

3. Surface chemistry and catalysis

Nanoparticles and surface chemistry

a. Surface chemistry and non-innocent ligands

One of the characteristics of the group is to have developed an approach to the surface chemistry of NPs using the tools of molecular chemistry ([Acc Chem Res 2018](#)). This made possible to characterize the surface state of Ru ([Chem Eur J 2014](#)) and Pt NPs ([Nanoscale 2014](#)), to follow the evolution of Ru NPs surface during the hydrogenation of CO by a combined XPS and solid NMR approach ([ACS Catal 2014](#)) and, in collaboration with the MPC group, to propose a phase diagram of CO and H₂ on a Ru particle as a function of temperature and pressure ([Nanoscale 2016](#)). This also allowed the characterization of the surface state of bimetallic NPs such as RuRe ([Dalton 2017](#)).

An important work has also been performed on the study of a family of original non-innocent ligands: secondary phosphine oxides (SPOs). These are versatile ligands that participate in the heterolytic activation of H₂ in catalytic reactions of hydrogenation, H₂ transfer or hydroformylation (Fig. 1b).

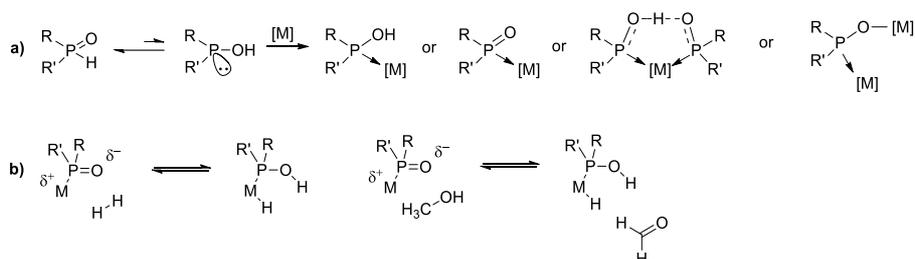


Fig. 1 a. Coordination modes of SPOs, b. Examples of heterolytic cleavage reactions involving SPOs.

This remarkable property has been exploited in association with Ru NPs in various catalytic systems to promote the hydrogenation of the ketone function in unsaturated (olefinic or aryl) ketones. While these tests confirm the contribution of the SPOs, the selectivity remains modest and a drop in activity is observed. On the other hand, very promising results have been obtained with iridium. First, this concerns the question of the actual catalytic species in systems involving NPs: in other words is it the NPs or leaching molecular complexes? This has been examined in detail in the case of iridium where the selectivity and activity of Ir NPs and complexes of Ir (I) (homochiral hydride mono and dimer complexes) and iridium NPs (coll. Y. Coppel, [PCCP 2017](#)) synthesized under analogous conditions (Fig. 2) ([Chem Eur J 2017](#)) have been compared.

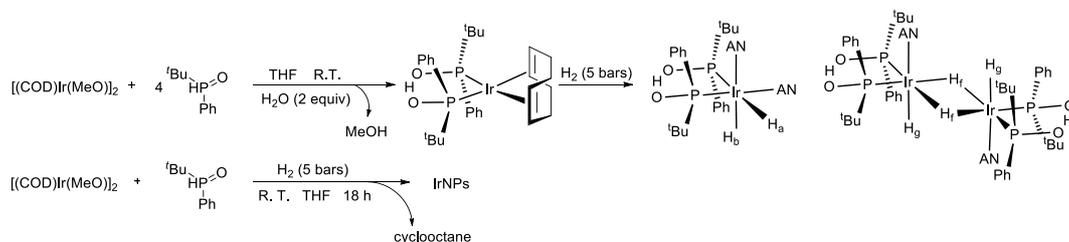
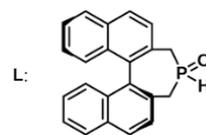


Fig. 2. Synthesis of complexes of Ir(I) and NPs of Ir.

While these two entities are active for the hydrogenation of ketones, they exhibit a totally different behavior with bifunctional reagents (enals, nitro-aldehydes, cyano-aldehydes, alkynals, etc.), thus showing that they are distinct catalysts, the complexes being more active and selective for the hydrogenation of the aldehyde function to unsaturated aldehydes (cinnamaldehyde, citral, furfural, etc.) ([Catal. Sci. & Technol. 2018](#)). The extension to systems of Ir NPs / chiral ligands was performed with the chiral SPO L (4,5-dihydro-3H-dinaphtho)[2,1-c:1',2'-e] phosphepine-4-oxide) giving rise to NPs of 1.4 (0.2) nm active in the enantioselective hydrogenation (56% ee) of prochiral ketones. This is the first example of an asymmetric hydrogenation by an unsupported catalyst and by Ir NPs ([Catal. Sci. Technol. 2016](#)).



A last part of the use of the SPO ligands concerns their association with the chemistry of the elements of the group 11 (Ag and Au) and the exploitation of the formal analogy existing between the anion derived from SPO (or basic form of SPO: phosphinito) and thiolates. In the case of gold, clusters of small size (50-100 atoms) are obtained. The nature of the SPO ligands varies according to the functionalization: thus in the case of aryl SPOs, only the anionic form is observed, whereas a mixture of the acidic and basic forms is observed for the alkyls as it is often observed in the molecular complexes. The latter, of composition Au₅₅(SPO)₃₀, are very selective for the hydrogenation of unsaturated

aldehydes leading to the corresponding unsaturated alcohols. The ligand plays a central role in the selectivity of the hydrogenation of enal or nitro groups ([JACS 2015](#)) and the mechanism studied by DFT confirms a transition state involving heterolytic cleavage ([ACS Catal. 2017](#)). The combination of silver and SPO ligands (but also SPS - secondary phosphine sulfide) was studied in collaboration with the University of Porto Alegre (Brazil). DFT studies show that the synthesis of complexes derived from SPO should be possible but in practice the procedures conventionally used for thiolates lead to the formation of polymeric species ([J Phys Chem C 2018](#)). In the case of SPS, the reactivity follows that observed for thiolates: two molecules of SPS react with each other and with the silver salt to form Ag₂S nanoclusters covered by "SPS-Ag staples". Alternative synthesis routes (in the presence of sulphide) are being studied and have provided access to new fluorescent clusters of the formula Ag₅₄S₂₀(SPS)₂₄ (Coll.Burrow, Federal University of Santa Maria, Brazil).

b. Synthesis of NPs stabilized par by carbene ligands

The N-heterocyclic carbenes (NHCs) are the ligands of choice for the stabilization of small-sized metallic NPs that present catalytic properties. The stability of the metal carbene bond on the NPs is surprising and, because of the absence of possible oxidation of this ligand under the usual conditions of use, the carbene-stabilized NPs are proved to be excellent catalysts, stable in air and water, for hydrogenation, CH activation and even oxidation reactions. We now have a very important range of systems that includes Ru, Rh, Pd, Ir, Pt, PtRu, and even Ni bimetals. The three main NHCs used are NHCs substituted on nitrogen by cyclohexyl, mesityl and di-isopropylphenyl radicals. Finally, a new class of ligands, the betaines, allowed the stabilization of NPs of small sizes. Without detailing all these results, we may mention the use of NHCs-stabilized NPs of Ru and Rh for the hydrogenation of aromatic and polyaromatic derivatives, in collaboration with S. Castillon in Tarragona ([ChemCatChem 2014](#), [Catalysis Sc&Tec 2015](#), [J. Cata. 2017](#)), the development of a method to prepare NPs systems stabilized by non-isolatable carbenes ([Chem Eur J 2015](#)), the synthesis of NPs containing long-chain carbenes that can be used in one-pot oxidation reactions followed by hydrogenation or the opposite, in collaboration with F. Glorius (Münster). Furthermore, betaine ligands have been used to stabilize Ru NPs of very small sizes. ([Chem Comm 2015](#)) and Pt NPs ([Chem Science 2017](#)) for which we have been able to highlight the transition from the molecular state to the metallic state by a follow-up of the Knight shift by NMR.

c.- NPs stabilized by hydrosoluble NHC ligands

In addition to the ligands presented previously, water-soluble carbenes, developed with Prof. E. de Jesus from the University of Alcalá, are used to maintain the NPs stability in the water and in the air while preserving their catalytic reactivity in hydrogenation and CH activation reactions. Controlling the synthesis of stable metal NPs in water is still a challenge in nanochemistry. The strategy used here involves a sulfonated NHC ligand to stabilize platinum and palladium NPs in water and in air, for an indefinite period of time. For this purpose, we have decomposed organometallic complexes containing the NHC ligand by different methods: by thermal decomposition or reduction under CO. In both cases, the coordination of NHC ligands on the surface of NPs has been demonstrated by solid state NMR. For Pt, a ¹³C-¹⁹⁵Pt coupling constant was unequivocally determined for the first time in a nanosystem (Fig. 3), the metal-ligand bond being of the same type as the one observed in molecular complexes. For Pd, the coordination of the NHC ligand could be unambiguously established by the Knight shift observation in the ¹³C resonance of the carbene carbon. Finally, we have shown that the surface of the NPs of Pd and Pt is still accessible to carry out catalytic reactions by testing them in the chemoselective hydrogenation of styrene to ethylbenzene. This work was done in collaboration with E. de Jesus. All these experiments required a strong expertise in MAS NMR (coll. Y. Coppel, LCC, [Angew Chem 2014](#), [Angew Chem 2017](#), [Chem Eur J 2017](#), [Dalton Trans 2018](#)).

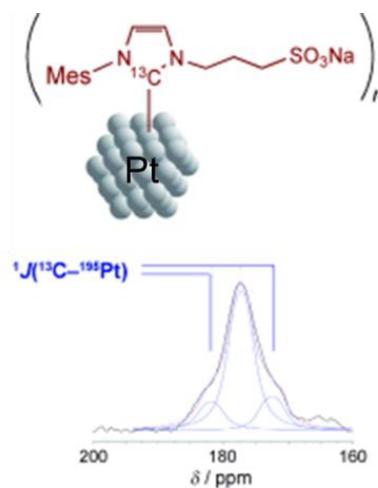


Fig. 3 : RMN ¹³C spectrum of Pt NPs stabilized by a water-soluble NHC.

d. NPs stabilized on SILP (Supported Ionic Liquid Phases)

The preparation of bimetallic NPs is an efficient strategy for modulating the catalytic properties of heterogeneous catalysts. In this context, FeRu NPs were synthesized on SILP on silica matrices. The presence of iron in the Ru NPs not only makes it possible to control their selectivity by suppressing their ability to hydrogenate aromatic rings, but also increases their activity for the reduction of ketones. The addition of an acidic ionic liquid phase allowed the hydrodeoxygenation of the carbonyl groups, while preserving the aromatic cycles (coll. W. Leitner du Max Planck Institute de Mülheim, [ACS Catal 2016](#), [Angew Chem 2018](#)).

e. CH activation for the deuteration of molecules of biological interest

C-H bond activation is a powerful tool for the synthesis or the functionalization of organic compounds. This method allows, among other things, rapid access to deuterium labeled compounds, which may be of interest for mechanistic studies in biology and organic or organometallic chemistry. Besides, the emergence of metabolomics and the research for new drugs has increased the demand for isotopically labeled compounds. For the synthesis of such molecules, the isotopic exchange after synthesis is much preferable to a synthetic route from constituent blocks. Recently, the group developed a methodology for the efficient labeling of nitrogen substrates, by catalytic H / D exchange reactions with ruthenium NPs, in a regioselective manner. ([Angew Chem 2013](#)). By using Ru NPs stabilized with water-soluble carbenes, we realized, in D₂O, the first enantioselective labeling of amino acids and small peptide fragments. ([Angew Chem 2015](#)). We have shown that this chemistry can be also applied to molecules containing sulfur ([Chem Comm 2018](#)) and to nucleic bases and oligonucleotides ([Angew Chem 2019](#)). Finally, in collaboration with G. Lippens (LISBP, INSA Toulouse), we have developed an NMR method (Chemical Shift Disturbance) to highlight the interaction of amino acids and peptides with NPs and to explain the selectivity of the catalytic reactions. ([Chem Comm 2017](#)). The H/D exchange was also used for the catalytic preparation of deuterated phosphine des ligands ([Chem Comm 2015](#)).

The continuation of the project consists in quantifying the reactivity of these NPs by controlling the nature of the catalyst (in particular NPs of Ir and Ni, Fig. 4) and their chemical order (RuPt), to extend the range of possible substrates (alcohols, phospholipids, etc.) and avoid undesirable reactions (reduction of aromatic rings, hydrogenolysis, etc.). This work is part of a PhD thesis funded by the European project ITN ISOTOPICS. Several collaborations were established within the framework of this project: G. Pieters from CEA Saclay, V. Derdau from Sanofi Frankfurt, and S. Roy from Sanofi Chilly-Mazarin.

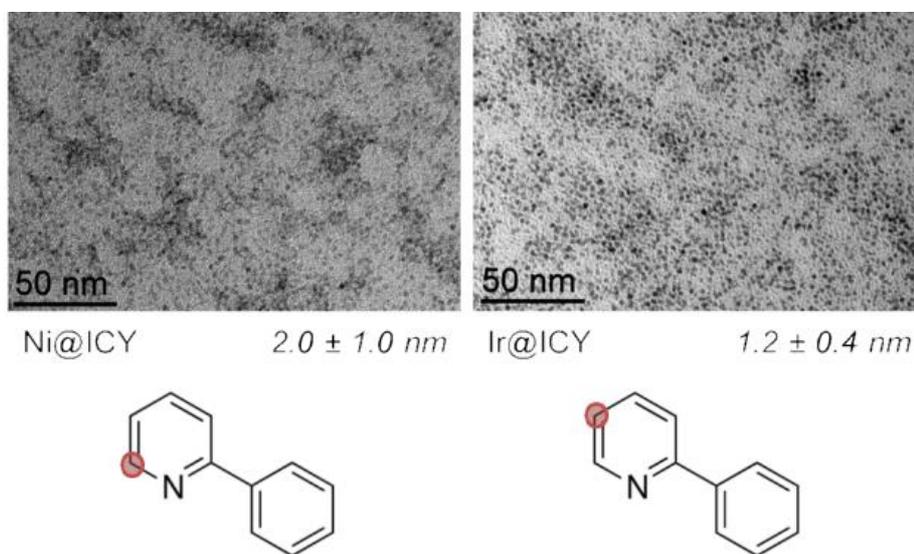


Fig. 4 : TEM images of nickel and iridium NPs stabilized by NHC ligands et regioselectivity in H/D exchange.