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A – Catalysis and the Periodic Table

Hybrid Ligands for Metal Complexes, Catalysts and Nanomaterials

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ACADEMIA DAS CIÊNCIAS
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Celebratory Symposium

A – Catalysis and the Periodic Table

Hybrid Ligands for Metal Complexes, Catalysts and Nanomaterials

Pierre Braunstein[4]

Pierre Braunstein received his PhD in Inorganic Chemistry from the University Louis Pasteur (ULP) Strasbourg (France) and then spent a year at University College London, with Profs. R. S. Nyholm and R. J. H. Clark, as a Royal Society/CNRS post-doctoral fellow. After earning his State Doctorate from ULP, he was awarded an Alexander-von-Humboldt post-doctoral fellowship to spend a year at the Technical University Munich with Prof. E. O. Fischer (Nobel Laureate).

He rose through the ranks at the CNRS, became Research Director Exceptional Class and is now Emeritus Research Director and «professeur conventionné» of the University of Strasbourg. He also holds various positions in China: at Qingdao University of Science and Technology, Zhejiang University, Soochow University and Yangzhou University.

His broad research interests lie in the inorganic and organometallic chemistry of the transition and main group elements, where he has (co)authored ca. 600 scientific publications and review articles. They cover the synthesis and coordination/organometallic chemistry of heterofunctional ligands, the study of hemilabile metal-ligand systems, of strongly dipolar quinonoid zwitterions, of low oxidation state metal-metal bonded (hetero)dinuclear and cluster complexes and of magnetic coordination clusters. Focused on fundamental aspects, his research has also led to numerous applications, ranging from homogeneous catalysis, e.g. ethylene oligomerization, to cluster-derived nanoparticles for heterogeneous catalysis and nanosciences.

He has received numerous awards and honors from France, China, Germany, India, Italy, Japan, Portugal, Singapore, Spain, The Netherlands and the United Kingdom. He is a member i.a. of the French Academy of Sciences, of the German National Academy of Sciences Leopoldina and Foreign Corresponding Member of the Academy of Sciences of Lisbon (Portugal) and Zaragoza (Spain). Since 2015, he is Head of the Chemistry Division of the European Academy of Sciences.

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INTRODUCTION

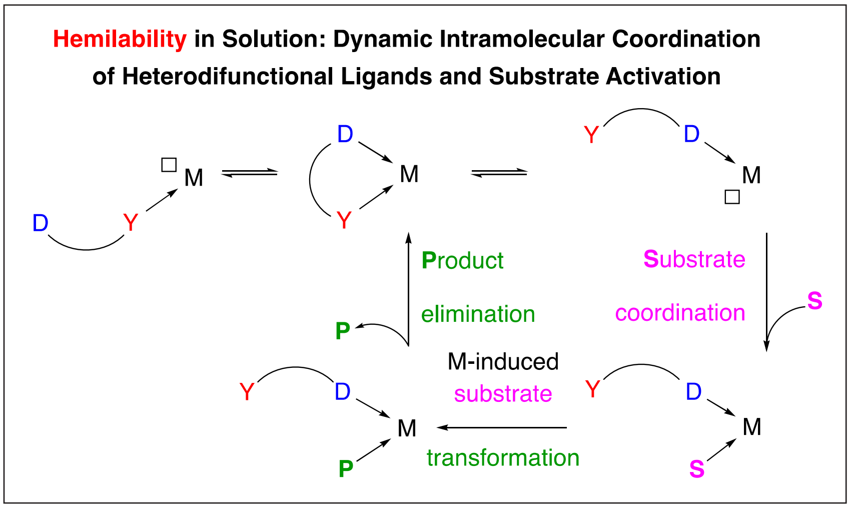
To celebrate the 150th Anniversary of the publication of *The Principles of Chemistry* by Mendeleev, UNESCO has declared 2019 the International Year of the Periodic Table. Numerous publications have recalled the history of its development and events have been organized on this occasion around the world. For example, the Academy of Sciences of Lisbon contributed to this celebration through a Symposium held on October 3, 2019,[1] and the French *Académie des Sciences* also dedicated an afternoon to this celebration on November 19, 2019.[2] The classification of the elements certainly represents one of the most fruitful achievements in modern science and the Periodic Table occupies an iconic position in chemistry, knowing no linguistic or geographical border since the language of chemistry is international. Its current form is reproduced in almost every undergraduate inorganic textbook and displayed in chemistry classrooms and lecture theatres.

Through the publication of his book "*The Principles of Chemistry*" in 1869, Dmitri Ivanovitch Mendeleev offered a classification of the 63 elements known that allowed him not only to rationalize several properties and explain similarities between elements but also to predict the existence of elements that remained to be discovered. Although Mendeleev has been rightly given the major credit for this achievement, he recognised the major role played over an 80-year timespan by scientists such as Lavoisier, Dalton, Berzelius, Prout, Döbereiner, Dumas, Cannizzaro, von Pettenkofer, Gmelin, Odling, Béguyer de Chancourtois, Newlands and Meyer. The predictive power of Mendeleev's classification was beautifully demonstrated when François Lecoq de Boisbaudran discovered gallium in 1875, the existence of which had been predicted by Mendeleev 6 years earlier (under the name eka-aluminum), when Lars Fredrik Nilson discovered scandium in 1879 (the eka-boron of Mendeleev) and Clemens Winkler discovered germanium in 1886 (eka-silikon). In 1875 Mendeleev published in the *Comptes Rendus de l'Académie des sciences* a version of his classification that prefigures the Periodic Table as we know it today, with 118 elements organized in 7 periods and 18 columns.[3]

The year 2019 also marks the 100th anniversary of the death of the Nobel laureate Alfred Werner (12 Dec. 1866 – 15 Nov. 1919), the founder of Coordination Chemistry. He was the first to propose correct structures for coordination compounds containing complex ions, in which a central transition metal atom is surrounded by neutral or anionic ligands, such as NH_3, H_2O or Cl^-, respectively. Since these pioneering days, the design of new functional ligands and complexes has become a major endeavour in chemistry, only limited by the chemists' imagination and triggered by fast developments in synthetic organic methodologies and increasing (catalytic) use of metals, that provide access to new molecules or solids endowed with remarkable chemical or physical properties.[4] Furthermore, the growing research effort directed toward the study of the structural, catalytic and physical properties of coordination/organometallic metal complexes is rewarded by their ever-increasing diversity of applications and performances. In the following, we shall provide an extended abstract of the lecture given on the occasion of the Celebration of the 150th Anniversary of the Periodic Table by the Academy of Sciences of Lisbon on October 3, 2019.

HEMILABILITY: A POWERFUL CONCEPT RELEVANT TO HOMOGENEOUS CATALYSIS

Catalysis is gaining increasing significance, both in academia and in industry, because it allows chemical transformations to be performed with lower activation energies, higher selectivity and atom economy, thus reducing energy costs and waste production. Catalysis is a major component of the guiding principles of green or sustainable chemistry.[5-7] To achieve a better fine-tuning of the stereoelectronic properties of the metal centres involved in stoichiometric or catalytic transformations, a huge diversity of functional ligands has been designed to control their coordination sphere. In particular, various hybrid ligands, which contain chemically different donor groups, such as hard and soft donors, have been developed. After coordination to one or more metal centres, their potential ability to undergo dynamic behaviour resulting from partial de-coordination of the weaker link is directly relevant to key steps in homogeneous catalysis processes (Scheme 1). This phenomenon, which is readily monitored by variable-temperature NMR spectroscopy, temporarily liberates a coordination site that can be used by a substrate molecule, which upon coordination to the active metal site, will be transformed and the liberation of the product will be assisted by chelation of the hybrid ligand.[8,9] This dynamic feature characterizes a ligand/metal couple and has been coined hemilability *ca*. 40 years ago,[10] although the phenomenon itself had been observed earlier.[11]

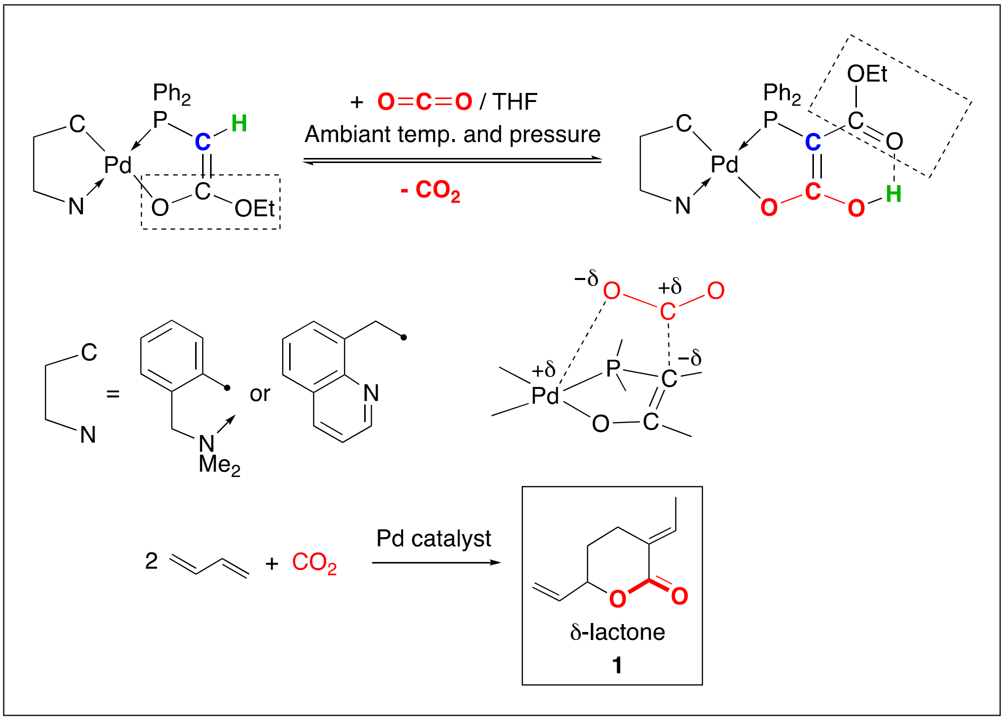


Scheme 1.
Relevance of hemilability of a coordinated hybrid ligand to catalytic steps.

ACTIVATION AND TRANSFORMATION OF CO_2

Using hybrid phosphine ligands containing an ester-enolate group,[12] we unexpectedly discovered a Pd(II) complex that is capable of reversibly binding CO_2 at room temperature and under atmospheric pressure (Scheme 2).[13]

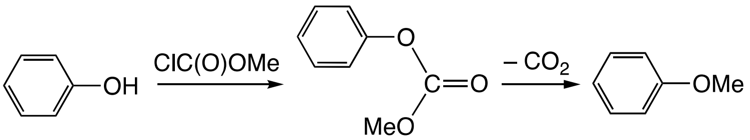
In this process, the P-donor arm remains coordinated to Pd throughout whereas the O-Pd bond opens and liberates a site for one of the oxygen atoms of the CO_2 molecule after nucleophilic attack of the enolate carbon atom to the carbon atom of CO_2 has led to C-C bond formation. Migration of the PCH proton results in a stabilizing H-bonding interaction in a six-membered ring. The reverse steps occur when nitrogen is bubbled through a solution of the complex under ambient conditions, which causes the liberation of the CO_2 molecule. In both forward and backward reactions, the oxygen-palladium bond formed and broken is in trans position to the σ–bonded carbon atom of the



Scheme 2.
Activation and valorisation of CO_2

cyclometallated spectator ligand, which has a strong trans-effect and trans-influence. These CO_2 carriers provided the first examples where reversible CO_2 fixation by a transition-metal complex has been fully characterized by X-ray diffraction and shown to occur by carbon-carbon bond formation.[14] Interestingly, no fixation of CO_2 was observed when the ester-enolate group was replaced by a keto-enolate (OEt replaced by Ph), illustrating the importance of the nucleophilicity of the enolate carbon centre that undergoes nucleophilic attack on the carbon atom of CO_2 while the electrophilic centres (Pd(II) and H^+) stabilize the oxygen atoms of CO_2. Thus, each atom of this triatomic molecule is involved in the process, which can be viewed as a trifunctional activation of CO_2. These palladium complexes were used to catalyse the telomerisation of CO_2 with butadiene to afford the δ–lactone **1** (Scheme 2).[15] This work also showed that CO_2 activation by a metal complex was necessary for catalytic activity but may not always be sufficient. After catalyst optimisation, we achieved a 49% yield and 96% selectivity in δ–lactone. Selectivity is the major issue since unreacted butadiene can be readily recycled whereas the formation of other CO_2-containing products, *e.g.* acids and esters, requires subsequent separation steps. It is interesting to note that more than 30 years later, this chemistry remains of prime interest and while the catalyst performances have not been significantly improved,[16] applications of the product appear promising.[17]

The properties and reactivity of alkyl carbonates remain of high academic and industrial interest because they are important, versatile and biodegradable chemical intermediates with moderate toxicity and environmental impact.[18] They may be used *e.g.* for the alkylation of various organic substrates. We reported a rare case of a Lewis acid catalysed formation of anisole or ethoxybenzene by decarboxylation of methyl or ethyl phenyl carbonate, respectively.[19] An Al(III) compound, such as $AlCl_3$ or $Al(OAr)_3$, was used as catalyst in a [Al]/[methyl phenyl carbonate] molar ratio of 0.0036. Facilitating this difficult decarboxylation step is important and O-alkylation of phenol can then be readily achieved in 2 steps using first an alkyl chloroformate and then catalytic decarboxylation of the organic carbonate (Scheme 3).

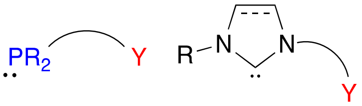


Scheme 3.
O-Alkylation of phenol by reaction of methyl chloroformate followed by catalytic decarboxylation of methyl phenyl carbonate affording anisole.

PHOSPHINO-ENOLATES AND FUNCTIONAL N-HETEROCYCLIC CARBENES

It is noteworthy that phosphino-enolates of the type seen above behave as 3 electron donor P,O-type chelating ligands with numerous metals and, together with closely related P,N-type chelates, lead to an impressive scope of very diverse catalytic applications,[12] ranging from CO_2 activation (see above) when coordinated to Pd(II), ethylene oligomerization with Ni(II) (SHOP-type industrial process),[20,21,22] transfer-hydrogenation with Ru(II) (with related 3 electron donor anionic phosphinooxazoline chelates)[23] to alkane activation with Rh(I).[24] These examples serve to illustrate the remarkable impact of hybrid ligands in homogeneous catalysis.[8,9,12]

Triggered in particular by the similarities between phosphine and N-heterocyclic carbene (NHC) donors – notwithstanding their differences – the field of NHC ligands is enjoying exponential growth and an increasing number of hybrid ligands are reported that associate NHC with other types of donor functions (Scheme 4). NHC ligands offer advantages over phosphines, such as a lower oxygen--sensitivity and formation of generally more robust bonds to metals. Recent examples illustrate the very interesting and often unique features and properties that functional NHC ligands confer to their metal complexes.[25-34]



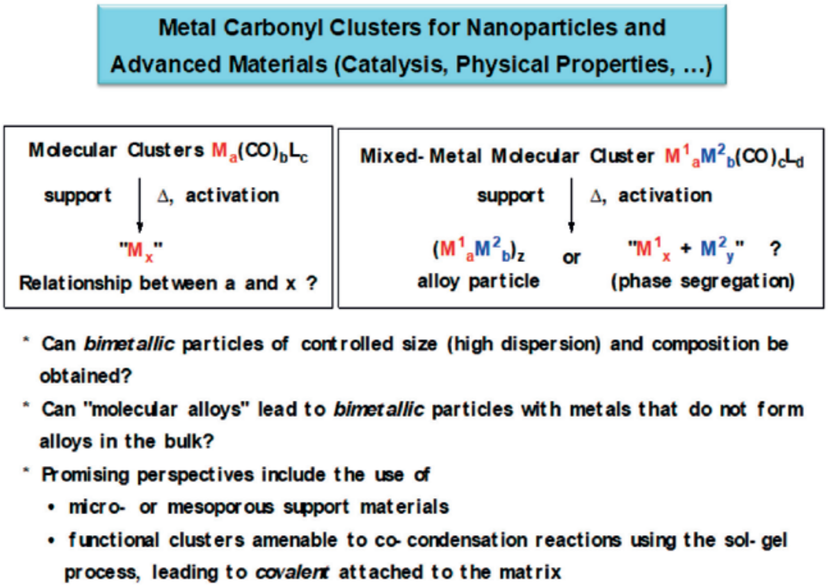
Scheme 4.

METAL CARBONYL CLUSTERS: WELL-DEFINED PRECURSORS TO NANOPARTICLES

Although the notion of metal-metal bonds in molecules was inexistent in the days of Alfred Werner, the field of metal clusters is now well established in chemistry and thousands of molecules containing metal-metal bonds between similar (homometallic) or different (heterometallic) metal centres have been prepared and characterized, usually by X-ray diffraction, the « ultimate » method.[35]

Metal clusters are fascinating objects, and both experimentalists and theoreticians worldwide aim at unravelling and understanding their often aesthetically most pleasing structures, their bonding features, the occurrence within their core of metallophilic interactions at distances inferior to the sum of the van der Waals radii,[36] their stoichiometric and catalytic properties in chemistry,[37] including in the gas phase,[38] and their physical, electronic, magnetic and optical properties of relevance to physics and material sciences.

Starting from well-defined carbonyl clusters where the metals are in a low oxidation state, thermal activation allows easy removal of the ligands to afford metal nanoparticles, without drastic rearrangements of the metal core that would occur if redox reactions were involved in the process. The central question was to investigate whether their size and composition, in case of heterometallic systems, could keep the "memory" of the metal core composition of their molecular precursor or whether phase segregation would occur (Figure 1).

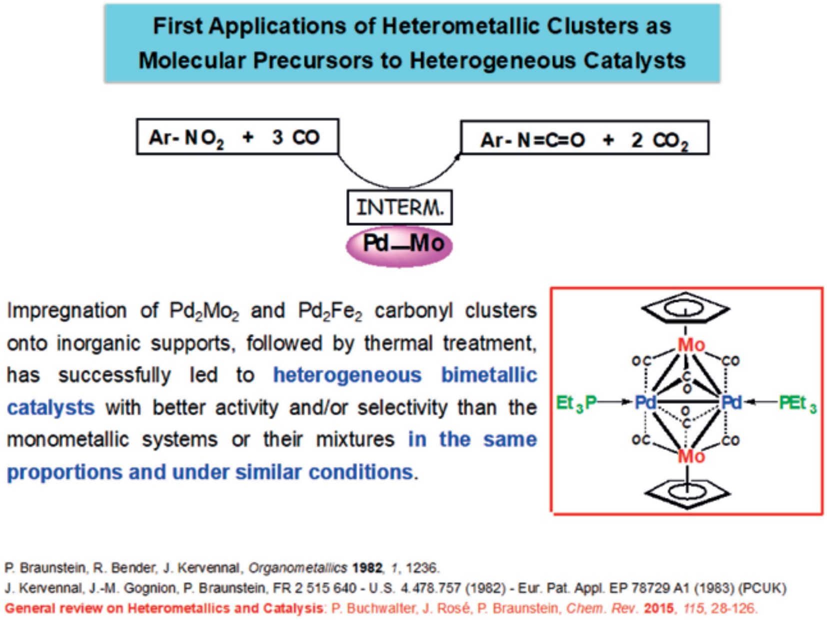


- Can *bimetallic* particles of controlled size (high dispersion) and composition be obtained?
- Can "molecular alloys" lead to *bimetallic* particles with metals that do not form alloys in the bulk?
- Promising perspectives include the use of
  - micro- or mesoporous support materials
  - functional clusters amenable to co-condensation reactions using the sol-gel process, leading to *covalent* attached to the matrix

Figure 1.
Molecular clusters as precursors to well-defined nanoparticles

This approach led us to report in 1982 the first application of heterometallic clusters as molecular precursors to heterogeneous catalysts in the form of alloy nanoparticles.[39] We investigated the carbonylation of organic nitro derivatives into isocyanates, catalysed by nanoparticles derived from the planar, centrosymmetric bimetallic cluster $[Mo_2Pd_2Cp_2(CO)_6(PPh_3)_2]$ (Figure 2).

Gratifyingly, these nanoparticles very not only very active but their selectivity for phenyl isocyanate (71–80%) was higher than that of conventional catalysts prepared by mixing the individual components (62–67%). These studies were extended to the use of Fe–Pd clusters impregnated on silica or alumina as precursors to heterogeneous bimetallic catalysts for the conversion of *o*-nitrophenol to benzoxazol-2-one.[40] All the particles obtained by thermal decomposition of the clusters $[FePd_2(CO)_4(\mu\text{-dppm})_2]$ or $[Fe_2Pd_2(CO)_5(NO)_2(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$



First Applications of Heterometallic Clusters as Molecular Precursors to Heterogeneous Catalysts

Ar-NO$_2$ + 3 CO → Ar-N=C=O + 2 CO$_2$

INTERM.

Pd—Mo

Impregnation of Pd$_2$Mo$_2$ and Pd$_2$Fe$_2$ carbonyl clusters onto inorganic supports, followed by thermal treatment, has successfully led to **heterogeneous bimetallic catalysts** with better activity and/or selectivity than the monometallic systems or their mixtures **in the same proportions and under similar conditions**.

P. Braunstein, R. Bender, J. Kervennal, *Organometallics* **1982**, *1*, 1236.
J. Kervennal, J.-M. Gognion, P. Braunstein, FR 2 515 640 - U.S. 4.478.757 (1982) - Eur. Pat. Appl. EP 78729 A1 (1983) (PCUK)
General review on Heterometallics and Catalysis: P. Buchwalter, J. Rosé, P. Braunstein, *Chem. Rev.* **2015**, *115*, 28-126.

Figure 2.
This Mo$_2$Pd$_2$ cluster was the first mixed-metal cluster containing palladium and used as a precursor to catalytic bimetallic nanoparticles.

(bis(diphenylphosphino)methane) were shown by analytical electron microscopy to have a diameter of 20-50 Å and to be all bimetallic.[41] In contrast, no small bimetallic particles were detected in conventional catalysts prepared by co-impregnation of palladium and iron salts. The preparation of heterogeneous, bimetallic catalysts from well-defined, mixed-metal clusters has become a very successful field of research.[37]

If impregnation of clusters on inorganic oxides, followed by thermal activation under controlled atmosphere, to avoid oxidation of the highly reactive metallic nanoparticles obtained, is a straightforward approach, it also appeared attractive to chemically anchor the clusters to the host matrix, with the hope to better control the distribution of the particles in the solid. Bifunctional ligands may be used for that purpose and we explored and compared complementary approaches to this aim.[4] Starting from the versatile short-bite diphosphine ligand $Ph_2PNHPPh_2$ (bis(diphenylphosphino)amine, dppa),[42] we prepared the alkoxysilyl-functionalized diphosphine ligands $(Ph_2P)_2N(CH_2)_3Si(OMe)_3$, $(Ph_2P)_2N(CH_2)_4SiMe_2(OMe)$ and $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ which were used to decorate the pore walls of nanoporous alumina membranes.[43,44] The ligand alkoxysilyl end-group allows covalent attachment to the inorganic matrix by formation of strong Si–O bonds. This procedure was also applied to the functionalization of an ordered mesoporous silica of the type SBA-15 and the anchoring of the tetrahedral cluster $[Co_4(CO)_{10}(\mu\text{-dppa})]$ (Figure 3).[45] This cluster was selected because interesting magnetic properties were expected for the resulting cobalt nanoparticles. The bridging dppa ligand not only stabilizes the cluster but also selectively orients the substitution of the alkoxysilyl-functionalized diphosphine to the opposite edge of the tetrahedron.

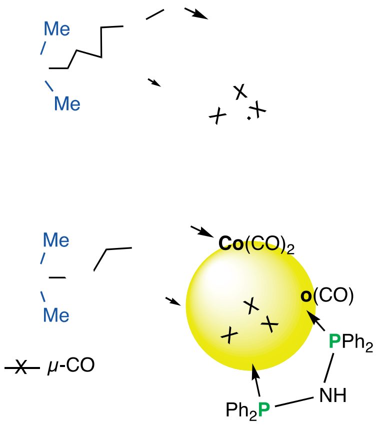


Figure 3.
Anchoring of a Co4 carbonyl cluster onto mesoporous silica.

Subsequent thermal treatment of the functionalized mesoporous silica under H_2 led unexpectedly to pure nanocrystalline, orthorhombic Co_2P particles.[45,46] Their spatial repartition, size, and shape were more regular than when a silica xerogel, obtained by the sol–gel process, was used. Interestingly, the narrow size distribution of the particles of *ca*. 6 nm corresponds to the pore size diameter of SBA-15, consistent with a controlled confinement exerted by the matrix on particle formation. The preparation of transition-metal phosphides is attracting much interest owing to their various properties and it generally requires the direct combination of the elements at higher temperatures, although molecular precursors are being increasingly used.

Heterometallic clusters were also used as precursors to nanoparticles, such as $[RuCo_3(CO)_{12}]^-$ which is isoelectronic to $[Co_4(CO)_{12}]$.[47,48] Starting from the cluster $[Mo_2Pd_2Cp_2(CO)_6(PPh_3)_2]$ depicted in Figure 2, its impregnation in two different silica matrices, amorphous xerogels and ordered SBA-15, followed by thermal activation led to the identification of a new lacunar ternary compound Pd_xMo_yP, isostructural with Mo_3P. Interestingly, the nanoparticles were more uniformly distributed in the SBA-15 framework than in the amorphous xerogels and presented a narrower size distribution.[49]

Clearly, there are several advantages associated with stepwise approaches leading to the anchoring of well-characterized metal clusters in mesoporous materials. They facilitate the subsequent controlled generation of metal nanoparticles, which can be homo- or hetero-metallic depending on the nature of the molecular precursor. Mixed-metal clusters can be viewed as ligand-stabilized "molecular alloys" and convenient precursors to alloy nanoparticles. The study of their catalytic and electronic properties is attracting increasing attention.[37]

CONCLUSION

Molecular chemistry is a fast expanding and unlimited field of research that deals with all the elements of the Periodic Table. In this presentation, we wished to illustrate, by selecting recent and less recent but still relevant examples from our research activities, how specific ligands associated with mono- or polynuclear metal centres can bring about novel and sometimes unexpected properties.

Serendipity is an important and exciting component of fundamental research and, as quoted by Louis Pasteur, « In the fields of observation, chance favors only the prepared mind ».

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REFERENCES

1. https://www.youtube.com/watch?v=qgdOqeGZEEI.
2. https://www.academie-sciences.fr/fr/Colloques-conferences-et-debats/variations-autour-du-tableau-periodique.html.
3. D. Mendeleev, Remarques à propos de la découverte du gallium, *C. R. Hebd. Séances Acad. Sci.*, 1875, 969-972.
4. P. Braunstein, Functional ligands and complexes for new structures, homogeneous catalysts and nanomaterials, *J. Organomet. Chem.*, 2004, **689**, 3953-3967.
5. P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.
6. I. T. Horvath and P. T. Anastas, Innovations and green chemistry, *Chem Rev*, 2007, **107**, 2169-2173.
7. P. Anastas and N. Eghbali, Green Chemistry: Principles and Practice, *Chem. Soc. Rev.*, 2010, **39**, 301-312.
8. P. Braunstein and F. Naud, Hemilability of hybrid ligands and the coordination chemistry of oxazoline-based systems, *Angew. Chem. Int. Ed.*, 2001, **40**, 680-699.
9. W. H. Zhang, S. W. Chien and T. S. A. Hor, Recent advances in metal catalysts with hybrid ligands, *Coord. Chem. Rev.*, 2011, **255**, 1991-2024.
10. J. C. Jeffrey and T. B. Rauchfuss, Metal complexes of hemilabile ligands. Reactivity and structure of dichlorobis(*o*--(diphenylphosphino)anisole)ruthenium(II), *Inorg. Chem.*, 1979, **18**, 2658-2666.
11. P. Braunstein, D. Matt, F. Mathey and D. Thavard, Functional Phosphines. New Synthesis of Diphenylphosphinoacetonitrile and Ethyl Diphenylphosphinoacetate; Some of Their Complexes with Iron(0), Gold(I), Nickel(II), Palladium(II), Platinum(II), Rhodium(III), and Iridium(III). Stereodynamic Behavior of $[Rh(Ph_2PCH_2CO_2Et)(Ph_2PCH_2CO_2Et)Cl_3]$, *J. Chem. Res. (S)*, 1978, 232-233; (*M*) 1978, 3041-3063.
12. P. Braunstein, Bonding and organic and inorganic reactivity of metal-coordinated phosphinoenolates and related functional phosphine-derived anions, *Chem. Rev.*, 2006, **106**, 134-159.
13. P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, Coordination Properties of (Diphenylphosphino) acetonitrile, Ethyl (Diphenylphosphino)acetate, and Corresponding Carbanions. Characterization of a New Facile Reversible CO_2 Insertion into Pd(II) Complexes, *J. Am. Chem. Soc.*, 1981, **103**, 5115-5125.
14. P. Braunstein, D. Matt and D. Nobel, Reactions of Carbon Dioxide with Carbon Carbon Bond Formation Catalyzed by Transition-Metal Complexes, *Chem. Rev.*, 1988, **88**, 747-764.
15. P. Braunstein, D. Matt and D. Nobel, Carbon Dioxide Activation and Catalytic Lactone Synthesis by Telomerization of Butadiene and CO_2, *J. Am. Chem. Soc.*, 1988, **110**, 3207-3212.
16. M. Sharif, R. Jackstell, S. Dastgir, B. Al-Shihi and M. Beller, Efficient and selective Palladium-catalyzed Telomerization of 1,3-Butadiene with Carbon Dioxide, *ChemCatChem*, 2017, **9**, 542-546.
17. R. Nakano, S. Ito and K. Nozaki, Copolymerization of carbon dioxide and butadiene via a lactone intermediate, *Nat. Chem.*, 2014, **6**, 325-331.
18. S. Huang, B. Yan, S. Wang and X. Ma, Recent advances in dialkyl carbonates synthesis and applications, *Chem. Soc. Rev.*, 2015, **44**, 3079-3116.
19. P. Braunstein, M. Lakkis and D. Matt, Synthesis of Anisole by Lewis Acid-Catalyzed Decarboxylation of Methyl Phenyl Carbonate, *J. Mol. Catal.*, 1987, **42**, 353-355.
20. W. Keim, Oligomerization of Ethylene to α-Olefins: Discovery and Development of the Shell Higher Olefin Process (SHOP), *Angew. Chem. Int. Ed.*, 2013, **52**, 12492-12496.

21. P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, Intramolecular O-H···O-Ni and N-H···O-Ni Hydrogen-Bonding in Nickel Diphenylphosphinoenolate Phenyl Complexes: Role in Catalytic Ethene Oligomerization. Crystal-Structure of [NiPh{Ph$_2$PCH···C(···O)(*o*-C$_6$H$_4$NHPh))(PPh$_3$)], *J. Chem. Soc., Chem. Commun.*, 1994, 2203-2204.
22. P. Braunstein, Y. Chauvin, S. Mercier and L. Saussine, Influence of intramolecular N-H···O-Ni hydrogen bonding in nickel(II) diphenylphosphinoenolate phenyl complexes on the catalytic oligomerization of ethylene, *C. R. Chimie*, 2005, **8**, 31-38.
23. P. Braunstein, F. Naud and S. J. Rettig, A new class of anionic phosphinooxazoline ligands in palladium and ruthenium complexes: catalytic properties for the transfer hydrogenation of acetophenone, *New J. Chem.*, 2001, **25**, 32-39.
24. P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, Rhodium(I) and iridium(I) complexes with ß-keto phosphine or phosphino enolate ligands. Catalytic transfer dehydrogenation of cyclooctane, *Organometallics*, 1996, **15**, 5551-5567.
25. C. Fliedel and P. Braunstein, Recent advances in S-functionalized N-heterocyclic carbene ligands: From the synthesis of azolium salts and metal complexes to applications, *J. Organomet. Chem.*, 2014, **751**, 286-300.
26. F. He, A. A. Danopoulos and P. Braunstein, Trifunctional pNHC, Imine, Pyridine Pincer-Type Iridium(III) Complexes: Synthetic, Structural, and Reactivity Studies, *Organometallics*, 2016, **35**, 198-206.
27. T. Simler, P. Braunstein and A. A. Danopoulos, Cobalt PNC$^{\mathrm{NHC}}$ 'Pincers': Ligand Dearomatisation, Formation of Dinuclear and N$_2$ Complexes and Promotion of C-H Activation, *Chem. Commun.*, 2016, **52**, 2717-2720.
28. V. Charra, P. de Frémont and P. Braunstein, Multidentate N-Heterocyclic Carbene Complexes of the 3d Metals: Synthesis, Structure, Reactivity and Catalysis, *Coord. Chem. Rev.*, 2017, **341**, 53-176.
29. S. Hameury, P. de Frémont and P. Braunstein, Metal Complexes with Oxygen-Functionalized NHC Ligands: Synthesis and Applications, *Chem. Soc. Rev.*, 2017, **46**, 632-733.
30. P. Ai, K. Yu. Monakhov, J. van Leusen, P. Kögerler, C. Gourlaouen, M. Tromp, R. Welter, A. A. Danopoulos and P. Braunstein, Linear Cu$^{\mathrm{I}}_{2}$Pd^{0}, Cu$^{\mathrm{I}}$Pd$^{0}_{2}$, and Ag$^{\mathrm{I}}_{2}$Pd^{0} Metal Chains Supported by Rigid N,N′-Diphosphanyl N-Heterocyclic Carbene Ligands and Metallophilic Interactions, *Chem. Eur. J.*, 2018, **24**, 8697-8697.
31. T. Simler, S. Choua, A. A. Danopoulos and P. Braunstein, Reactivity of a Dearomatised Pincer Co$^{\mathrm{II}}$Br Complex with PNC$^{\mathrm{NHC}}$ Donors: Alkylation and Si-H Bond Activation via Metal-Ligand Cooperation, *Dalton Trans.*, 2018, **47**, 7888-7895.
32. A. A. Danopoulos, A. Massard, G. Frison and P. Braunstein, Iron and Cobalt Metallotropism in Remote-Substituted NHC Ligands: Metalation to Abnormal NHC Complexes or NHC Ring Opening, *Angew. Chem. Int. Ed.*, 2018, **57**, 14550-14554.
33. A. A. Danopoulos, T. Simler and P. Braunstein, N-Heterocyclic Carbene Complexes of Copper, Nickel, and Cobalt, *Chem. Rev.*, 2019, **119**, 3730-3961.
34. K. J. Evans and S. M. Mansell, Functionalised N-Heterocyclic Carbene Ligands in Bimetallic Architectures, *Chem. Eur. J.*, 2020, **26**, in press.
35. P. Braunstein, L. A. Oro and P. R. Raithby, *Metal Clusters in Chemistry*, Wiley-VCH, Weinheim, 1999.
36. S. Sculfort and P. Braunstein, Intramolecular d^{10}-d^{10} interactions in heterometallic clusters of the transition metals, *Chem. Soc. Rev.*, 2011, **40**, 2741-2760.
37. P. Buchwalter, J. Rosé and P. Braunstein, Multimetallic Catalysis Based on Heterometallic Complexes and Clusters, *Chem. Rev.*, 2015, **115**, 28-126.
38. S. Zhou, X. Sun, L. Yue, M. Schlangen and H. Schwarz, Tuning the Reactivities of the Heteronuclear [Al$_{n}$V$_{3-n}$O$_{7-n}$]$^{+}$ (n = 1, 2) Cluster Oxides towards Methane by Varying the Composition of the Metal Centers, *Chem. Eur. J.*, 2019, **25**, 2967-2971.
39. P. Braunstein, R. Bender and J. Kervennal, Selective Carbonylation of Nitrobenzene over a Mixed Pd-Mo Cluster Derived Catalyst, *Organometallics*, 1982, **1**, 1236-1238.
40. P. Braunstein, J. Kervennal and J. L. Richert, Reductive Carbonylation of Ortho-Nitrophenol with a Fe-Pd Cluster-Derived Heterogeneous Catalyst; CO Migration in [FePdPt(CO)$_4$(Ph$_2$PCH$_2$PPh$_2$)$_2$], *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 768-770.
41. P. Braunstein, R. Devenish, P. Gallezot, B. T. Heaton, C. J. Humphreys, J. Kervennal, S. Mulley and M. Ries, Silica-Supported Fe-Pd Bimetallic Particles: Formation from Mixed-Metal Clusters and Catalytic Activity, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 927-929.
42. C. Fliedel, A. Ghisolfi and P. Braunstein, Functional Short-Bite Ligands: Synthesis, Coordination Chemistry, and Applications of N-Functionalized Bis(diaryl/dialkylphosphino)amine-type Ligands, *Chem. Rev.*, 2016, **116**, 9237-9304.
43. I. Bachert, P. Braunstein and R. Hasselbring, Alkoxysilyl-functionalized mixed-metal carbonyl clusters, *New J. Chem.*, 1996, **20**, 993-995.
44. P. Braunstein, H.-P. Kormann, W. Meyer-Zaika, R. Pugin and G. Schmid, Strategies for the anchoring of metal complexes, clusters, and colloids inside nanoporous alumina membranes, *Chem. Eur. J.*, 2000, **6**, 4637-4646.

45. F. Schweyer-Tihay, P. Braunstein, C. Estournès, J. L. Guille, B. Lebeau, J. L. Paillaud, M. Richard-Plouet and J. Rosé, Synthesis and characterization of supported Co_2P nanoparticles by grafting of molecular clusters into mesoporous silica matrixes, *Chem. Mater.*, 2003, **15**, 57-62.
46. P. Buchwalter, J. Rosé, B. Lebeau, O. Ersen, M. Girleanu, P. Rabu, P. Braunstein and J.-L. Paillaud, Characterization of cobalt phosphide nanoparticles derived from molecular clusters in mesoporous silica, *J. Nanopart. Res.*, 2013, **15**, 2132.
47. F. Schweyer, P. Braunstein, C. Estournès, J. Guille, H. Kessler, J.-L. Paillaud and J. Rosé, Metallic nanoparticles from heterometallic Co-Ru carbonyl clusters in mesoporous silica xerogels and MCM-41-type materials, *Chem. Commun.*, 2000, 1271--1272.
48. F. Schweyer-Tihay, C. Estournès, P. Braunstein, J. Guille, J. L. Paillaud, M. Richard-Plouet and J. Rosé, On the nature of metallic nanoparticles obtained from molecular Co_3Ru-carbonyl clusters in mesoporous silica matrices, *PCCP*, 2006, **8**, 4018-4028.
49. S. Grosshans-Vielès, P. Croizat, J. L. Paillaud, P. Braunstein, O. Ersen, J. Rosé, B. Lebeau, P. Rabu and C. Estournès, Molecular clusters in mesoporous materials as precursors to nanoparticles of a new lacunar ternary compound Pd_xMo_yP, *J. Cluster Sci.*, 2008, **19**, 73-88.