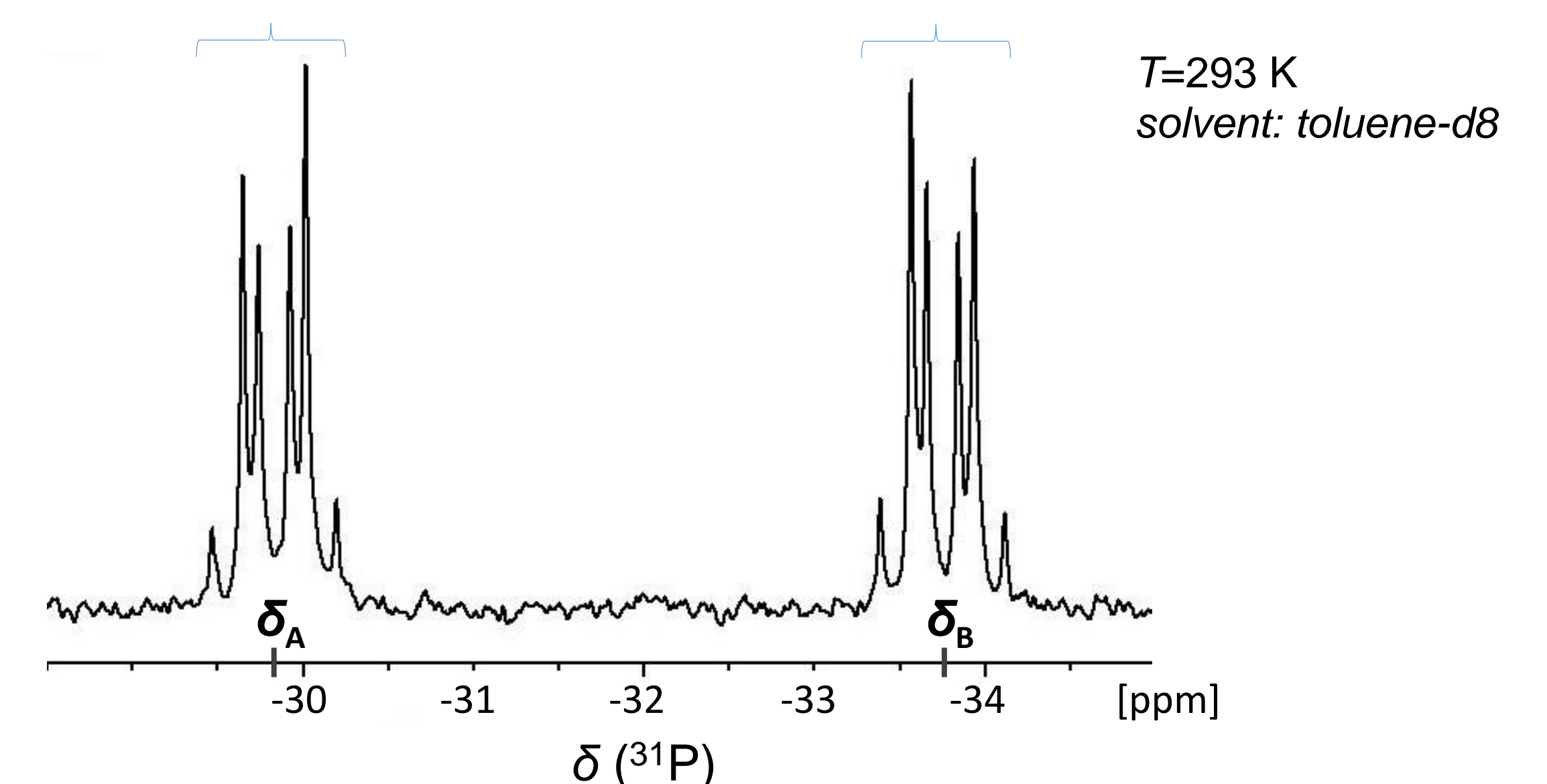
NMR spectroscopy!



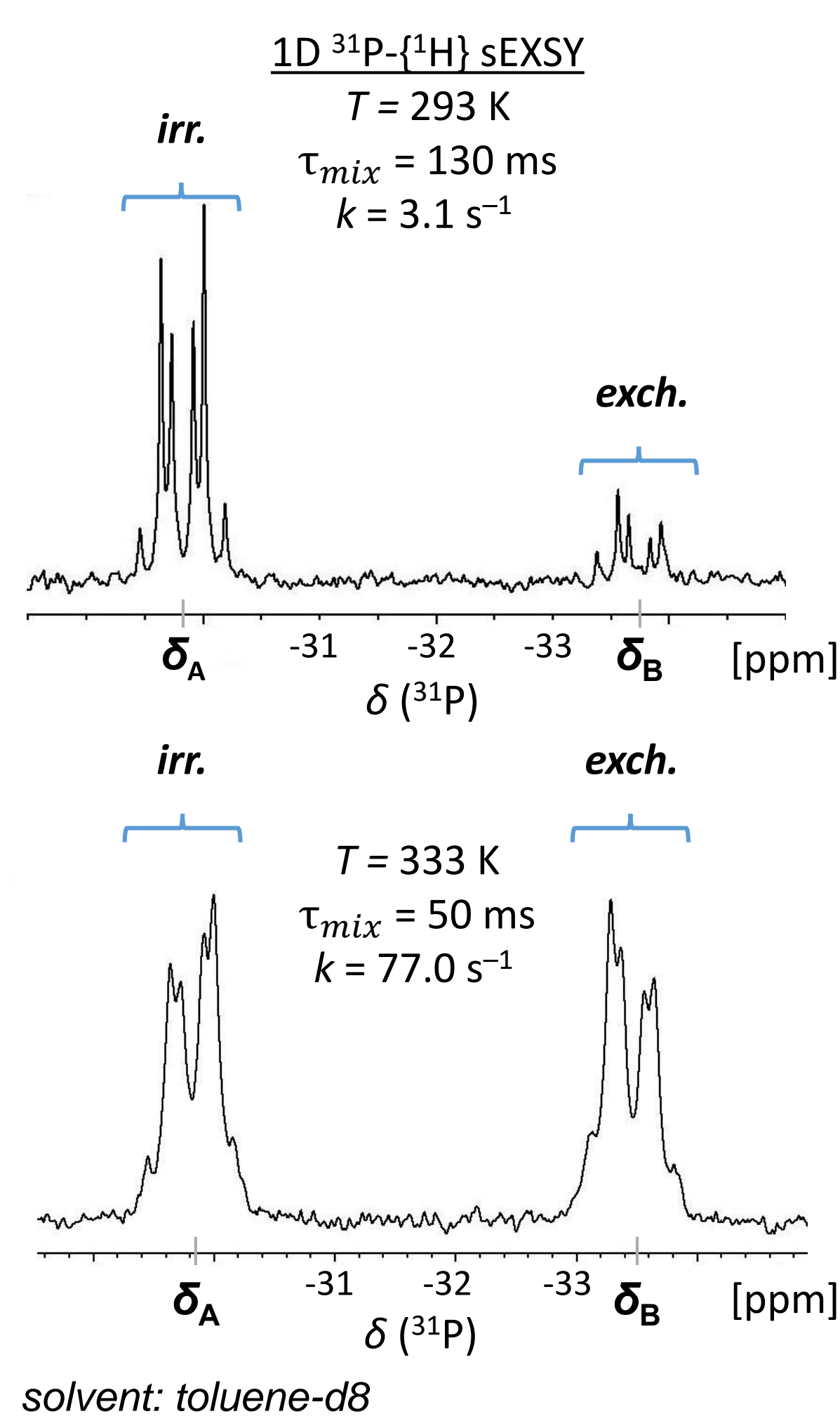
³¹P-{¹H} NMR spectrum of Fc(P)₄tBu*

- 2 chemical environments (red and green) for the 4 phosphorus nuclei due to symmetry

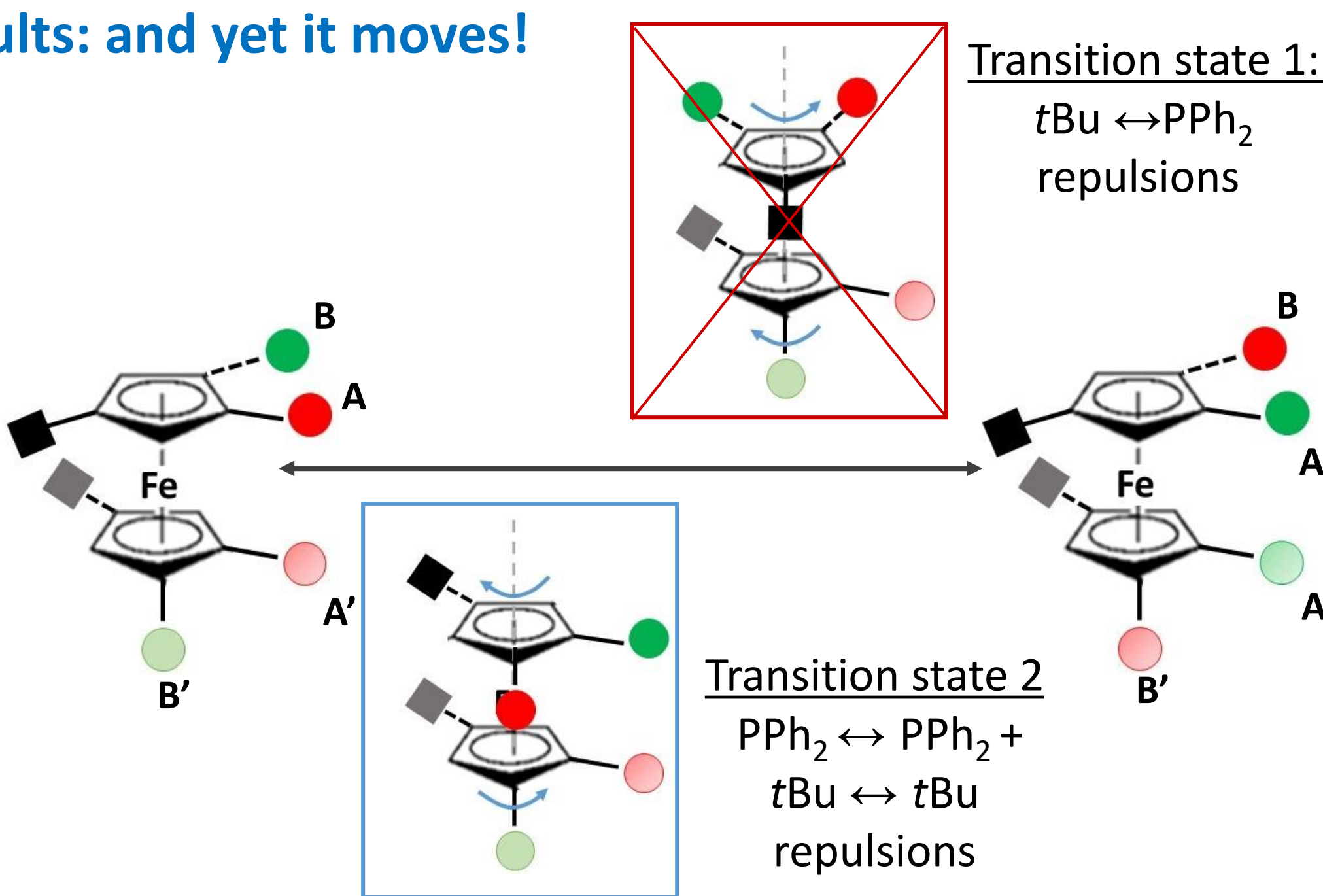
central positions ● = A
● = A' side positions ● = B
● = B'



Results: and yet it moves!



- Elevation of $T \rightarrow$ line broadenings
- 1D selective ³¹P EXSY experiments
- $\rightarrow A(A') \leftrightarrow B(B')$ dynamic exchange
- \rightarrow **Relative twisting of the rings**

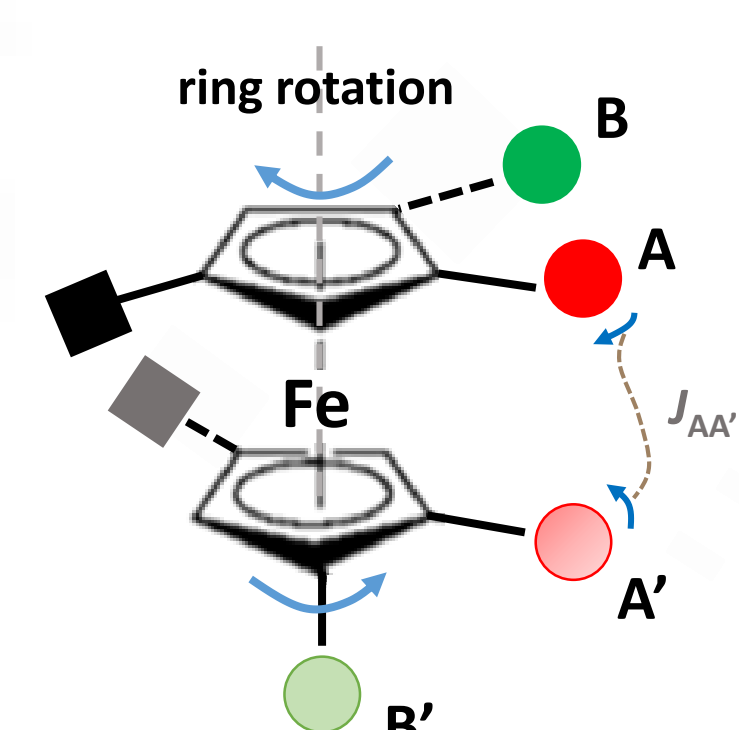


- From $k_{rot}(T) \rightarrow \Delta H_{rot}^\ddagger$ and ΔS_{rot}^\ddagger (via Eyring-plot [3])
- $\rightarrow \Delta G_{rot,298 K}^\ddagger$ (exp.) = 69.0 kcal·mol⁻¹
- According to DFT calculations (PBE1PBE/Def2SVP-w06)
- $\Delta G_{298 K}^\ddagger$ (theor.) = 68.9 kcal·mol⁻¹ for transition state 2
- \rightarrow **Preferred way of (hindered) rotation keeps the coordinative sites close**

$J_{AA'}$: through space or not?

$$k_{rot}(333 K) = 77.0 \pm 0.2 \text{ Hz} > 59.5 \text{ Hz} = J_{AA'}$$

and still AA'BB'!



$$Q_1 : Q_3 : Q_5 = (2C^2 - 1) : (2C\sqrt{1 - C^2}) : 1$$

$$\rightarrow Q_3 = 75 \text{ Hz} = Q_4$$

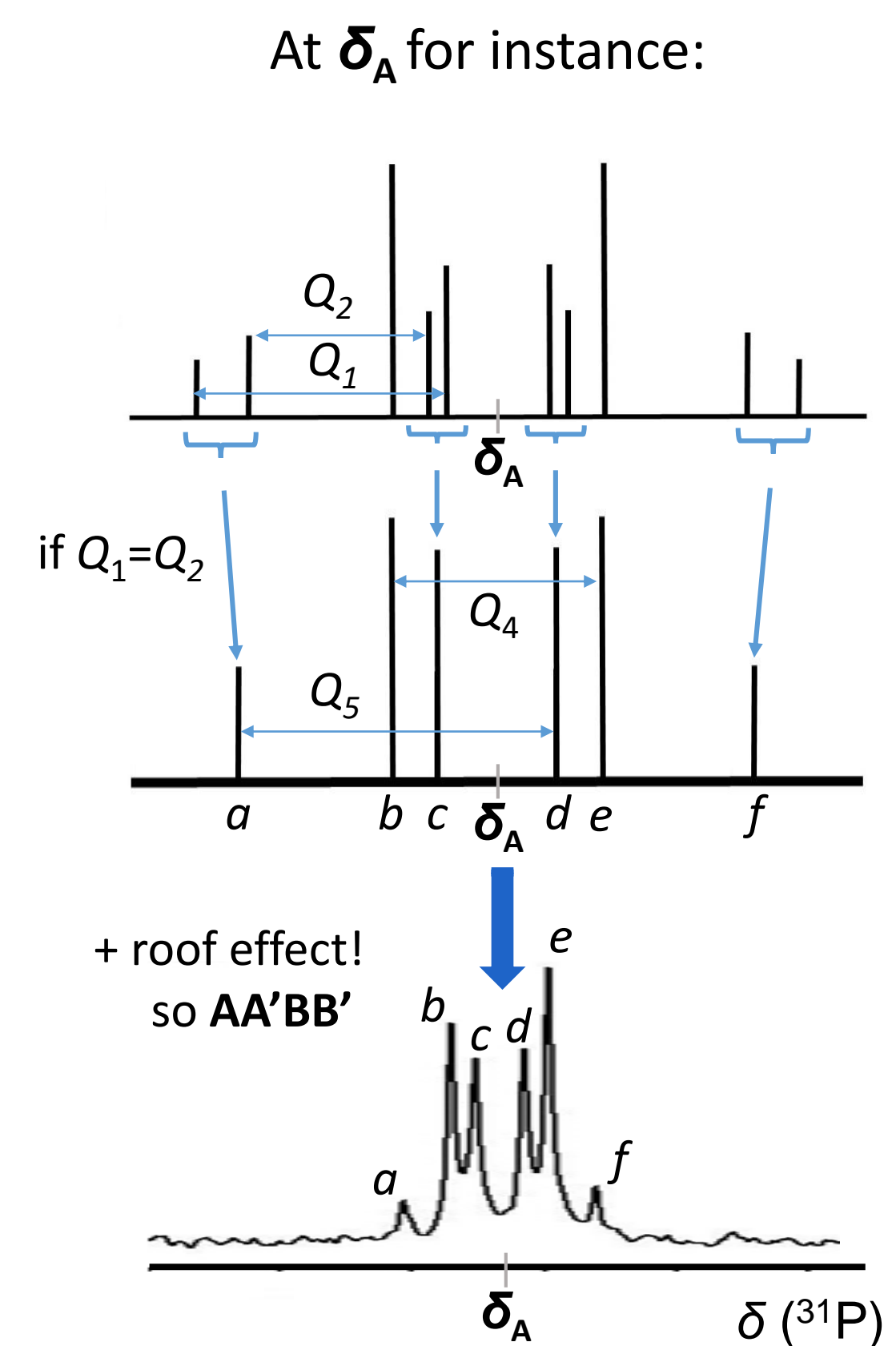
$$J_{AX'} = J_{A'X} = \frac{1}{2}(Q_4 - Q_3) = 0 \text{ Hz}$$

$$J_{AA'} = \frac{1}{2}(Q_1 + Q_2) = 59.5 \text{ Hz}$$

$$J_{AX} = J_{A'X'} = \frac{1}{2}(Q_3 + Q_4) = 75 \text{ Hz}$$

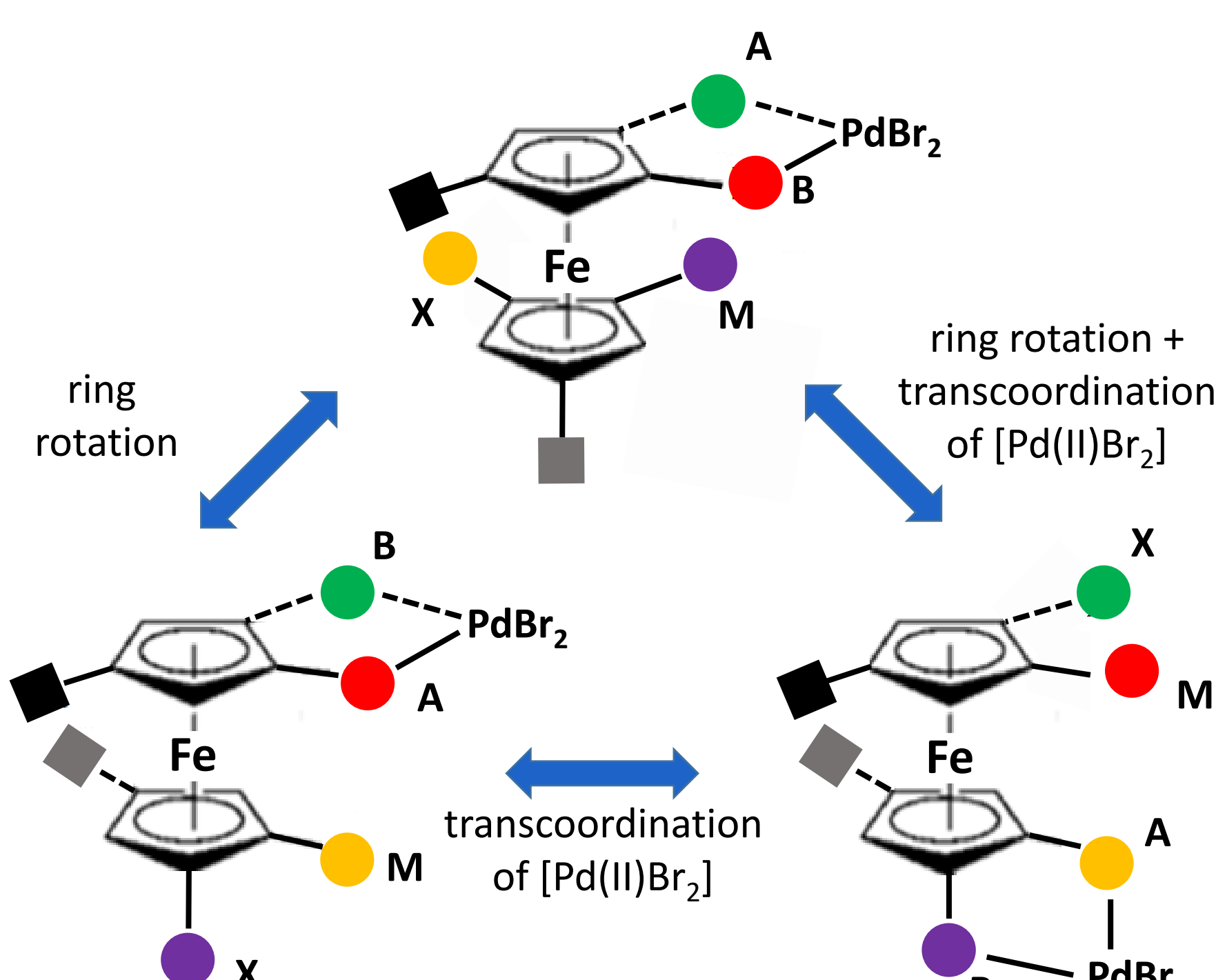
$$J_{XX'} = \frac{1}{2}(Q_1 - Q_2) = 0 \text{ Hz}$$

- ³ $J_{AA'}$ is reported to be *through space* [4]



Results II – [Pd(II)Br₂-Fc(P)₄tBu]

- [Pd(II)Br₂-Fc(P)₄tBu]: 16 e⁻ state of Pd
- ABMX ³¹P spin system (4 peaks)
- 1D ³¹P and 2D ¹H EXSY-s
- $\rightarrow A \leftrightarrow B \leftrightarrow M \leftrightarrow X$ are in dynamic exchange
- \rightarrow **Ring rotation + transcoordination of =PdBr₂**
- Benefits of multiple coordinative sites
- $k(\text{rot}) > k(\text{transc.})$



Conclusions

- The 'rigidity' of the Cp scaffold in Fc(P)₄tBu was quantified experimentally and *in silico*
- The preferred pathway of the hindered Cp ring twisting supports the existence of a permanent multidentate coordinative 'cage'
- Transition metal transcoordination between distinct coordinative sites was directly shown in case of [Pd(II)Br₂-Fc(P)₄tBu]

Acknowledgements

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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] Bain, A., *Chemical Exchange in NMR*, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2003, **43**, 63-103 [4] Hierso, J.-C., Fihri, A., Ivanov, V. V., Hanquet, B., Piriou, N., et al., *J. Am. Chem. Soc.*, 2004, **126**, 11077-11087

*Note: the assignments of the ³¹P NMR spectra were adapted from [4]. However, the interpretation of the peak multiplicities and the investigation of dynamic properties are novel results and the product of the authors of this work.