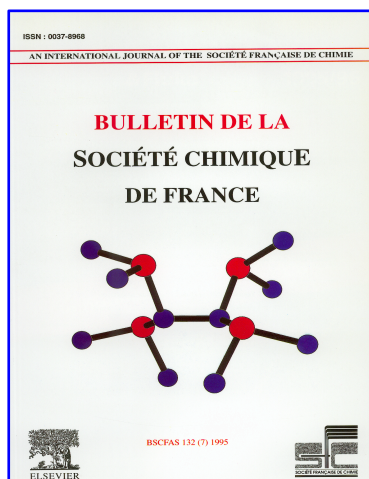


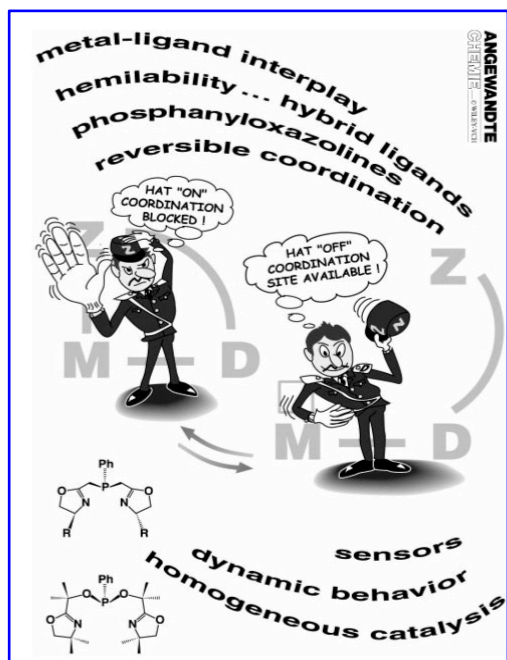
## 2) Functional Ligands, Hemilability, Metal Complexes and Applications.

Our interest for short-bite, assembling ligands led us to study the reactivity of the anion derived from  $\text{CH}_2(\text{PPh}_2)_2$  (dppm). We found that oxidative P-C coupling leads to ylids, whereas C-C coupling yielded this new  $\text{C}_2$  chiral tetraphosphine, whose existence has long been questioned in the literature.



P. Braunstein, R. Hasselbring, A. DeCian, J. Fischer.  
Polyfunctional Ligands: Carbon-Carbon Oxidative  
Coupling of  $[\text{HC}(\text{PPh}_2)_2]^-$  and Crystal Structure of the  
New Tetraphosphine Ligand  $(\text{Ph}_2\text{P})_2\text{CH}-\text{CH}(\text{PPh}_2)_2$   
*Bull. Soc. Chim. Fr.* **1995**, 132, 691.

We were also pioneers in the use and conceptual classification of hemilabile ligands. In this context, we developed new ligands that allow better control of the metal-ligand interactions and of the reactivity of the metal complexes in several important stoichiometric/catalytic reactions.



P. Braunstein, F. Naud  
Hemilability of Hybrid Ligands and the Coordination  
Chemistry of Oxazoline-Based Systems  
*Angew. Chem. Int. Ed.* **2001**, 40, 680-699.

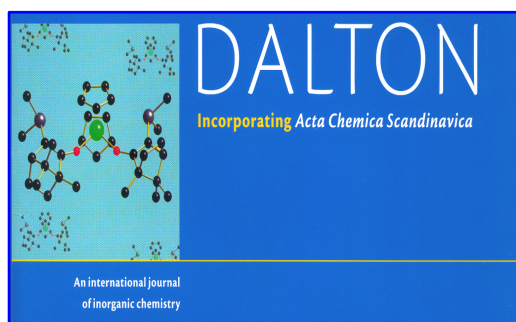
Surprisingly, some N,P,N phosphine-oxazoline tridentate ligands were found to behave as N,N rather than P,N chelates towards metal centres like Fe or Co, which otherwise readily form phosphine complexes. Such observations have a direct impact on the ligand bite angle and the subsequent reactivity of the metal complex.



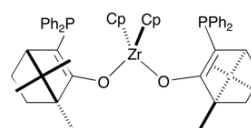
A. Kermagoret, P. Braunstein  
 Contrasting Bonding Modes of a Tridentate Bis(oxazoline)phosphine Ligand in Cobalt and Iron vs. Palladium Complexes: Unprecedented *N,N*-coordination for a N,P,N Ligand.  
*Dalton Trans.* **2008**, 585-587.

Our group developed over the years a very rich chemistry of functional ligands of the P,O-, P,N-, and N,O-type. Such phosphine ligands, in particular the ketophosphines and their corresponding enolates, are relevant to the industrial SHOP process of ethylene oligomerisation. An overview is provided in *Chem. Rev.* 2006, *106*, 134-159.

A new chiral metalladiphosphine for early-late chemistry was obtained, and a D-camphor-based zirconium enolato phosphine was structurally characterised and led to an interesting rearrangement in heterobimetallic Zr/Pd complexes.

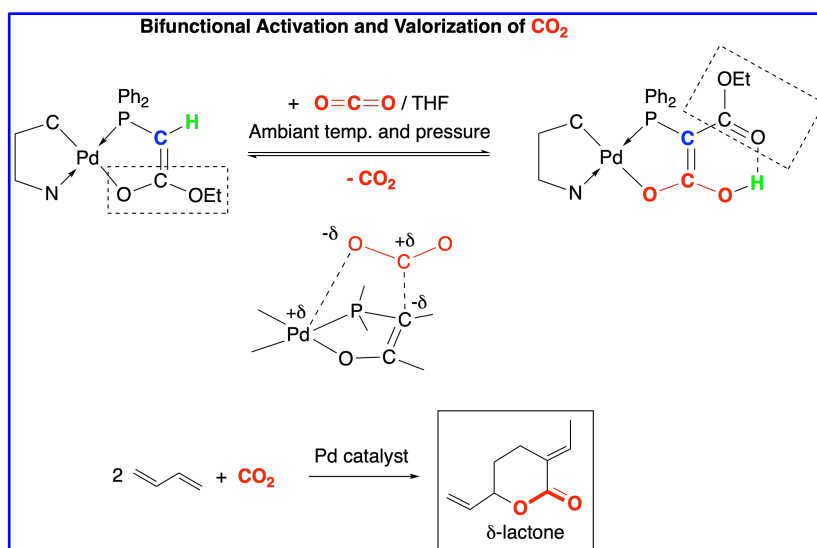


C. Mattheis, P. Braunstein, A. Fischer. A New Chiral Metalladiphosphine for Early-Late Chemistry. Crystal Structure of a D-Camphor-Based Zirconium Enolato Phosphine and Rearrangement of Heterobimetallic Zr/Pd Complexes.  
*J. Chem. Soc., Dalton Trans.* **2001**, 800-805.

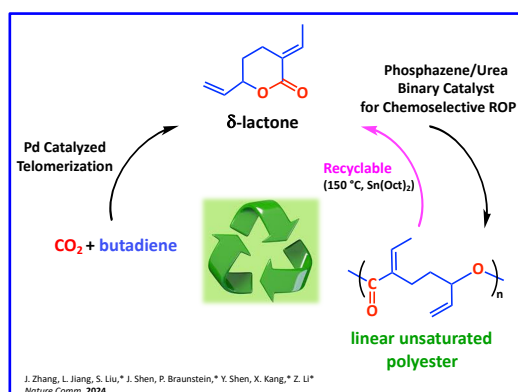


We isolated rare monohapto-allyl Pd(II) complexes and found that their occurrence may be triggered by the nature of the solvent. We evidenced their enhanced reactivity compared to that of the ubiquitous  $\eta^3$ -allyl complexes, which is of direct relevance to several catalytic transformations involving allyl intermediates (*Organometallics*, 2001, *20*, 2966; *J. Chem. Soc., Dalton Trans.* 2003, 507-509).

In the early 1980s, our group **converted CO<sub>2</sub> into a higher-added-value  $\delta$ -lactone** by telomerization with butadiene, using a Pd(II) catalyst, which was the first metal complex to allow reversible CO<sub>2</sub> fixation under ambient conditions through C-C bond formation. He reviewed this area in *Chem. Rev.* 1988, *88*, 747. This lactone was recently used for **the synthesis of polyesters that can be recycled back to the original monomer**.



- \* P. Braunstein, D. Matt, Y. Dusaouy, J. Fischer, A. Mitschler, L. Ricard. Coordination properties of (diphenylphosphino)acetonitrile, ethyl (diphenylphosphino)acetate, and corresponding carbanions. Characterization of a new facile reversible CO<sub>2</sub> insertion into palladium(II) complexes. *J. Am. Chem. Soc.* **1981**, *103*, 5115.
- \* P. Braunstein, D. Matt, D. Nobel. Carbon dioxide activation and catalytic lactone synthesis by telomerization of butadiene and CO<sub>2</sub>. *J. Am. Chem. Soc.* **1988**, *110*, 3207.
- \* P. Braunstein, D. Matt, D. Nobel. Reactions of Carbon Dioxide with C-C Bond Formation Catalyzed by Transition Metal Complexes. *Chem. Rev.* **1988**, *88*, 747-764.



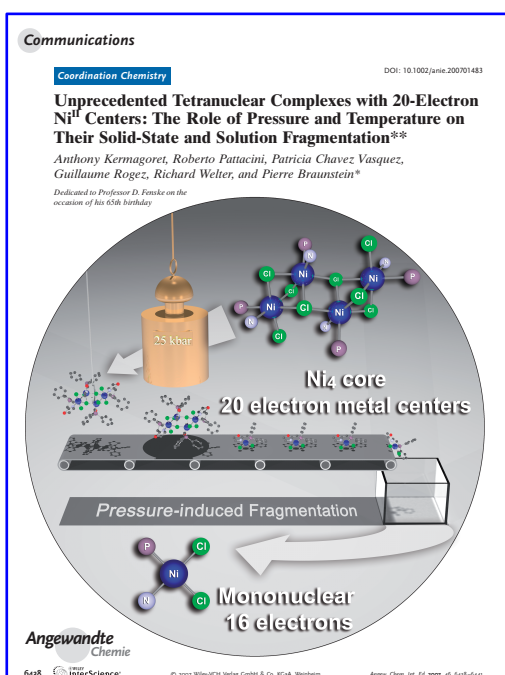
J. Zhang, L. Jiang, S. Liu, J. Shen, P. Braunstein, Y. Shen, X. Kang, Z. Li. Bifunctional and Recyclable Polyesters by Chemoselective Ring-Opening Polymerization of a  $\delta$ -Lactone Derived from CO<sub>2</sub> and Butadiene. *Nature Comm.*, **2024**, 15:8698.

We also reported a novel **double C-Cl activation** of CH<sub>2</sub>Cl<sub>2</sub> promoted by cobalt or nickel phosphine complexes, leading to transfer of the CH<sub>2</sub> group to phosphorus (*Chem. Commun.* 2009, 890; *Dalton* 2013, 42, 4208; *Organometallics*, 2015, 34, 2255).

Other achievements in homogeneous catalysis include the **selective oligomerisation of ethylene** with Ni(II) catalysts (*Acc. Chem. Res.* 2005, 38, 784), and more recently, with a novel class of Fe-based catalysts (Feature Article in *Chem. Commun.*, 2014, 50, 1398-1407), the **activation of alkanes** with phosphinoenolate Rh(I) complexes which are soluble in neat alkanes, the **transfer hydrogenation of ketones** using new phosphinooxazoline Ru(II) complexes, and Fe-Pd and Fe-Ni bimetallic catalysts which are currently the most active for the **dehydrogenative coupling of stannanes** (*Chem. Rev.* 2000, 100, 3541).

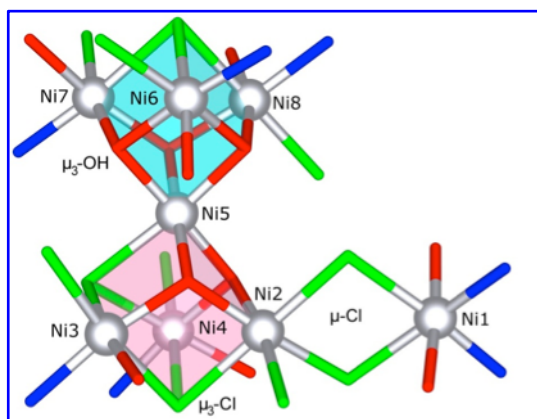
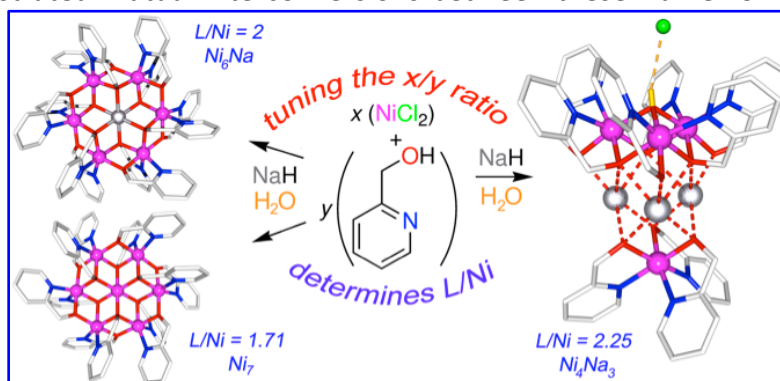
In the course of recent studies on Ni(II) precatalysts for ethylene oligomerisation, we discovered an unusual phenomenon of pressure-induced, unprecedented decrease in the nuclearity

of a tetranuclear coordination complex. Also, we found novel coordination clusters endowed with Single-Molecule Magnet behaviour.



A. Kermagoret, R. Pattacini, P. Chavez-Vasquez, G. Rogez, R. Welter, P. Braunstein. Unprecedented Tetranuclear Complexes with 20-Electron  $\text{Ni}(\text{II})$  Centers: The Role of Pressure and Temperature on Their Solid-State and Solution Fragmentation. *Angew. Chem. Int. Ed.* **2007**, 46, 6438–6441.

Using pyridine-alcohol and oxazoline-alcohol ligands with different stereoelectronic properties, we characterised a range of polynuclear  $\text{Ni}(\text{II})$  complexes based on incomplete or connected cubane-type frameworks endowed with catalytic properties for ethylene oligomerisation and magnetic behaviour. The demonstrated mutual interconversions between these frameworks are very relevant to their reactivity and *in-situ* catalytic behaviour. These studies have further emphasised the importance of isolating and fully characterising metal complexes before studying their reactivity because their structures are often unpredictable.

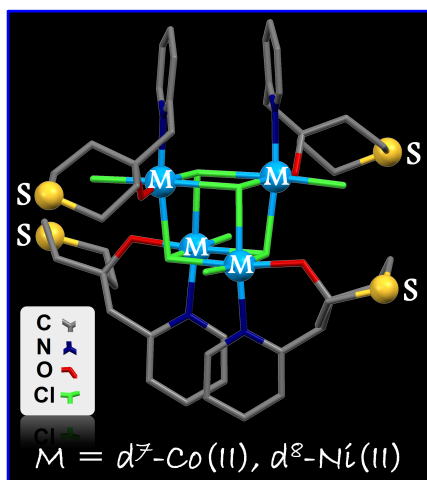


J. Zhang, P. Teo, R. Pattacini, A. Kermagoret, R. Welter, G. Rogez, T. S. A. Hor, P. Braunstein. Structural Effects of Sodium Cations in Polynuclear, Multicubane-Type Mixed  $\text{Na-Ni}$  Complexes. *Angew. Chem. Int. Ed.* **2010**, 49, 4443.

S. Hameury, L. Kayser, R. Pattacini, G. Rogez, W. Wernsdorfer, P. Braunstein. Synthesis of cubane-type  $\text{Ni}(\text{II})$  complexes from pyridyl-alcohol ligands; their single-molecule magnet behaviour. *Dalton Trans.*, **2013**, 42, 5013.



The addition of thioether functions to pyridine-alcohol ligands yielded new  $M_4Cl_4$  cubane-type cobalt(II) and nickel(II) complexes and allowed their subsequent binding to Au surfaces (*Dalton Trans.* 2014, 43, 7847).



A. Ghisolfi, K. Yu. Monakhov, R. Pattacini, P. Braunstein, X. López, C. De Graaf, M. Speldrich, J. Van Leusen, H. Schilder, P. Kögerler. A Comparative Synthetic, Magnetic and Theoretical Study of Functional  $M_4Cl_4$  Cubane-Type Co(II) And Ni(II) Complexes. *Dalton Trans.* **2014**, 43, 7847.

Combined Magnetic and Theoretical Studies of the New Isostructural  $M_4Cl_4$  Cubane-Type Co (**1**) and Ni (**2**) Complexes Emphasize their Different Spin Behaviour and **2** is Considered a Single Molecule Magnet.

We used metalloligands not only to assemble higher nuclearity metal complexes in a controlled manner, but also to connect Au-coated silica Janus-type micro-spheres, observable under an optical microscope, and thus validate the anchoring procedures applied to nano-objects. This approach allows testing of anchoring ability through optical visualisation of the pairing of the spheres and to translate at the microscopic level events occurring at the nanoscale without requiring sophisticated equipment.

