

ORGANOCATALYSTS CONFINED WITHIN THE CAVITY OF CYCLODEXTRINS

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Cyclodextrins (CDs) have been studied as platforms for selective catalytic reactions. The bridging of CDs with a *N*-heterocyclic carbene (NHC) ligand led to a rigidification and a deformation of their cavities, conferring them a helicoidal chirality.^{[1],[2]} The presence of the NHC moiety allowed the formation of diverse metallic complexes pointing inside the cavity. Reactions involving coinage metals (Cu, Ag, Au) have been described and showed great regio- or enantioselectivities towards hydroboration, cycloisomerization and alkoxy cyclization reactions.^{[3],[4]}

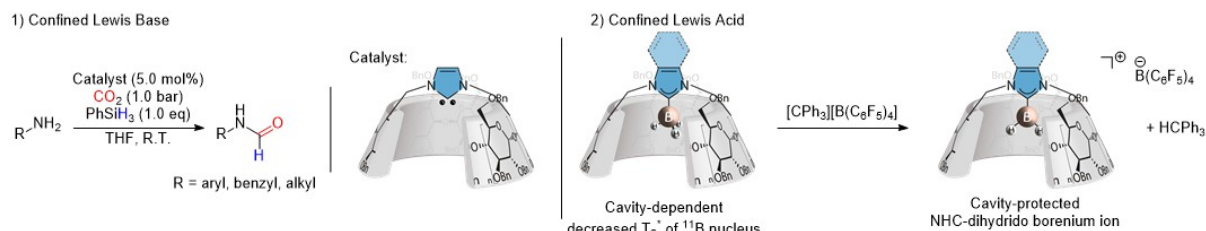
We recently turned our interest towards the confinement of organocatalysts to study the influence of the cavity in metal-free reactions.

We have therefore used the free NHCs as Lewis bases in catalysis and have synthesized NHC-boranes, precursors to strongly Lewis acidic borenium ions, to first study their structural features.

The Lewis basic free carbenes are used as catalysts and showcase an enhanced cavity influence regarding the formylation of amines by CO₂ hydrogenation.^[5]

The confinement of NHC-boranes in the cavity of the CD reveals a strong decrease, up to a 64-fold, of the NMR transverse relaxation time (T_2^*) of the boron nucleus, depending on the size of the cavity. The influence of a cavity regarding relaxation times has been described for dipolar nuclei but it has, to our knowledge, never been for quadrupolar nuclei.^[6]

The protection brought by the cavity of the CD allows us to form the elusive NHC-BH₂⁺ borenium ion that was thought to be non-isolable.^[7] This borenium ion is also active towards catalysis for the hydrosilylation of ketones and shows different selectivities in function of the size of the cavity.



References

- 1) M. Guitet, P. Zhang, F. Marcelo, C. Tugny, J. Jiménez-Barbero, O. Buriez, C. Amatore, V. Mourès-Mansuy, J.-P. Goddard, L. Fensterbank, Y. Zhang, S. Roland, M. Ménand, M. Sollogoub, *Angew. Chem. Int. Ed.* 2013, 52, 7213–7218.
- 2) P. Zhang, C. Tugny, J. Mejjide Suárez, M. Guitet, E. Derat, N. Vanthuyne, Y. Zhang, O. Bistri, V. Mourès-Mansuy, M. Ménand, S. Roland, L. Fensterbank, M. Sollogoub, *Chem* 2017, 3, 174–191.
- 3) S. Roland, J. Mejjide Suárez, M. Sollogoub, *Chem. Eur. J.* 2018, 24, 12464–12473.
- 4) C. Tugny, N. del Rio, M. Koohgard, N. Vanthuyne, D. Lesage, K. Bijouard, P. Zhang, J. Mejjide Suárez, S. Roland, E. Derat, O. Bistri-Aslanoff, M. Sollogoub, L. Fensterbank, V. Mourès-Mansuy, *ACS Catal.* 2020, 10, 5964–5972.
- 5) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem. Int. Ed.* 2012, 51, 187–190.
- 6) G. Huber, L. Beguin, H. Desvaux, T. Brotin, H. A. Fogarty, J.-P. Dutasta, P. Berthault, *J. Phys. Chem. A* 2008, 112, 11363–11372.
- 7) B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo, *Angew. Chem. Int. Ed.* 2011, 50, 8400–8403.