5) *Homogeneous Catalysis*

Over the years, our group examined several catalytic reactions, some of which have already been mentioned above.

In the early 1980s, we converted CO_2 into higher-added-value lactones by telomerization with butadiene, using a Pd(II) catalyst which was the first metal complex to allow reversible CO_2 fixation under ambient conditions through C-C bond formation (*J. Am. Chem. Soc.* 1981, *103*, 5115; *J. Am. Chem. Soc.* 1988, *110*, 3207). This area was reviewed in *Chem. Rev*. 1988, *88*, 747. The resulting δ-lactone could be converted into recyclable polyesters (see section 2) (*Nature Comm*., 2024, 15:8698).

The isolation of rare monohapto-allyl Pd(II) complexes, a bonding mode shown to be triggered by the nature of the solvent, led to the demonstration of their enhanced reactivity compared to the ubiquitous η^3-allyl complexes (*Organometallics*, 2001, *20*, 2966; *J. Chem. Soc., Dalton Trans.* 2003, 507). This is of direct relevance to several catalytic transformations involving allyl intermediates.

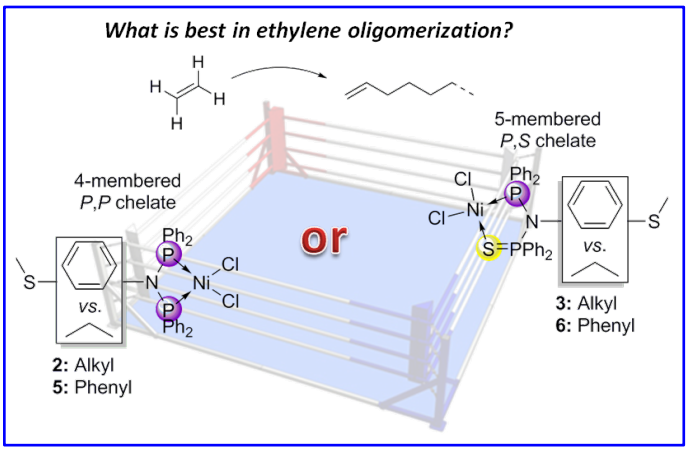
Using functional phosphinooxazoline ligands, wee obtained very active Ru complexes for hydrogenation transfer of ketones (*J. Chem. Soc., Dalton Trans.* 1999, 589).

We also reported Fe-Pd and Fe-Ni bimetallic catalysts which were the most active catalysts known for the dehydrogenative coupling of stannanes (see above). The field was reviewed in *Chem. Rev*. 2000, *100*, 3541-3552.

Alkane activation using neutral phosphinoenolate Rh(I) complexes, which are soluble in neat alkanes, was successfully investigated (*Organometallics* 1996, *15*, 5551).

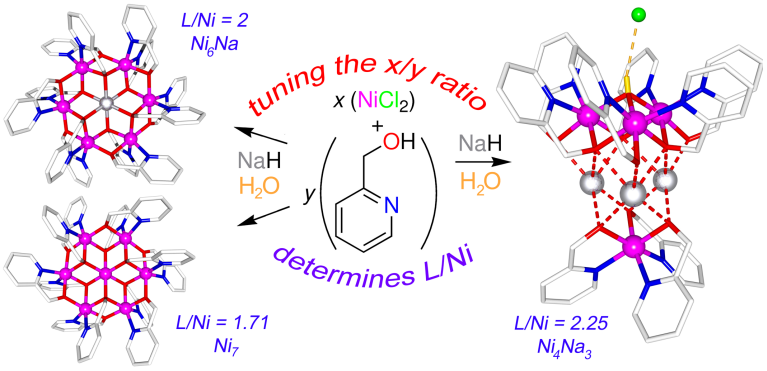
Our group also reported a novel cobalt phosphine complex-promoted double C-Cl activation of CH_2Cl_2 leading to transfer of the CH_2 group to phosphorus (*Chem. Commun*. 2009, 890). It extended this reaction to Ni(II) complexes (*Organometallics*, 2015, *34*, 2255).

As part of a long-standing collaboration in homogeneous catalysis with the Institut Français du Pétrole (now IFP Energies nouvelles), first with Yves Chauvin (Nobel laureate) and then Hélène Olivier-Bourbigou, to study selective catalysts for the oligomerisation of ethylene. Some of his results have been summarised in *Acc. Chem. Res*. 2005, *38*, 784. Functional ligands have led to efficient and selective Ni catalysts and systematic comparisons between structurally related precatalysts have been very fruitful. Ethylene oligomerisation using iron complexes was also investigated (*Chem. Commun*. 2014, *50*, 1398-1407).

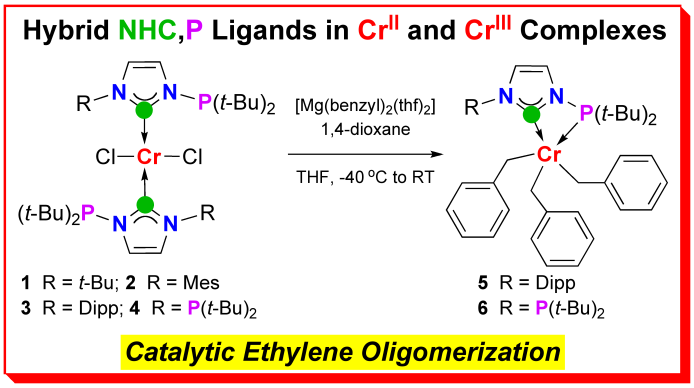


A. Ghisolfi, C. Fliedel, V. Rosa, K. Yu. Monakhov, P. Braunstein. Combined Experimental and Theoretical Study of Bis(diphenylphosphino)(*N*-thioether)amine-Type Ligands in Nickel(II) Complexes for Catalytic Ethylene Oligomerization.
Organometallics, **2014**, *33*, 2523-2534.

In the course of these studies, unexpected mixed Ni-Na coordination clusters were isolated that shed light on the nature of species produced in situ during catalytic transformations. Some of these clusters are endowed with Single-Molecule Magnet behaviour (*Angew. Chem. Int. Ed.* 2010, *49*, 4443; *Chem. Commun*. 2010, *46*, 6461; *ChemPlusChem*. 2015, *80*, 1312).



Developing the use of functional NHC ligands, our group reported novel *N*-phosphanyl- and *N*,*N*'-diphosphanyl-NHC chromium complexes and their properties in catalytic ethylene oligomerisation. In some cases, exclusively 1-hexene and 1-butene were formed.



P. Ai, A. A. Danopoulos, P. Braunstein *N*-Phosphanyl- and *N*,*N*'-Diphosphanyl-N Heterocyclic Carbene Chromium Complexes: Synthesis, Structures and Catalytic Ethylene Oligomerization. *Organometallics*, **2015**, *34*, 4109-4116.

We also performed early studies on the stepwise Pd-promoted coupling of ethylene, CO and functional monomers (*Angew. Chem. Int. Ed*. 2000, *39*, 2867-2870).

Our pioneering work related to mixed-metal clusters-derived **heterogeneous catalysis** was mentioned in section 1).