



Michel ETIENNE

**Professor at Université Paul Sabatier, Toulouse III
Laboratoire de Chimie de Coordination du CNRS, UPR 8241
205 Route de Narbonne
31077 Toulouse Cedex 4**

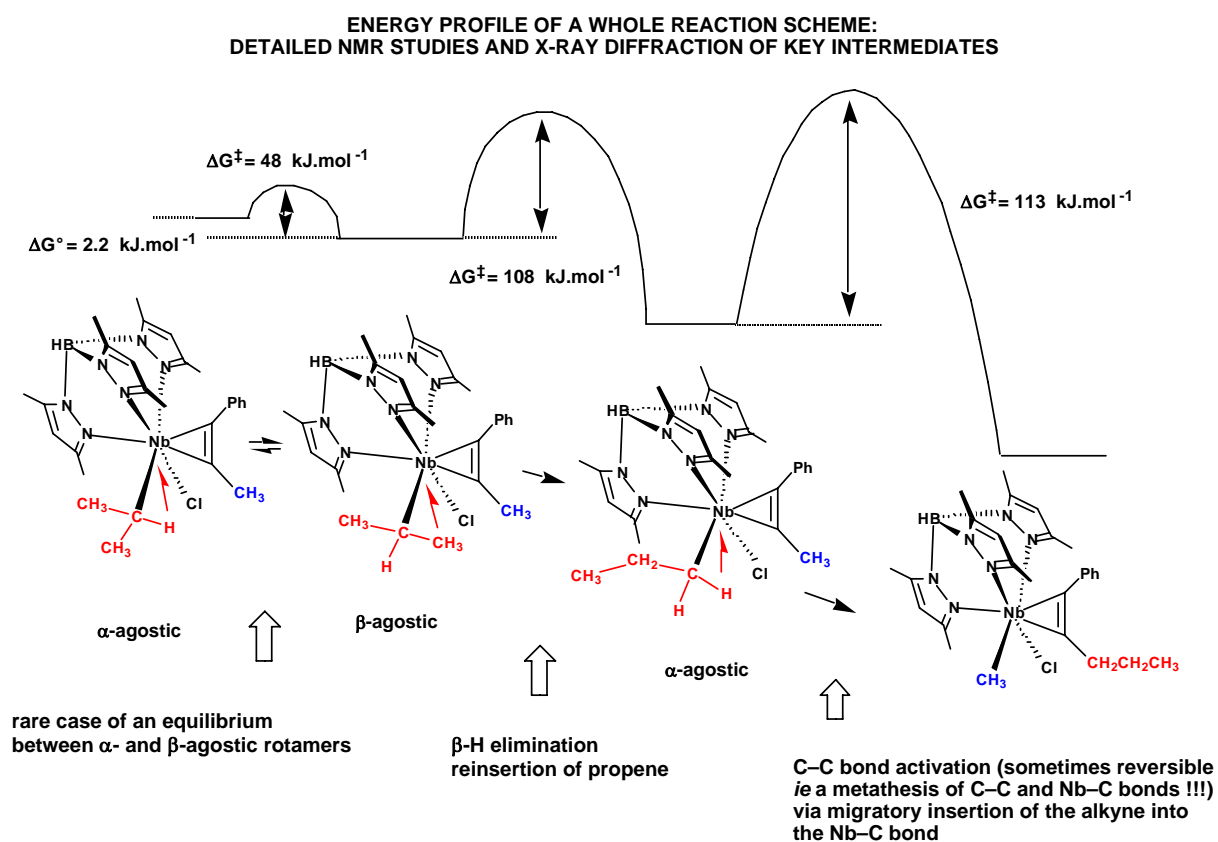
**+33 (0)5 61 33 31 76
michel.etienne@lcc-toulouse.fr**

After studies at the Université Paris XI-Orsay and Université Paul Sabatier 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 position at Université Paul Sabatier as Professor but 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 early transition metal centres and their possible consequences on the polymerisation of olefins and C–H and C–C bond activation. The use of "scorpionate" ligands [hydrotris(pyrazolyl)borates] niobium alkyne complexes is a central theme in these studies. More recently he became interested in low valent complexes of these metals, to highly fluorinated scorpionate ligands and their use in late transition metal chemistry.

Tris(pyrazolyl)borate (Tp') complexes of the group 5 metals: dynamics of alkyl groups, CH and CC agostic interactions, CH and CC activation

We use the fantastic possibilities of tuning the steric and electronic properties of tris(pyrazolyl)borate ligands to induce unusual ligand coordination, stabilise 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 the catalytic polymerisation of olefins, and CH and CC bond activation.

A summary of directly observed events related to the existence of α -CH or β -CH agostic interactions, sometime in equilibrium, is presented in the following Scheme. A remarkable metathesis of M-C and C-C bonds has been observed in this system.



Thanks to fruitful collaborations with groups of computational chemists (Prof John E. McGrady, Glasgow, UK; Dr Feliu Maseras, ICIQ, Tarragona, Spain), we have been able to gain a better insight of the factors governing this behavior. Also we have proposed a more intimate view on the nature of these so-called α -CH or β -CH agostic interactions.

- On the Origin of α - and β -Agostic Distortions in Early Transition Metal Alkyl Complexes.

D. A. Pantazis, J. E. McGrady, M. Besora, F. Maseras, M. Etienne.

Organometallics, 2008, 27, 1128-1134.

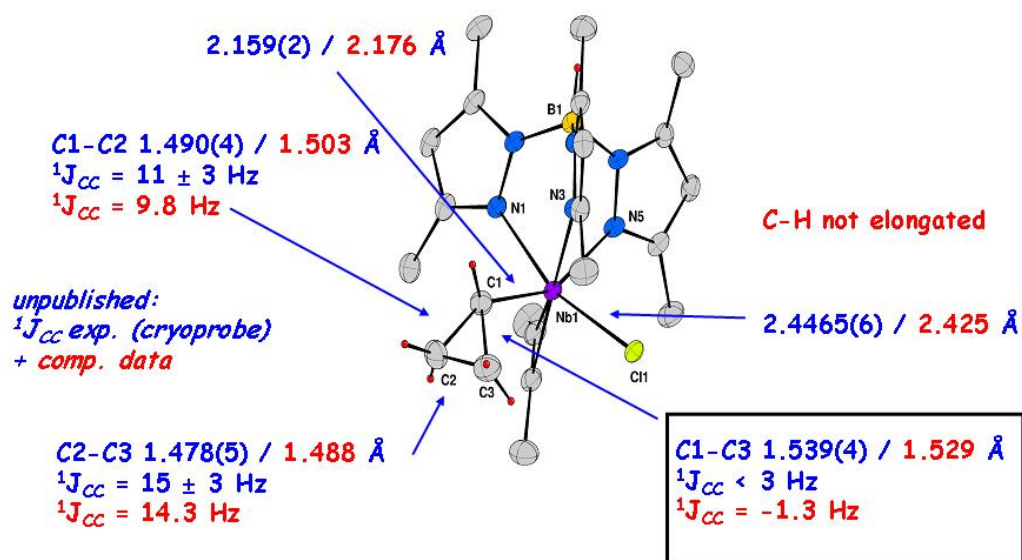
- Equilibria Between α - and β -Agostic Stabilized Rotamers of Secondary Alkyl Niobium Complexes.

J. Jaffart, M. Etienne, F. Maseras, J. E. McGrady, O. Eisenstein.

J. Am. Chem. Soc. 2001, 123, 6000-6013.

More recently, a rare case of an α -CC agostic complex has been described. The importance of the constraint in the cyclopropyl group of $\text{Tp}^*\text{NbCl}(\text{c-C}_3\text{H}_5)(\text{MeCCMe})$ has been emphasized, and again strong interactions with theoretical chemists have been central to this research.

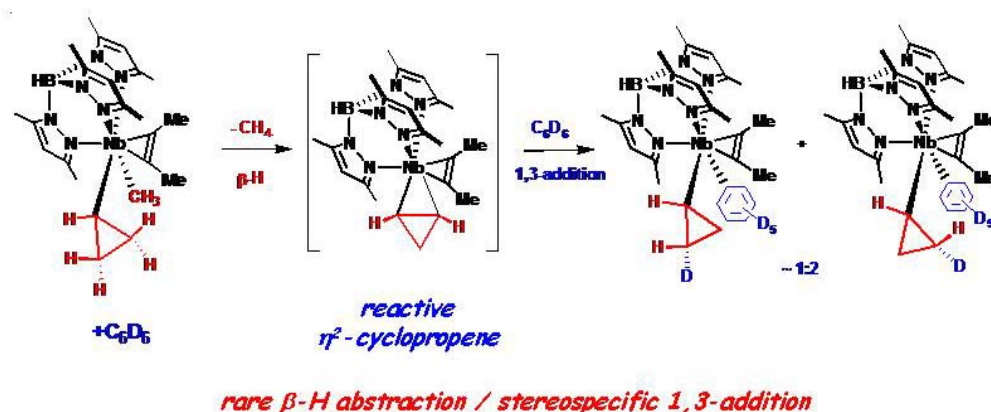
cyclopropyl complex: calculations (full QM, PBE1PBE)
 α -C-C agostic is preferred over either α - or β -C-H interactions!
 suggestion: destabilization of C-C bonds in the C3 ring



- An Unprecedented α -C-C Agostic Interaction in a Cyclopropyl Tris(pyrazolyl)boratoniobium Complex.

J. Jaffart, M. Etienne, M. Reinhold, J. E. McGrady, F. Maseras.
Chem. Commun. 2003, 876-877.

Remarkably, related cyclopropyl methyl complexes were shown to activate under very mild conditions (room temperature!) the CH bond of benzene via a rare β -H abstraction / 1,3-addition sequence, linking the structure of the complex to its reactivity.



- CH Bond Activation by a Transient η^2 -Cyclopropene Niobium Complex.

P. Oulié, C. Boulho, L. Vendier, Y. Coppel, M. Etienne.
J. Am. Chem. Soc., 2006, 128, 15962-15963.

Publications of Michel Etienne 2009-1997

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- Reinvestigation of the Spin Crossover Phenomenon in the Ferrous Complex [Fe(HB(pz)₃)₂].
L. Salmon, G. Molnár, S. Cobo, P. Oulié, M. Etienne, T. Mahfoud, P. Demont, A. Eguchi, H. Watanabe, K. Tanaka, A. Bousseksou.
New J. Chem., **2009**, *33*, 1283-1289.

- A High-Spin Fe(II) / Low-Spin Fe(III) Redox Couple Featuring the Hydrotris[(4-chloro-3,5-dimethylpyrazolyl)]borate Ligand: Synthesis, Spectroscopic and Crystallographic Characterization.
P. Hamon, A. Mari, J.-F. Meunier, L. Toupet, O. Cador, M. Etienne, J.-R. Hamon.
Inorganica Chim. Acta, **2009**, *362*, 4389-4395.

- Amine-Phenolate Ligands in Niobium Chemistry: π -Interactions Probed by an Ancillary Alkyne Ligand.
E. Despagne-Ayoub, S. Schigand, L. Vendier, M. Etienne.
Organometallics, **2009**, *28*, 2188-2194.

- 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.
Organometallics, **2009**, *28*, 940-943.

- Agostic Interactions in Sterically Hindered Early Transition Metal Alkyl Complexes.
M. Etienne, J. E. McGrady, F. Maseras.
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2008

- Agostic Interactions in Sterically Hindered Early Transition Metal Alkyl Complexes.
M. Etienne, J. E. McGrady, F. Maseras.
Coord. Chem. Rev. in press.

- A New Perfluorinated F₂₁-Tp Scorpionate Ligand: Enhanced Alkane Functionalization by Carbene Insertion with (F₂₁-Tp)M Catalysts (M = Cu, Ag).
E. Despagne-Ayoub, K. Jacob, L. Vendier, M. Etienne, E. Álvarez, A. Caballero, M. M. Díaz-Requejo, P. J. Pérez.
Organometallics, **2008**, *27*, 4779-4787.

- On the Origin of α - and β -Agostic Distortions in Early Transition Metal Alkyl Complexes.
D. A. Pantazis, J. E. McGrady, M. Besora, F. Maseras, M. Etienne.

Organometallics, **2008**, *27*, 1128-1134.

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- The Critical Role of the Correlation Functional in DFT Descriptions of an Agostic Niobium Complex.

D. A. Pantazis, J. E. McGrady, F. Maseras, M. Etienne.

J. Chem. Theor. Comput. **2007**, *3*, 1329-1336.

- The Structure of Fluorinated Indazoles: The Effect of the Replacement of an H by a F Atom on the Supramolecular Structure of NH-Indazoles.

J. Teichert, P. Oulié, K. Jacob, L. Vendier, M. Etienne, R. M. Claramunt, C. López, C. P. Medina, I. Alkorta, J. Elguero.

New J. Chem. **2007**, *31*, 936-946.

2006

- Synthesis and structural characterisation of $[\text{Tp}^{\text{Me}_2}\text{Nb}(\text{CH}_3)_2(\text{CH}_3\text{C}\equiv\text{CCH}_3)]$ and $[\text{Tp}^{\text{Me}_2}\text{NbCl}(\text{CH}_3)(\text{CH}_3\text{C}\equiv\text{CCH}_3)]$: is there an intrinsic α -agostic interaction in alkyl complexes of the $[\text{Tp}^{\text{Me}_2}\text{Nb}(\text{alkyne})]$ moiety?

E. Teuma, M. Etienne, B. Donnadiou, G. S. McGrady.

New J. Chem. **2006**, *30*, 409-415.

- Aromatic interactions in hydrotris(3-methylindazolyl)borate organoniobium complexes: control of an alkyne ligand orientation in the crystal.

P. Oulié, J. Teichert, L. Vendier, C. Dablemont, M. Etienne.

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- Structure and bonding in a cyclobutyl tris(pyrazolyl)boratoniobium complex and the variation in agostic behaviour with ring size in the series $\text{Tp}^{\text{Me}_2}\text{NbCl}(c\text{-C}_n\text{H}_{2n-1})(\text{MeC}\equiv\text{CMe})$, $n = 3-6$.

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D. de Caro, M. Basso-Bert, H. Casellas, M. Elgaddari, J.-P. Savy, J.-F. Lamère, A. Bachelier, C. Faulmann, I. Malfant, M. Etienne, L. Valade.

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P. Oulié, N. Bréfuel, L. Vendier, C. Duhayon, M. Etienne.

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- Mono and dinuclear hydrotris(pyrazolyl)borato tantalum complexes.

M. Etienne, J.-C. Hierso, P. J. Daff, B. Donnadiou, F. Dahan.

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- Elusive niobium alkyl cations related to ethylene polymerization.

H. M. Pritchard, M. Etienne, L. Vendier, G. S. McGrady.

Organometallics **2004**, *23*, 1203-1206.

- A one-pot method to prepare the carbene complex $[\text{Tp}^{\text{Me}_2, \text{Cl}}\text{RhCl}_2(\text{CHNiPr}_2)]$ from $[\text{Tp}^{\text{Me}_2, \text{Cl}}\text{Rh}(\text{CO})_2]$, CHCl_3 , and $\text{NH}i\text{Pr}_2$.

E. Teuma, F. Malbosc, M. Etienne, J.-C. Daran, P. Kalck.

J. Organomet. Chem. **2004**, *689*, 1763-1765.

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J. Jaffart, M. Etienne, M. Reinhold, J. E. McGrady, F. Maseras

Chem. Commun. **2003**, 876 - 877.

- Niobium and molybdenum-based molecular magnet grown as thin films by chemical vapor deposition.

E. Lamouroux, E. Alric, H. Casellas, L. Valade, D. de Caro, M. Etienne, D. Gatteschi

Electrochemical Society Proceeding **2003**, *8*, 1040-1046.

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J. Jaffart, M. L. Cole, M. Etienne, M. Reinhold, J. E. McGrady, F. Maseras.

J. Chem. Soc., Dalton Trans. **2003**, 4057-4064.

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E. Teuma, M. Loy, C. Serra-Le Berre, M. Etienne, J.-C. Daran, P. Kalck.

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- Stable formally zerovalent and diamagnetic monovalent niobium and tantalum complexes based on diazadiene ligands.

P. J. Daff, M. Etienne, B. Donnadieu, S. Z. Knottenbelt, J. E. McGrady
J. Am. Chem. Soc. **2002**, *124*, 3818-3819.

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- Solid state and solution structures of a series of [HBPz₃^{Me₂}]Rh(CO)(PR₃) and [HBPz₃^{Me₂,4Cl}]Rh(CO)(PR₃) complexes.

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M. Paneque, S. Sirol, M. Trujillo, E. Carmona, E. Gutierrez-Puebla, M. A. Monges, C. Ruiz, F. Malbosc, C. Serra-Le Berre, P. Kalck, M. Etienne, J.-C. Daran
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J.-C. Hierso, M. Etienne
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J. Fernandez-Baeza, F. A. Jalon, A. Otero, M. E. Rodrigo-Blanco, M. Etienne

J. Chem. Soc., Dalton Trans. **1998**, 769-773.

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- Observing and modelling energetically close α - and β -carbon-hydrogen agostic interactions in an isopropyl tris(pyrazolyl)boratoniobium complex.

J. Jaffart, R. Mathieu, M. Etienne, J. E. McGrady, O. Eisenstein, F. Maseras

Chem. Commun. **1998**, 2011-2012.

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Angew. Chem. Int. Ed. **1998**, *37*, 3169-3172.

1997

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J. Am. Chem. Soc. **1997**, *119*, 3218-3228.