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After studies at the Université Paris XI-Orsay and Université Paul Sabatier (UPS) in Toulouse (France), Michel Etienne got his PhD from the Université de Bretagne Occidentale in Brest (France) in 1988 where he was appointed as "Chargé de Recherche" for the CNRS. In 1989, he worked for one year at the University of North Carolina at Chapel Hill (USA) with Prof. J. L. Templeton as a NATO/CNRS research associate. He then returned to Toulouse to the Laboratoire de Chimie de Coordination (LCC). In 1999, he took a Professor position at UPS and still does his research at the LCC. His research interests include organometallic and coordination chemistry, with a special emphasis on the dynamics of agostic alkyl groups bound to s-block and early transition metal centres and their consequences on the activation of strong and inert bonds such as CH, CF and CC bonds. The use of "scorpionate" ligands [hydrotris(pyrazolyl)borates] niobium alkyne complexes is a central theme in these studies. He is also interested in low valent complexes of these metals, in highly fluorinated scorpionate ligands and their use in late transition metal chemistry and catalysis for alkane functionalization.

Keywords: Tris(pyrazolyl)borate (Tp') ligands, fluorinated ligands, CH and CC agostic interactions, CH activation and functionalization, heavy alkaline earth metals, Calcium, Lithium, Niobium Yttrium,

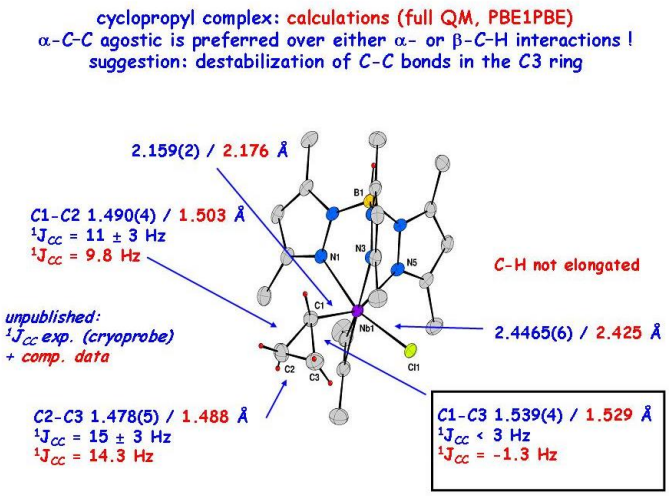
I- CC agostic interactions

We use the fantastic possibilities of tuning the steric and electronic properties of tris(pyrazolyl)borate ligands to induce unusual ligand coordination, stabilize reactive intermediates and eventually discover new reactions of Early Transition Metal complexes. In particular, C-H and C-C agostic interactions are studied with their consequence on the dynamics and reactivity of alkyl groups in the field of CH bond activation and functionalization.

Beyond α-CH or β-CH agostic interactions, rare cases of α-CC agostic complexes have been described. The importance of ring strain in the cyclopropyl group of $Tp^{Me2}NbCl(c\text{-}C_3H_5)(MeCCMe)$ has been emphasized. The key to assigning the α-CC agostic interaction was the ability to measure and compute J_{CC} coupling constants.

A review

- Intramolecular C–C Agostic Complexes: C–C Sigma Interactions by Another Name.
M. Etienne, A. S. Weller.
Chem. Soc. Rev. **2014**, *43*, 242



- C-C Coupling Constants, J_{CC}, are Reliable Probes for α-C-C Agostic Structures
C. Boulho, T. Keys, Y. Coppel, L. Vendier, M. Etienne, A. Locati, F. Bessac, F. Maseras, D. A. Pantazis, J. E. McGrady.
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J. Jaffart, M. Etienne, M. Reinhold, J. E. McGrady, F. Maseras.
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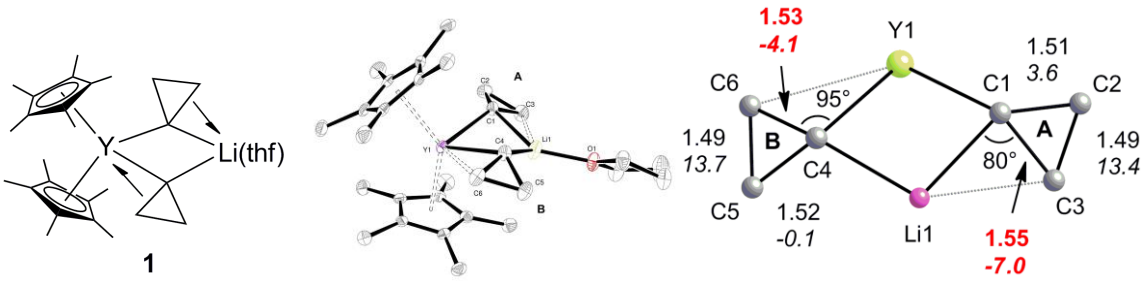
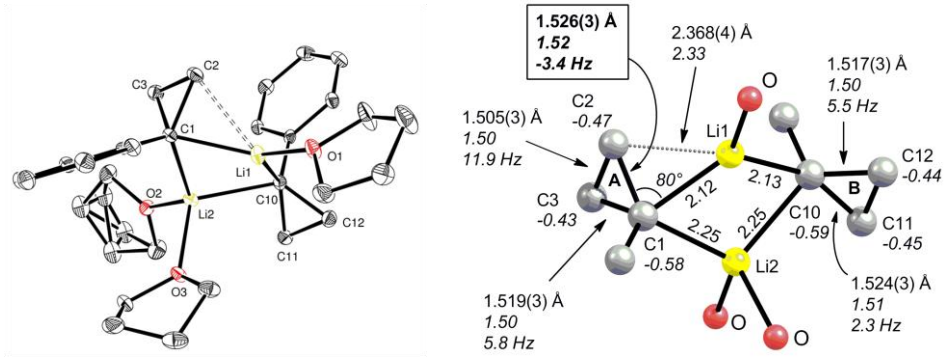
M. Etienne, J. E. McGrady, F. Maseras.
Coord. Chem. Rev. **2009**, *253*, 635.

A unique case of a heterobimetallic bis(cyclopropyl) LiY complex exhibiting two types of CC agostic interactions has been obtained. The interaction with Li has an electrostatic character whereas that with Y has a more covalent nature (DFT and NBO analysis). The latter is also supported by a CH agostic interaction in a Y(η^3-CCH) manner. The right hand side of the picture shows the optimized structure of **1** with relevant calculated parameters: CC bond length (Å), 1st line; J_{CC} (Hz), 2nd line, *italics*.



- An Unsymmetrical bis CC Agostic Heterobimetallic LiY Complex.
Y. Escudié, C. Dinoi, O. Allen, L. Vendier, M. Etienne.
***Angew. Chem. Int. Ed*, 2012**, *51*, 2461.

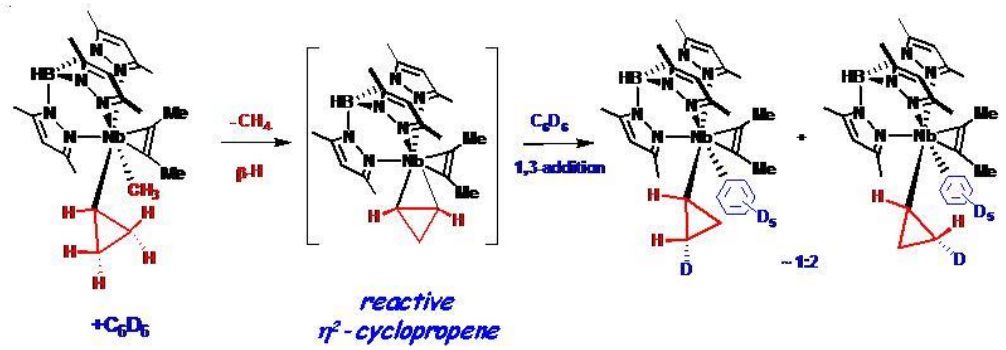
This has been extended to a homobimetallic bis[(1-phenylcyclopropyl)lithium] complex. The interaction is strong enough that a thf is expelled from the coordination sphere of lithium (X-ray structure, below left). The DFT computed structure reveals low J_{CC} and electrostatic interactions. The bimetallic structure is broken in thf solution (DOSY NMR).



- α-CC Agostic Structures and Aggregation Diversity in Cyclopropyllithium Derivatives.
Q. Dufrois, L. Vendier, M. Etienne.
***Chem. Commun. 2016*, *52*, 6781.**

II- CH activation and functionalization

Cyclopropyl methyl and related complexes of niobium activate the CH bond of benzene via a rare β-H abstraction / 1,3-addition sequence under very mild conditions (room temperature!), linking the structure of the complex to its reactivity. Methane and other hydrocarbons can be activated similarly. Cyclopropyl zirconocene complexes are also competent for some of these reactions.



rare β-H abstraction / stereospecific 1,3-addition

- CH Bond Activation of Methane by a Transient η^2-Cyclopropene / Metallabicyclobutane Complex of Niobium.
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- β-H Abstraction / 1,3-CH Bond Addition as a Mechanism for the Activation of CH Bonds at Early Transition Metal Centers.
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C. Boulho, P. Oulié, L. Vendier, M. Etienne, V. Pimienta, A. Locati, F. Bessac, F. Maseras, D. A. Pantazis, J. E. McGrady.
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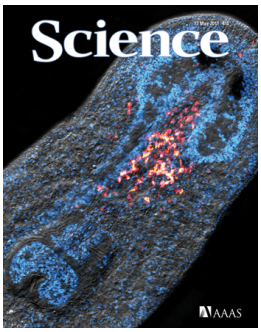
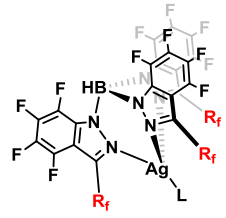
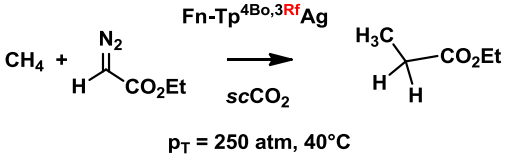
Our interest in CH bond activation expands to catalytic functionalization of alkanes. Highly fluorinated hydrotris(indazolyl)borates have been synthesized. Extremely electrophilic copper(I) and silver(I) complexes are catalysts for the insertion of carbene into alkane CH bonds. This includes a mild catalytic functionalization of methane to ethylpropanoate under supercritical conditions (*sc*-CO_2) with TON approaching 10^3, one of the most challenging problems of modern chemistry.







$R_f = CF_3, (CF_2)_nCF_3$
L= thf, Me=CO, CO, $\nu_{CO} = 2166\ cm^{-1}$

- Functionalization of Non-Activated C-H Bonds of Alkanes: an Effective and Recyclable Catalytic System Based on Fluorinated Silver Catalysts and Solvents.
M. Á. Fuentes, B. K. Muñoz, K. Jacob, L. Vendier, A. Caballero, M. Etienne, P. J. Pérez.
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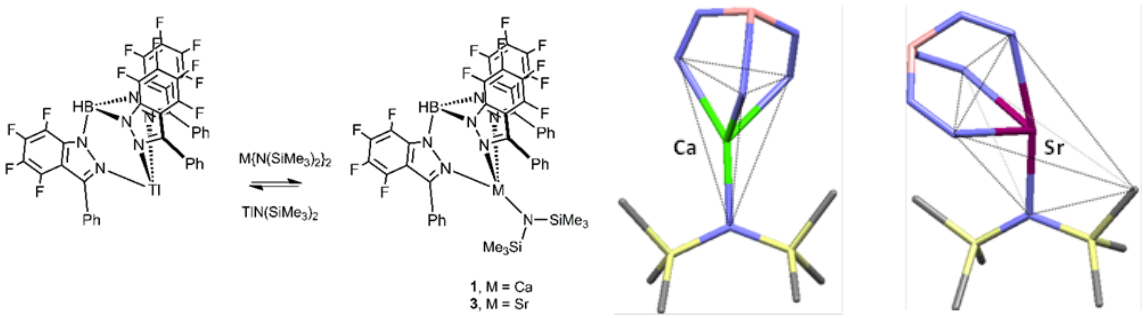
***Science* 2011**, *332*, 835.

III- Chemistry of the heavier alkaline earth metals

Ae metals are abundant, oxophilic and redox-inactive in their cationic form. They are characterized by a wide range of ionic radii and cation charge densities (Mg^{2+} = 0.72 Å; Ca^{2+} = 1.00 Å; Sr^{2+} = 1.18 Å, Ba^{2+} = 1.35 Å for six-coordinate ions). Their chemistry is therefore largely governed by electrostatic and steric factors, featuring highly ionic and essentially non-directional bonding. One consequence is the deleterious Schlenk equilibrium especially for the heavier Ae with their large ionic radii. One challenge here is to stabilize heteroleptic species that would be strongly electrophilic. With their electron-withdrawing properties and significant steric hindrance, the highly fluorinated hydrotris(indazolyl)borates have produced a variety of heteroleptic calcium and strontium complexes stabilized by different type of secondary interactions. The larger strontium has stronger agostic interactions than calcium has seen from the X-ray structures of silylamido complexes below. These complexes are good catalysts for intramolecular hydroamination reactions.



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N. Romero, S.-C. Roşca, Y. Sarazin, J.-F. Carpentier, L. Vendier, S. Mallet-Ladeira, C. Dinoi, M. Etienne.
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Y. Hu, N. Romero, C. Dinoi, L. Vendier, S. Mallet-Ladeira, J. E. McGrady, A. Locati, F. Maseras, M. Etienne.
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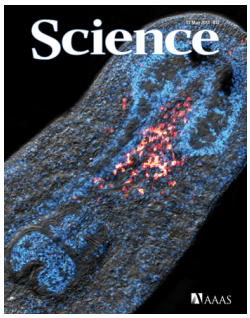

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