

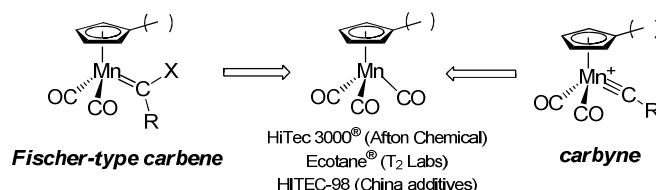
PhD proposal, Ministry of Higher Education and Research (MESR), october 2010

Team A « Molecular design of transition metal precatalysts » of the LCC
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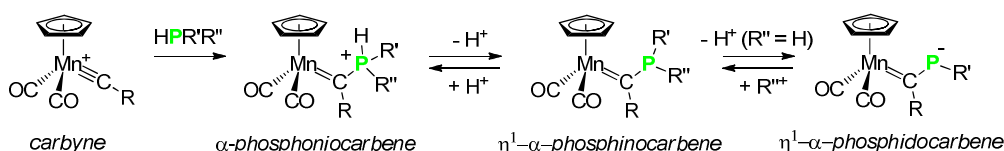
Carbyne complexes deriving from cymantrene - $\text{CpMn}(\text{CO})_3$ - in fine organic synthesis

Transition metals play a major role in organic synthesis as they offer a mean to stabilize short-lived organic fragments as *ligands* in *organometallic complexes*. Once stabilized, these organic fragments, can be further transformed within the coordination sphere of the metal, under steric and/or electronic control of the latter. Valuable chemicals are ultimately released upon de-coordination from the metal. Naturally, such a stoichiometric transition metal-mediated approach of organic synthesis is viable only if the metal-containing starting material is cost-effective. Cymantrene and methylcymantrene, $\text{CpMn}(\text{CO})_3$ and $\text{MeCpMn}(\text{CO})_3$, being produced on an industrial scale under the names of HITEC-98, and HiTec 3000 or Ecotane as antiknocking agents for gasoline, appear as suitable candidates. They are indeed reasonably priced (ca. 4-7 €/mole) and the metal fragment, $(\text{Me})\text{Cp}(\text{CO})_2\text{Mn}$, being relatively electron rich, is well suited to stabilize labile fragments such as carbene “ $\text{C}(\text{X})\text{R}$ ” and, even more importantly, *carbyne* fragments, “ CR ”, within cationic carbyne complexes $\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{R}$.

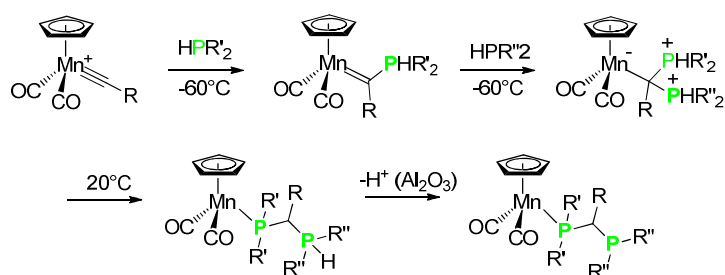


We are engaged in a program aimed at exploiting the availability and reactivity of such carbyne complexes with a view to valuable specific applications to fine organic synthesis.¹ Contrary to the generally accepted idea that such carbyne complexes are thermally unstable and difficult to handle, we have shown that they are actually totally insensitive to air and moisture provided they are associated with a bulky and inert counter-ion such as tetraphenylborate,² and yet remain extremely reactive once dissolved in organic solvents.

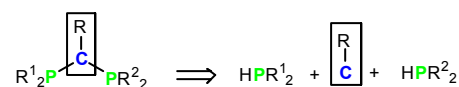
Our current objective is now to find applications of these complexes as sources of carbyne for the synthesis of original organophosphorus derivatives. Indeed, we have recently shown that a continuum α -P(III)-substituted transition metal carbene complexes – including scarce α -phosphonio- and η^1 - α -phosphinocarbene complexes, as well as hitherto unknown η^1 - α -phosphidocarbene complexes – is readily reachable from the highly electrophilic carbyne precursors $\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{R}$ upon simple addition of secondary or primary phosphines.³



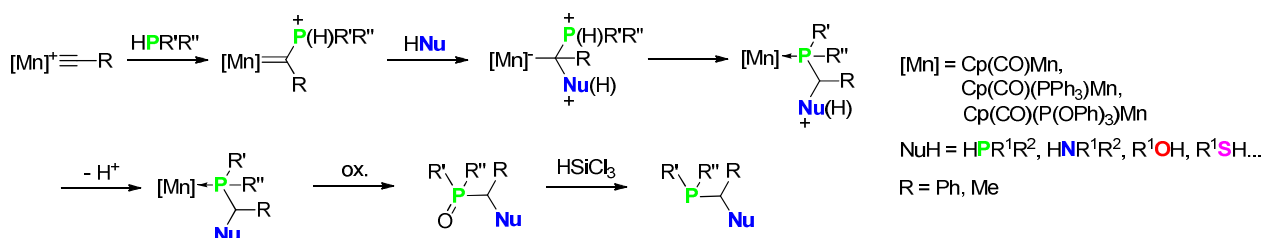
The main goal of the PhD work would be to define the reactivity of these unusual species, starting with α -phosphoniocarbene complexes, $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{R})\text{P}^+\text{HR}'_2$. Preliminary studies, have revealed that the latter species retain the very strong electrophilic character of their carbyne precursors, and are prone to uptake a second equivalent of phosphine to afford *in fine* the diphosphine complex $\text{Cp}(\text{CO})_2\text{MnPR}'_2\text{C}(\text{H})\text{RPR}''_2$ in a quantitative manner.



This unprecedented coupling reaction reveals manganese carbyne complexes may act as an effective source of carbyne fragment. We believe the present reaction has a strong potential for the specific design of valuable [hetero]bidentate ligands for use in catalysis.



The first objective of the PhD work will be to determine the scope and limitation of this new coupling reaction, opposing, in a sequential manner, a set of two mobile-H-containing nucleophiles, including secondary phosphines or diphosphine, and primary or secondary amines, thiols or alcohols, to cationic manganese carbyne complexes. The oxidative demetallation of the resulting phosphine-substituted manganese derivatives should afford the corresponding phosphinoyls, which should be easily converted into the target hetero-bidentate ligands by treatment with chlorosilanes, for instance.



In a first move, the reaction will be studied from *achiral* dicarbonyl carbyne species of the type $\text{Cp}(\text{CO})_2\text{Mn}^+\equiv\text{C}-\text{R}$, then from *chiral* $\text{Cp}(\text{CO})(\text{PR}_3)\text{Mn}^+\equiv\text{C}-\text{R}$ derivatives we have the experience of,⁴ and finally from optically active carbyne derivatives,⁵ the ultimate goal being to produce optically active heterobidentate ligands for use in asymmetric catalysis.

Requested profile: The candidate should be fluent in French or English. He/she should possess a good background in organic and organometallic chemistry, and have a definite interest for the *synthesis* aspect of research in chemistry. The experimental work will involve intensive use of Schlenk tube/vacuum line technique for the synthesis part, thin plate or column chromatography, selective crystallisation, or distillation techniques for the purification aspects, and IR, multinuclear NMR and X-ray diffraction techniques for the characterisation of the new compounds.

¹ Sentets, S.; Serres, R.; Ortin, Y.; Lugan, N.; Lavigne, G. *Organometallics* **2008**, *27*, 2078.

² Ortin, Y.; Lugan, N.; Mathieu, R. *Dalton Trans.* **2005**, 1620.

³ Valyaev, D.; Lugan, N.; Lavigne, G.; Ustynyuk, N. A. *Organometallics* **2008**, *27*, 5180.

⁴ Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S. Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735.

⁵ Fischer, H.; Weissenbach, K.; Karl, C.; Geyer, V. *Eur. J. Inorg. Chem.* **1998**, 339.