STeRéO Group Seminar - RCC Julien Botton

X-ray Snapshot Observation of Palladium-Mediated Aromatic Bromination in a Porous Complex

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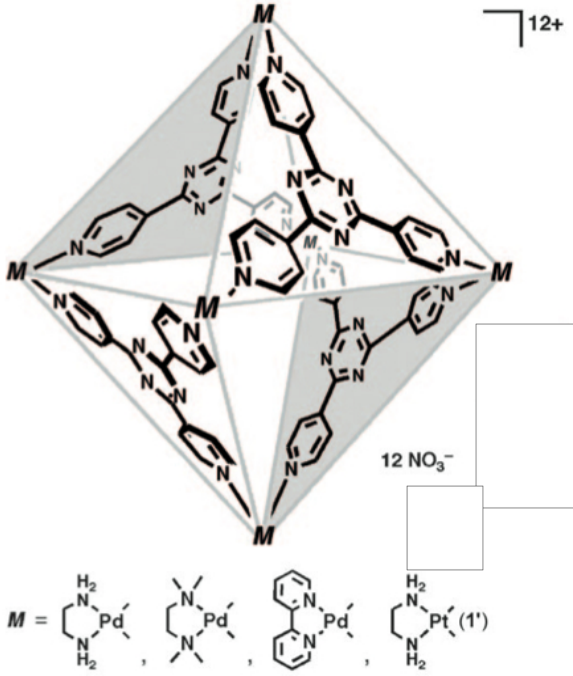
Molecular Vessels

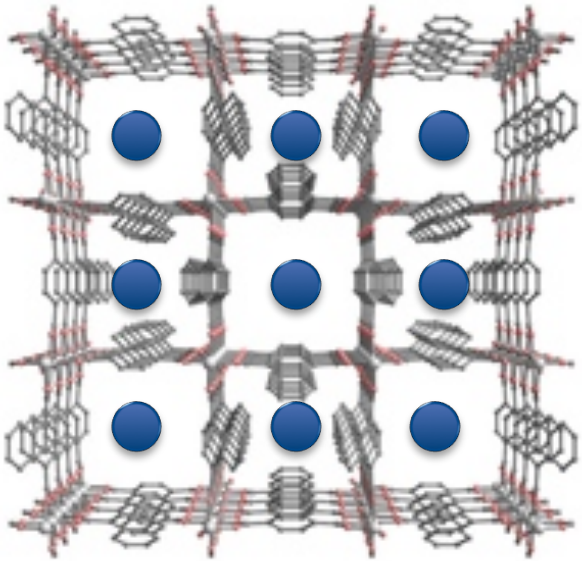


* Increase of the reaction rates
* New regioselectivities
* New reactivities
* Chiral induction
* Whole molecule protecting group

Fujita *et al.*, *Angew. Chem. Int. Ed.* **2009**, 48, 3418

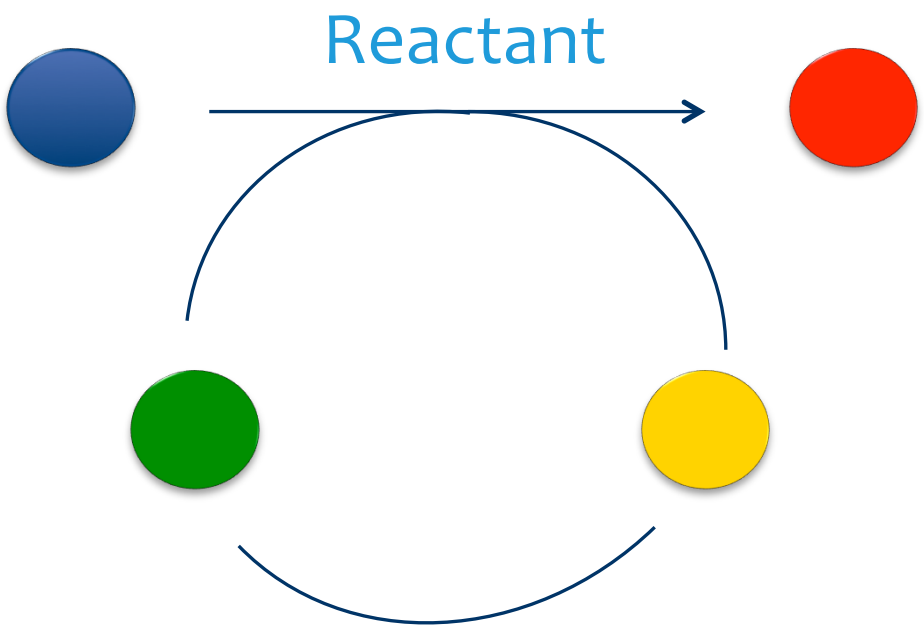
STEREO's Team Bibliographic Seminar: http://ism2.univ-amu.fr/fichiers_pdf/seminaires-stereo/

Key Concept: Crystalline Flasks

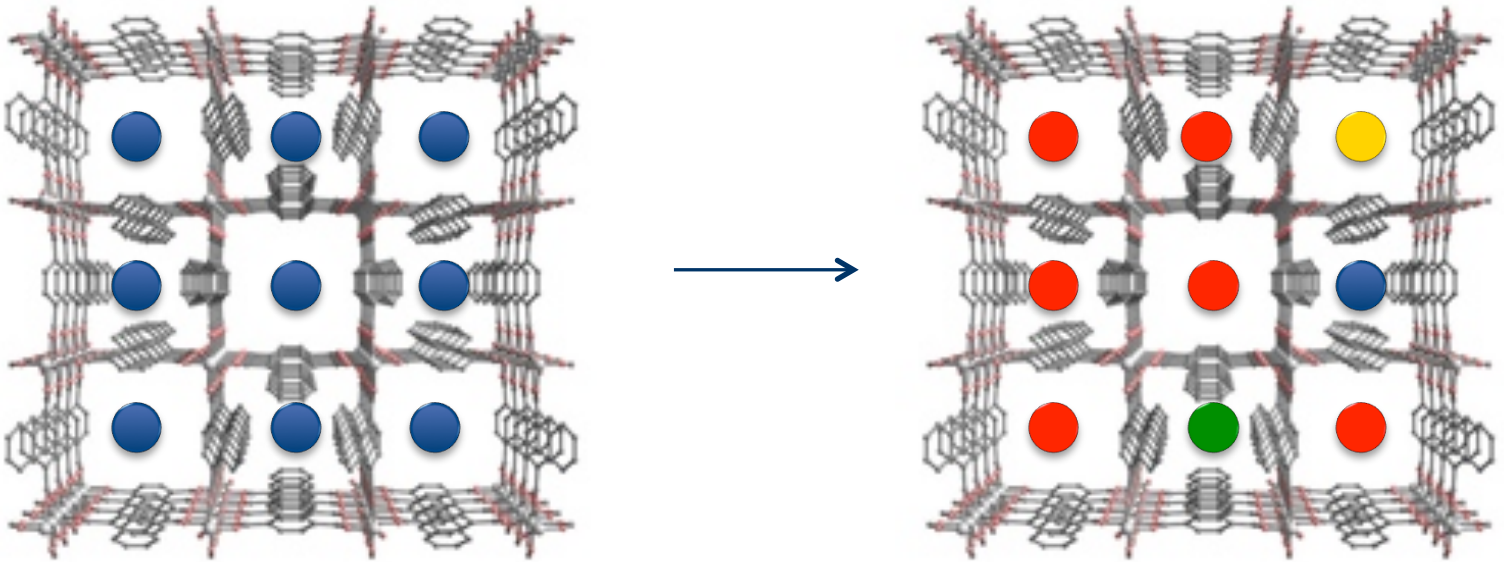


Crystalline porous template loaded with a substrate

Key Concept: Crystalline Flasks



Key Concept: Crystalline Flasks



Crystalline porous template loaded with a substrate

X-Ray analysis to picture the reactive intermediates

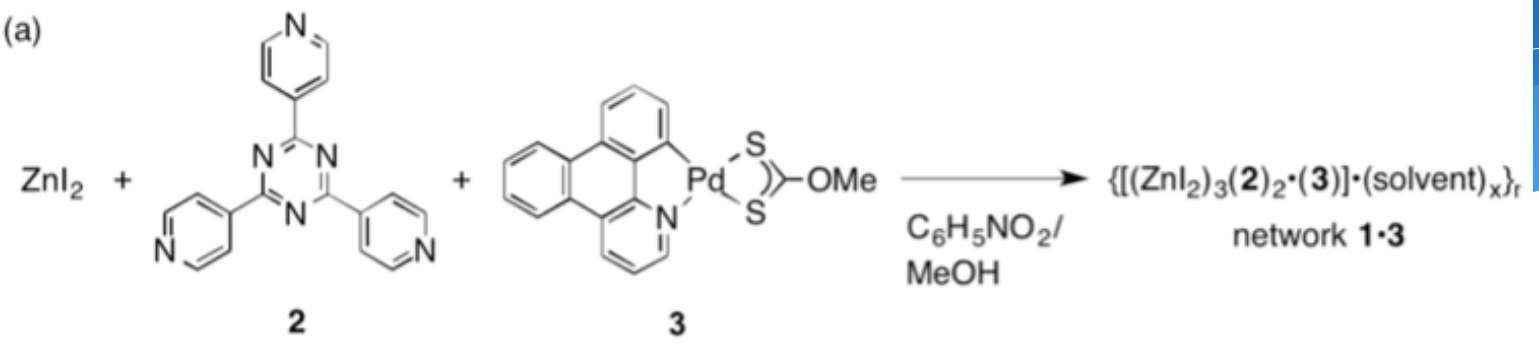
Pd-catalyzed Aryl-bromination

* Postulated mechanism:

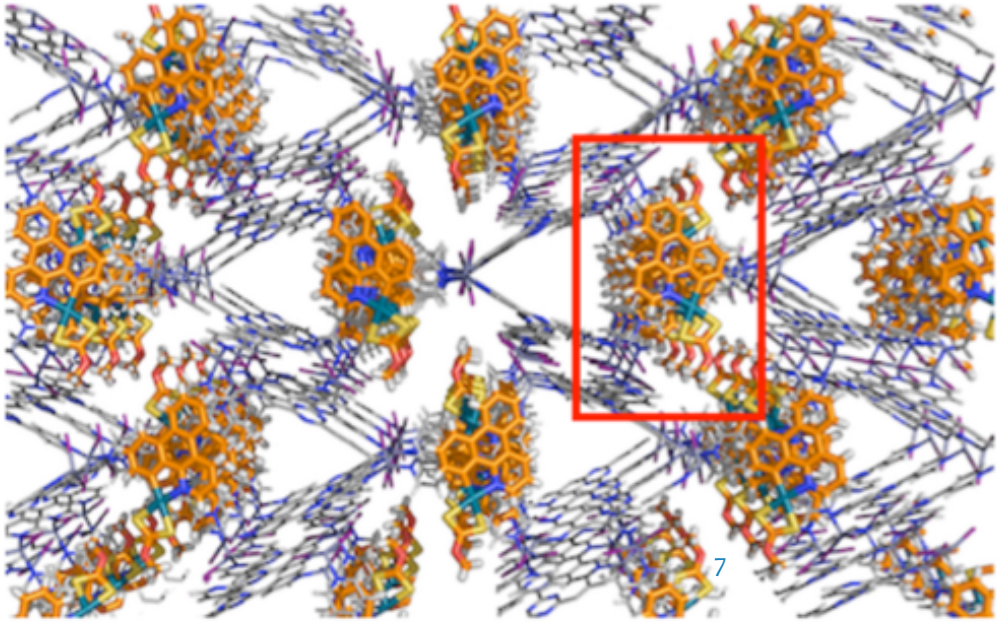
K. Muniz, *Angew. Chem. Int. Ed.* **2009**, *48*, 9412 – 9423

Assembling the system

(a)



(b)



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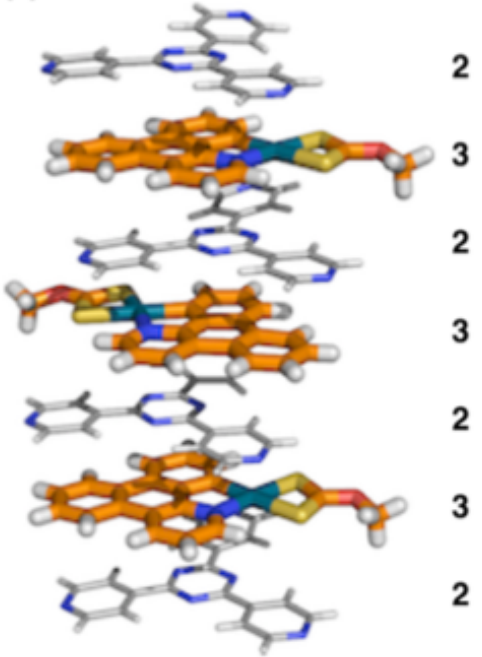
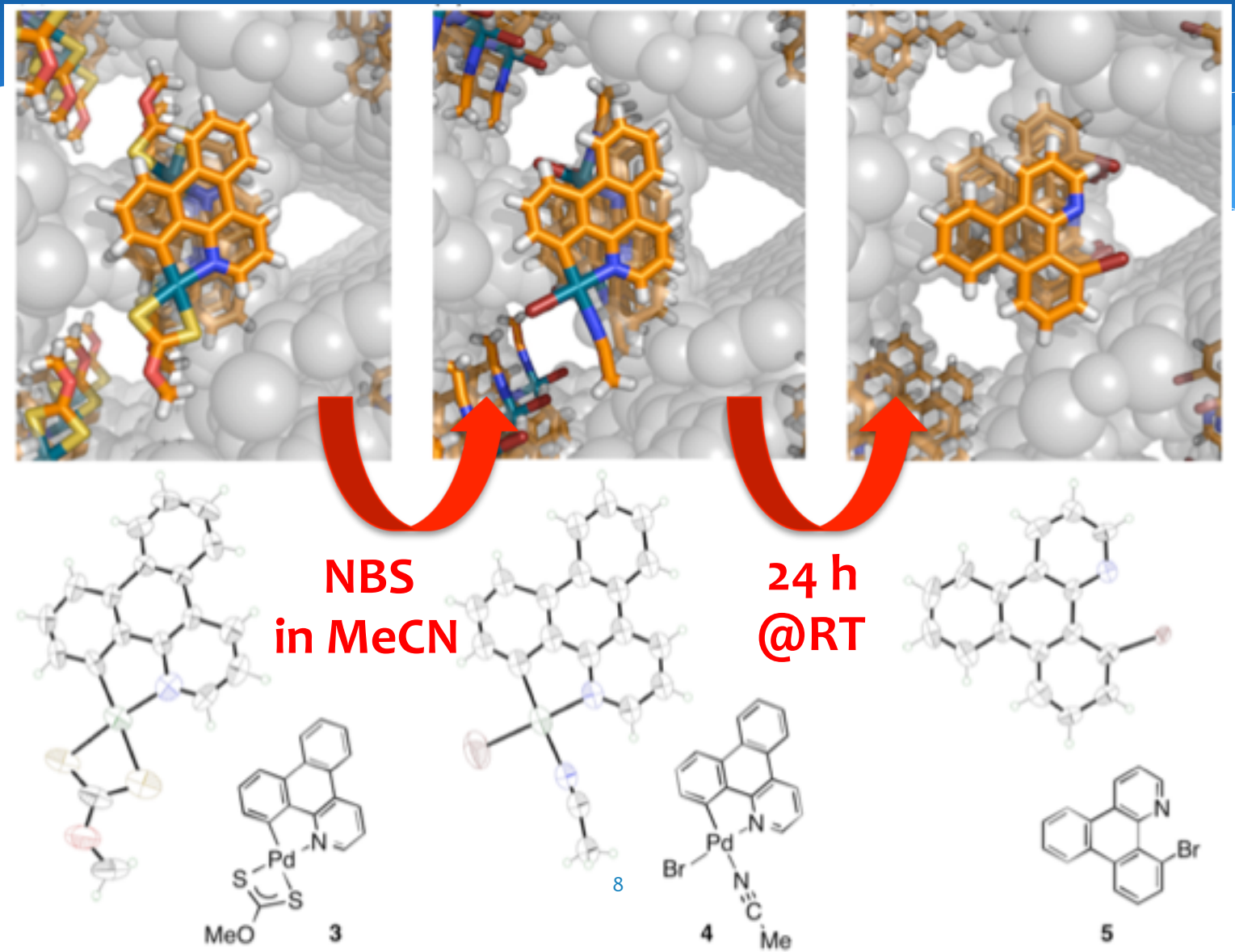


Observation of Intermediates



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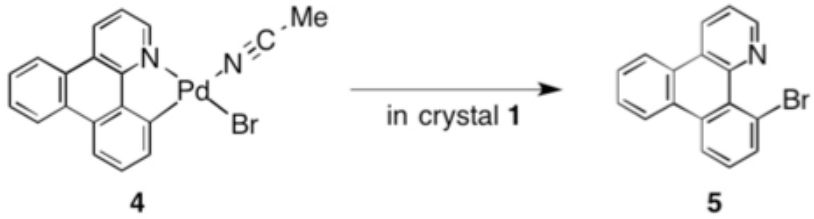

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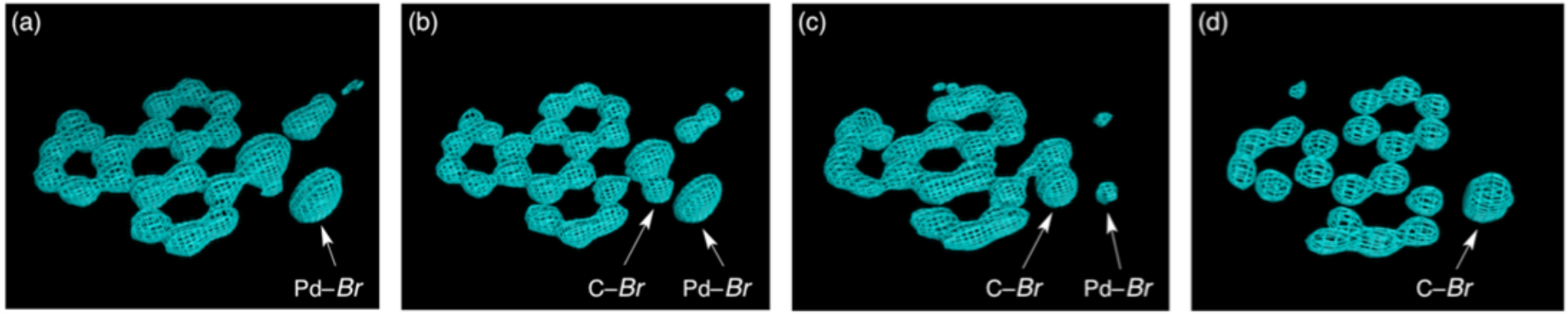

* Electron density mapping showed formation of C-Br bond from Pd-Br in a square plan shape
* No pyramidalization ➔ Pd(II) / Pd(0) mechanism

X-Ray Snapshot / Crystalline Flasks: a Powerful Technique ?

Advantages

* Visualisation of intermediates
* Possibility to cool the crystal
* Proposition of mechanism

Drawbacks

* Different reactivities inside the crystal
* Only long lifetime species are observed
* Steric constraint could prevent the Pd(IV) formation

➔ Impossible to exclude the Pd(II)/ Pd(IV) pathway

Thank you for your attention