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Molecular design of transition metal pre-catalysts

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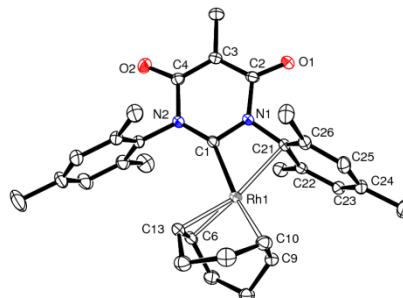
The major thrust of our research is on the design of reactive Transition-Metal pre-catalysts offering low activation energy pathways for challenging substrate transformations in relevance to organic synthesis.

These are constructed from conceptually new ligand architectures based on *N*-heterocyclic carbenes. One outgrowth of our work is on the development of new catalysts for various target CC bond forming reactions.

Keywords: Ruthenium - Organic synthesis
Homogeneous catalysis - Olefin metathesis –
Anionic *N*-heterocyclic carbenes - Zwitterionic catalysts - C-H / olefin coupling - Fischer-type carbenes – Manganese - Experimental charge density analyses .

Catalyst design begins with ligand design! See our new anionic NHCs exhibiting tunable electronic properties

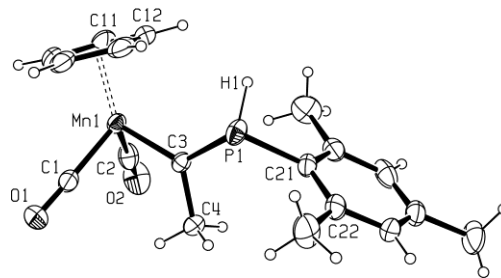
We have recently disclosed the archetype of a new family of *anionic N-heterocyclic carbenes* paving the way to the development of *zwitterionic catalysts*, exemplified here by the 14 e⁻ Rh complex {*mal*NHC}Rh(COD) (*JACS* **2008**; *Chem. Comm.* 2009)



α -phosphinocarbenes now tamed!

The unique α -phosphinocarbene complex shown below is constructed directly from a cationic carbyne complex by nucleophilic attack of a primary or secondary phosphine at the electrophilic carbynic center, followed by de-protonation. It is tantalizing that the archetype of this family, CpMn(CO)₂C(Me)PH(Mes)} was generated from mesitylphosphine, a primary phosphine!

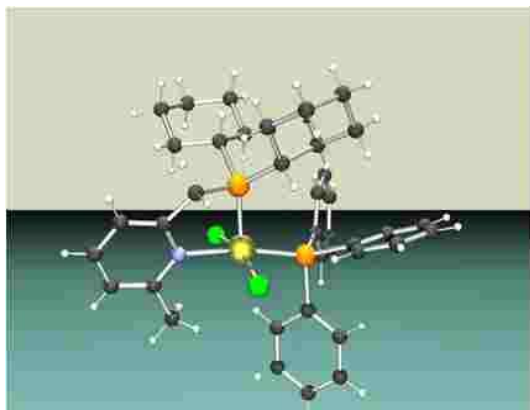
(*Organometallics*, **2008**, *27*, 5180)



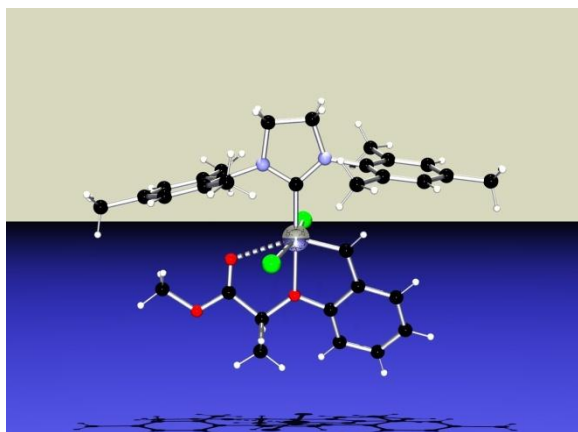
Catalytic reactions of Ru(II) complexes modified by hemi-labile ligands

Inspired by Grubbs III catalysts where a bromopyridine is acting as a leaving group, we have designed a series of “user-friendly pyridine-functionalized phosphine complexes formulated as RuCl₂(R₂PCH₂py)(PPh₃) (see structure next page). These function as efficient ROMP initiators for norbornene upon in situ activation by trimethylsilyldiazomethane. Such complexes also rank amongst the fastest transfer hydrogenation catalysts reported so far.

(*Organometallics*, **2008**, *27*, 1193)



In parallel, a Marie Curie project in collaboration with [Karol Grela](#) (Polish. Acad. Sci.) has led to the development of a new class of Hoveyda-Grubbs catalysts. These are incorporating a poly-chelating carbene bearing a weakly donating ester group as a terminal substituent of the ether, thereby allowing to reach the optimum balance between stability, activity and selectivity. These recoverable catalysts exhibit high efficiency in a number of challenging RCM and cross metathesis reactions ([JACS, 2006, 128, 13652](#))



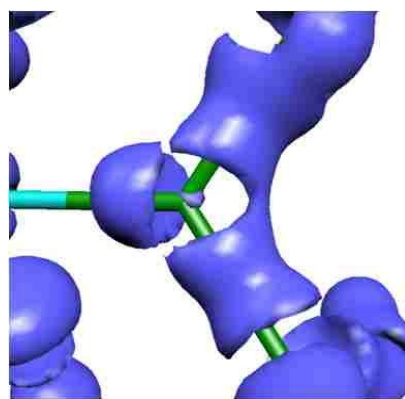
“Instant” generation of $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$ via hydroxide-promoted reduction of $\text{Ru}(\text{II})$ carbonyls to $\text{Ru}(0)$.

$\text{Ru}(\text{CO})_2(\text{PR}_3)_3$, the archetype of reactive $\text{Ru}(0)$ species, known as the best catalyst for C-H/olefin coupling (the Murai reaction), is now available within minutes from $\text{Ru}(\text{CO})_3\text{Cl}_2(\text{thf})$ via a simple reaction cascade where a CO ligand is oxidized to CO_2 and carbonate via the formation of a hydroxycarbonyl intermediate and its subsequent deprotonation by an excess of base ([JACS, 2005, 127, 14554](#)). A recent extension of this work in 2009 has led us to prepare hybrid NHC/olefin complexes of $\text{Ru}(0)$.



Direct visualisation of bonding electrons via experimental charge density analysis: a new challenge

The chemist's dream to see the bonding electrons is now becoming reality with the emerging development of this new technique.



Selected recent publications:

Instant generation of Roper's type $\text{Ru}(0)$ complexes

Sentets, S.; Rodriguez Martinez, M.; Vendier, L.; Donnadieu, B.; Huc, V.; Lugan, N.; Lavigne, G.

[J. Am. Chem. Soc. 2005, 127, 14554-14555](#)

Extension of the experimental electron density analysis to metastable states...

Legrand, V.; Pilllet, S.; Souhassou, M. Lugan, N.; Lecomte, C.

[J. Am. Chem. Soc. 2006, 128, 13922-13931](#)

Advanced fine-tuning of Grubbs/Hoveyda Olefin metathesis catalysts...

Bieniek, M.; Bujok, R.; Cabaj, M.; Lugan, N.; Lavigne, G.; Artl, D.; Grela, K.

[J. Am. Chem. Soc. 2006, 128, 13652-13653](#)

New insight into the reactivity of pyridine-functionalized phosphine complexes of $\text{Ru}(\text{II})$...

Mothes, E.; Sentets, S.; Luquin, M. A.; Mathieu, R.; Lugan, N.; Lavigne, G.

[Organometallics 2008, 27, 1193-1206](#)

Directed formation of allene complexes...

Sentets, S.; Serres, R.; Ortin, Y.; Lugan, N.; Lavigne, G.

[Organometallics 2008, 27, 2078-2091](#)

Generation of α -phosphinocarbene complexes...

Valyaev, D.; Lugan, N.; Lavigne, G.; Ustynyuk, N. A.

[Organometallics 2008, 27, 5180-5183](#)

A stable Anionic N-heterocyclic carbene...

César, V.; Lugan, N.; Lavigne, G.

[J. Am. Chem. Soc. 2008, 130, 11286-11287](#)

Imidazol-2-ylidene-4-olate: an anionic NHC pre-programmed for further derivatization.

Benhamou, L.; César, V.; Gornitzka, H.; Lugan, N.; Lavigne, G.

[Chem. Comm. 2009, 4720-4722](#)