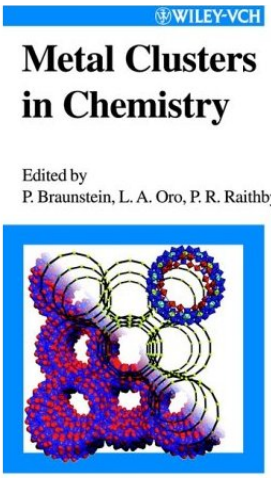
1) *Bimetallic and Cluster Chemistry*



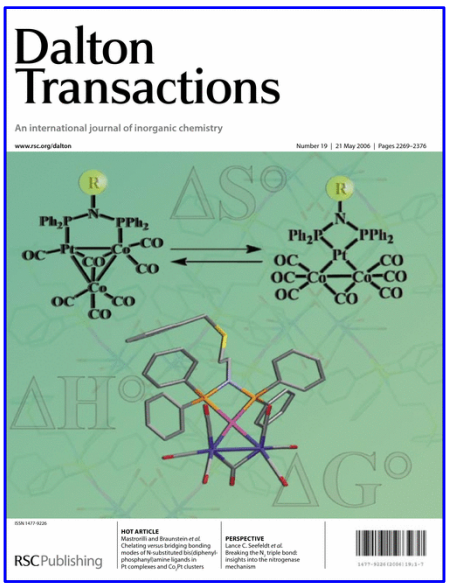
P. Braunstein, L. A. Oro and P. R. Raithby (Eds.)

"*Metal Clusters in Chemistry*", Wiley-VCH, **1999**, 3 vol., 1798 pages

Our group developed new approaches and concepts for the "bottom-up" construction of heterometallic clusters from organometallic building blocks with tunable electronic donicity, and used assembling ligands to increase selectivity and stability. We were the first to prepare *i.a.*, palladium-containing mixed-metal clusters, a platinum-gold cluster, and a trimetallic RuCoHg cluster in which the mercury atom was for the first time surrounded by 6 metal atoms, numerous new heterometallic bonds between transition metals such as Pd, Pt, Fe, Co, Cr, Mo, W, Au... We discovered the most dramatic reversible cluster isomerism known, where a change in crystallisation solvent results in a variation of a Pt-Pt distance in a Pt_3 cluster by more than 0.5 Å. The work on Pt_3 clusters was reviewed in *Inorg. Chim. Acta*, 2015, *424*, 20-28.

In the case of a Pt_2Mo_2 cluster, we analysed the reasons for the occurrence of equilibria between planar or butterfly structures, in violation of the Wade-Mingos electron counting rules (*J. Am. Chem. Soc.* 1991, *113*, 5282).

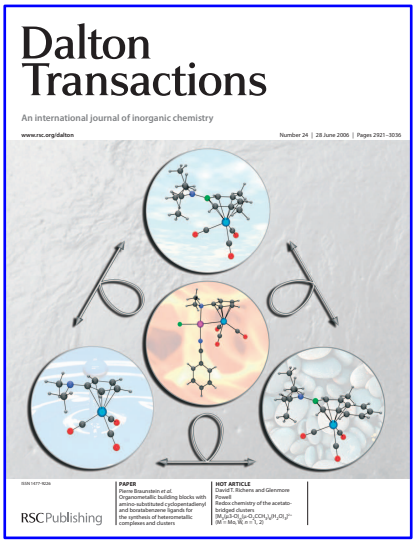
Using the isolobal analogy to compare the bonding behaviour and reactivity of carbonylmetallate reagents, we developed rational approaches to heterometallic clusters and produced several unprecedented bimetallic systems. Among the numerous and often beautiful clusters obtained, an unprecedented Pd_4Mn_4 cyano cluster with a double helical structure is noteworthy, which was the first molecular box of its type.



P. Braunstein, B. Oswald, A. Tiripicchio, M. Tiripicchio Camellini. Novel bonding mode for a cyanometallate ligand: synthesis and crystal structure of the Pd_4Mn_4 cluster $[(OC)Pd(\mu\text{-}CN)Mn(\eta\text{-}C_5H_4Me)(CO)_2]_4$ containing a *meso* arrangement of helical units.
Angew. Chem., Int. Ed. Engl. **1990**, *29*, 1140.

V. Gallo, P. Mastrorilli, C. F. Nobile, P. Braunstein, U. Englert. Chelating *versus* bridging bonding mode of N-substituted bis(diphenylphosphanyl) amine ligands in Pt complexes and Co_2Pt clusters. *Dalton Trans.* **2006**, 2342-2349.

A fruitful collaboration with G. Herberich (Aachen, Germany) revealed the potential of boron-containing organic π-systems in bimetallic and cluster chemistry.



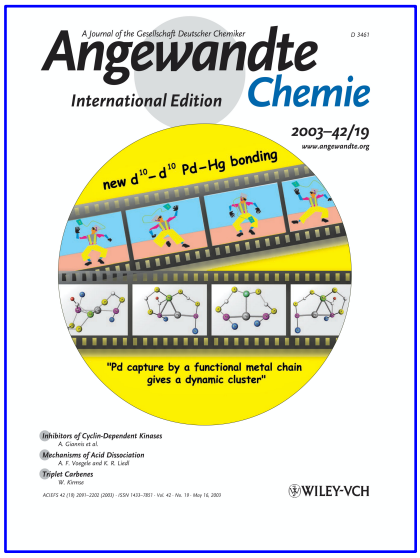
* P. Braunstein, U. Englert, G. E. Herberich, M. Neuschütz. First Mixed-Metal Borole Cluster; Stabilization of Formally 14e Pd Centers in the Re_2Pd_2 Electron Deficient $[\{\eta^5\text{-}C_4H_4BPh)(CO)_3Re\}Pd]_2$ Cluster. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1010.
* P. Braunstein, U. Englert, G. E. Herberich, M. Neuschütz, M. U. Schmidt. Heterometallic Complexes with Borole Ligands. *J. Chem. Soc., Dalton Trans.* **1999**, 2807-2812.
* P. Braunstein, E. Cura, G. E. Herberich. Heterometallic complexes and clusters with 2-boratanaphtalene ligands. *J. Chem. Soc., Dalton Trans.* **2001**, 1754-1760.
* N. Auvray, T. S. Basu Baul, P. Braunstein, P. Croizat, U. Englert, G. E. Herberich, R. Welter. Organometallic Building Blocks with Amino-Substituted Cyclopentadienyl and Boratabenzene Ligands for the Synthesis of Heterometallic Complexes and Clusters. *Dalton Trans.* **2006**, 2950-2958.
* P. Croizat, N. Auvray, P. Braunstein, R. Welter. Comparative Bonding Behavior of Functional Cyclopentadienyl Ligands and Boron-Containing Analogues in Heterometallic Complexes and Clusters. *Inorg. Chem.* **2006**, *45*, 5852-5866.

Our group has also developed unprecedented **heterobimetallic silicon chemistry** and discovered that trialkoxysilane ligands can bridge between two transition metals. We found that the resulting four-membered ring M-M'-Si-O is often kinetically labile, but thermodynamically stable (*Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1361). This has important implications in homogeneous and heterogeneous catalysis. We discovered the first intramolecular silyl group migration form one metal to another (*Angew. Chem., Int. Ed. Engl.* 1992, *31*, 1583), unprecedented intramolecular, metal-dependent substituent exchanges between phosphorus and silicon atoms, isolated unusual silylene metal complexes (*Angew. Chem., Int. Ed. Engl.* 1994, *33*, 2440; *J. Chem. Soc., Chem. Commun.* 1996, 2041-2042) and reported the most active catalysts for the dehydrogenative coupling of stannanes.

P. Braunstein, X. Morise. Dehydrogenative Coupling of Hydrostannanes Catalysed by Transition-Metal Complexes *Chem. Rev*. **2000**, *100*, 3541-3552.

The very rich and unusual bimetallic silicon chemistry developed by our group has been reviewed (P. Braunstein, M. Knorr, Ch. Stern, *Coord. Chem. Rev.* 1998, *178-180*, 903-965; see also P. Braunstein, M. Knorr**,** Reactivity of the metal-silicon bond in organometallic chemistry, *J. Organomet. Chem*. 1996, 500, 21-38).

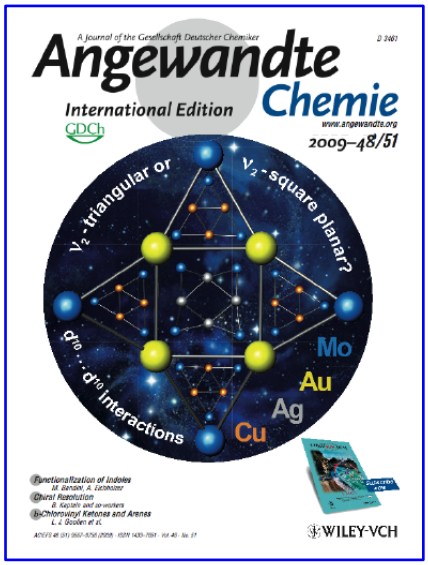
We also described unusual metal-metal bonded coordination polymers and identified novel heterometallic, metal-metal d^{10}-d^{10} interactions (Cu-Hg, Ag-Hg, Au-Hg, Pd-Hg) in mesocyclic structures as well as their dynamic behaviour (*Angew. Chem. Int. Ed*. 2003, *42*, 2161 and *J. Am. Chem. Soc*. 2005, *127*, 10250).



* W. Schuh, P. Braunstein, M. Bénard, M.-M. Rohmer, R. Welter. An Unusual Dynamic Fe-Hg-Pd Cluster with a Palladium(0) Fragment Stabilized by d^{10}-d^{10} Heterometallic Bonding. *Angew. Chem. Int. Ed*. **2003**, *42*, 2161.

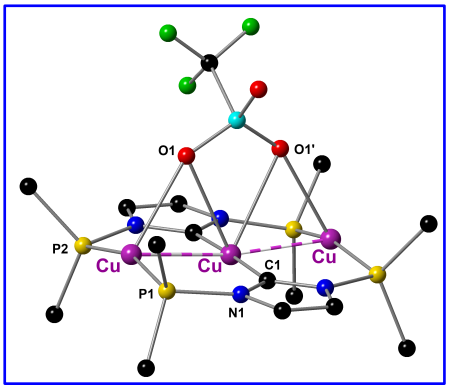
* W. Schuh, P. Braunstein, M. Bénard, M.-M. Rohmer, R. Welter. Metal « Capture» by a Heterotrimetalloligand, Heterometallic d^{10}-d^{10} Interactions, and Unexpected Iron-to-Platinum Silyl Ligand Migration: a Combined Experimental and Theoretical Study. *J. Am. Chem. Soc*. **2005**, *127*, 10250.

He reported a family of triangular M_3Mo_3 or square M_4Mo_4 heterometallic clusters of which the structure depends on the d^{10} ion present (M = Cu, Ag, Au), thus allowing an evaluation of the contribution of metallophilic interactions to the structure within a series of closely related complexes. Such investigations considerably extend the scope of the well-known aurophilic interactions.



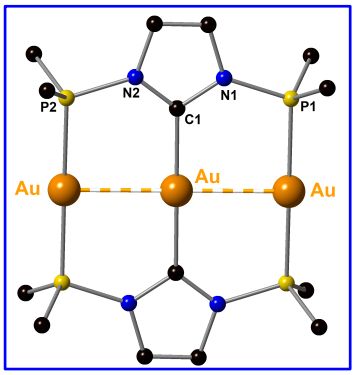
* S. Sculfort, P. Croizat, A. Messaoudi, M. Bénard, M.-M. Rohmer, R. Welter, P. Braunstein. 2-Dimensional Triangular and Square Heterometallic Clusters: the Influence of the Close-Shell d^{10} Electronic Configuration
  Angew. Chem. Int. Ed. **2009**, *48*, 9663-9667
* S. Sculfort, P. Braunstein. Intramolecular d^{10}-d^{10} interactions in heterometallic clusters of the transition metals
  Chem. Soc. Rev. **2011**, *40*, 2741-2760.

Our group also reported the use of bis(phosphine)-functionalized N-heterocyclic ligands as "double short-bite ligands" that provide a unique, constrained geometry favouring the assembling of unique Cu(I), Ag(I) and Au(I) metal chains displaying d^{10}-d^{10} interactions. In the Cu_3 complex, the triflate anion adopts an unprecedented bonding mode, bridging the metal chain. The metal chains display strong metallophilic interactions supported by the P-C^{NHC}-P ligands.



P. Ai, A. A. Danopoulos, P. Braunstein, K. Yu. Monakhov**.** A novel, rigid diphosphine with an active NHC spacer; di- and trinuclear complexes of d^{10} coinage metals. *Chem. Commun*. 2014, *50*, 103.

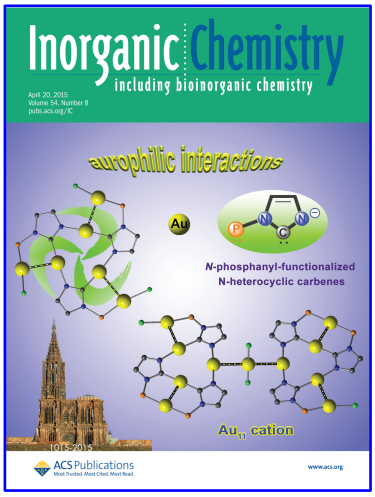
By suppressing phosphanyl migration during ligand synthesis from N to the NC^{NHC}N carbon, a novel rigid diphosphine with an NHC spacer was obtained as a hybrid PC^{NHC}P ligand favouring the constrained assembling of metals.

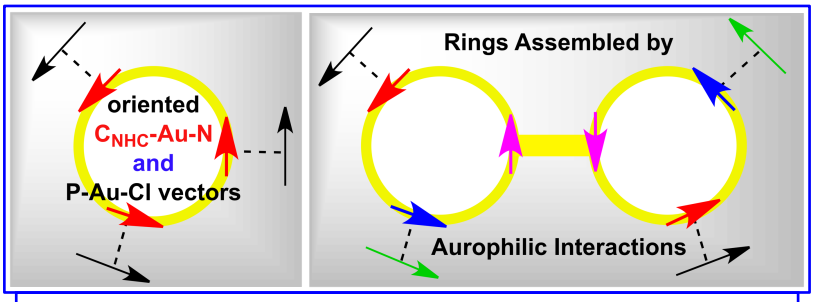


P. Ai, K. Yu. Monakhov, J. van Leusen, P. Kögerler, C. Gourlaouen, M. Tromp, R. Welter, A. A. Danopoulos, P. Braunstein. Linear Cu$^{I}_2$Pd^0, Cu^{I}Pd$^0_2$, and Ag$^{I}_2$Pd^0 Metal Chains Supported by Rigid *N,N'*-Diphosphanyl *N*-Heterocyclic Carbene Ligands and Metallophilic Interactions
Chem. Eur. J. **2018**, *24*, 8787 – 8796

The graphic illustrates the double short-bite nature of the functional NHC ligand system that stabilizes the metal chain and favors attractive d^{10}-d^{10} closed-shell interactions without restraining reactivity.

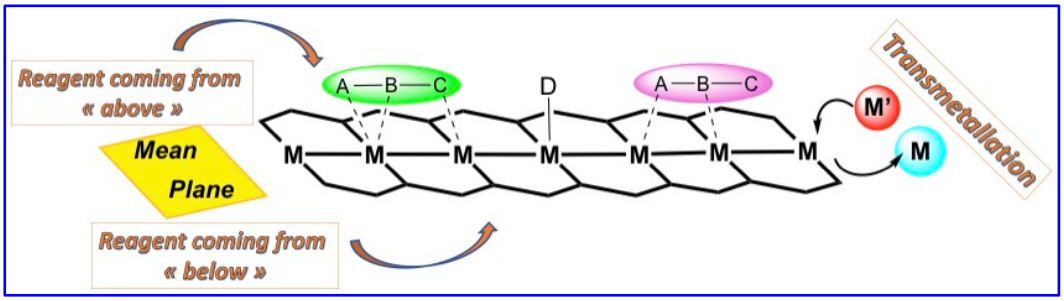
Related polynuclear Au(I) complexes supported by anionic PC^{NHC} ligands showing unique, oriented topologies were also characterised.





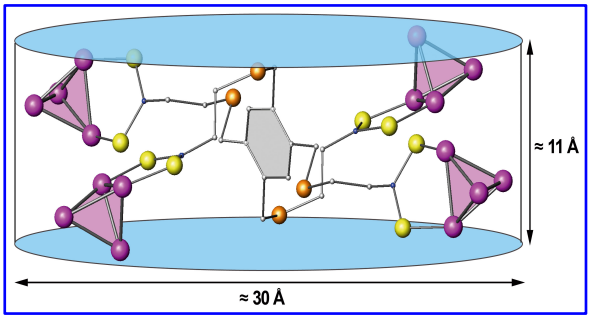
P. Ai, A. A. Danopoulos, P. Braunstein. Aurophilicity-Triggered Assembly of Novel Cyclic Penta- and Hexanuclear Gold(I) Complexes with Rigid Anionic NHC-Type Ligands. *Inorg. Chem.* **2015**, *54*, 3722-3724.

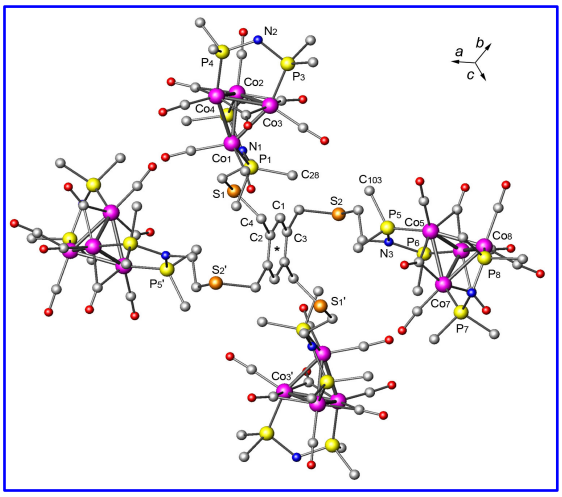
Metal chain complexes are generally supported by bridging ligands and diverse topologies can be targeted, enabling cooperativity between the metal centres, including in heterometallic chains, and between the metals and the ligands.



P. Braunstein, A. A. Danopoulos. Transition Metal Chain Complexes Supported by Soft Donor Assembling Ligands. *Chem. Rev*. **2021**, *121*, 7346–7397.

Noteworthy is also the preparation of unprecedented "branched clusters" where four tetranuclear Co clusters connected to a central dppa-type ($Ph_2PNHPPh_2$) organic core form a Co_{16} 'dendricluster', the largest structurally characterised molecule of its kind.

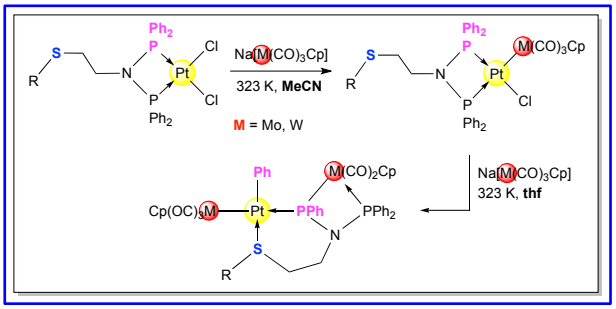




M. Rodriguez-Zubiri, V. Gallo, J. Rosé, R. Welter, P. Braunstein. Assembling Metals and Clusters around an Octaphosphine Ligand Based on *N*-substituted Bis(diphenylphosphanyl)amines: Structural Characterization of Dendrimer-like Co_{12} and Co_{16} Branched Clusters. *Chem. Commun.* **2008**, 64-66.

We also reported the first example of a bridging PF_6^- anion in which one fluorine atom bridges between two silver centres, thus demonstrating the generally overlooked possible "non-innocent" coordination behaviour of this anion (*Angew. Chem. Int. Ed.* 2008, *47*, 6856).

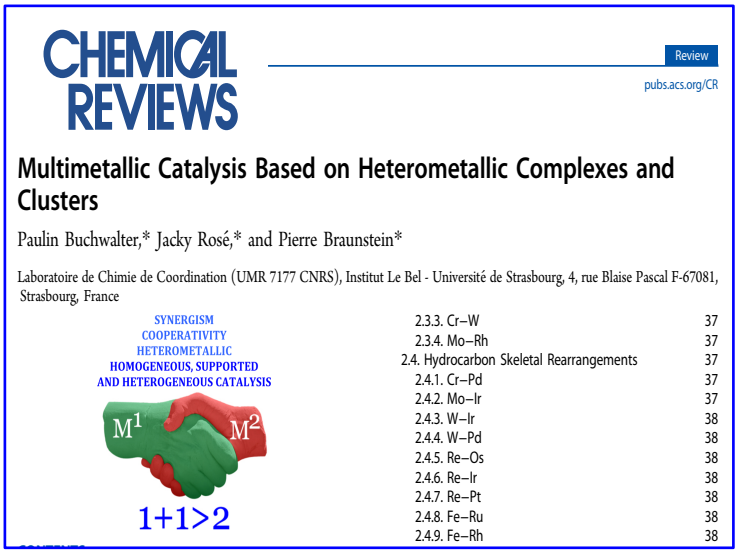
The *N*-functionalization of short-bite ligands of the dppa-type with thioether groups has allowed the synthesis of Fe(II) complexes in which the diphosphine ligand displays an unsymmetrical chelation mode which is not observed with the non-functionalized ligand. The resulting magnetic properties have been investigated (*Inorg. Chem.* 2015, *54*, 6547). Using such thioether-functionalized short-bite ligands, an unusual sulfur-assisted phenyl migration reaction from phosphorus to platinum was found to occur in PtW_2 and $PtMo_2$ clusters. Such reactions illustrate the potential of both heterometallic complexes and functional ligands in promoting unusual transformations.



S. Todisco, P. Mastrorilli, M. Latronico, V. Gallo, U. Englert, N. Re, F. Creati, P. Braunstein
Sulfur-Assisted Phenyl Migration from Phosphorus to Platinum in PtW_2 and $PtMo_2$ Clusters Containing Thioether-Functionalized Short-Bite Ligands of the Bis(diphenylphosphanyl)amine (dppa)-Type
Inorg. Chem. **2015**, *54*, 4777-4798

Dynamic Fe-Pd mixed-metal clusters containing a rare and probably first example of a terminal CO ligand bound to Pd were characterised by our group, and these clusters were used as molecular precursors to novel heterogeneous catalysts for the carbonylation of *o*-nitrophenol to benzoxazol-2-one (see below).

Our work established that new molecular associations between different transition metals could be achieved, even between metals that do not form alloys in the bulk. We contributed to the notion that "molecular alloys" could display properties different from those of bulk alloys. Metal clusters were soon recognised as unique chemical objects at the interface between molecular and colloidal systems and metal particles, whose nanometric dimensions were to arouse later considerable interest among physicists. Synergism and cooperativity between the different metals present in a cluster often lead to enhanced reactivity and greater selectivity with heterometallic clusters compared to their monometallic constituents. **We pioneered (1982) the use of heterometallic cluster-derived bimetallic metal particles in heterogeneous catalysis** and found, in collaboration with industry, first with a Pd-Mo and then Pd-Fe systems, that they were far superior to conventional catalysts containing the same metals in the same proportions for the carbonylation of organic nitro derivatives to isocyanates, thus avoiding the use of phosgene! The Ford Motor Company has gone on to prepare new catalysts in this way for abatement of automobile emissions from Pd-Mo and Pt-Mo trimetallic complexes and clusters prepared by our group (see *J. Phys. Chem*. 1995, *99*, 6926; *J. Phys. Chem*. 1996, *100*, 253 and *Phys. Chem. Chem. Phys.* 1999, *24*, 5725). The concept of **mixed-metal cluster-derived heterogeneous catalysts** is now increasingly used by the scientific community, and his recent review (*Chem. Rev.* 2015, *115*, 28 of *ca*. 100 pages!) on the topic demonstrates how successful this approach has been.


CHEMICAL REVIEWS

Review

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Multimetallic Catalysis Based on Heterometallic Complexes and Clusters

Paulin Buchwalter,* Jacky Rosé,* and Pierre Braunstein*

Laboratoire de Chimie de Coordination (UMR 7177 CNRS), Institut Le Bel - Université de Strasbourg, 4, rue Blaise Pascal F-67081, Strasbourg, France

SYNERGISM
COOPERATIVITY
HETEROMETALLIC
HOMOGENEOUS, SUPPORTED
AND HETEROGENEOUS CATALYSIS

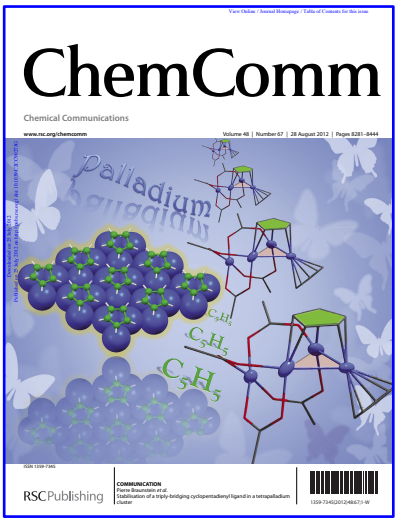
M1 M2

1+1>2

P. Buchwalter, J. Rosé, P. Braunstein
Multimetallic Catalysis Based on Heterometallic Complexes and Clusters
Chem. Rev. **2015**, *115*, 28-126.

Multidisciplinary research in the field of nanosciences also involved developing bimetallic monolayers from single-source precursors and using highly selective procedures to anchor molecular clusters onto inorganic mesoporous materials (MCM-41, SBA-15), thereby generating metal particles with a narrow size distribution and unusual magnetic properties. This approach was extended to the formation of cobalt-phosphide nanoparticles (*Inorg. Chim. Acta* 2014, *409*, 330–341).

Another very significant achievement was the discovery of a triply bridging Cp ligand in a palladium cluster, which extends the **cluster-surface analogy concept** to the cyclopentadienyl ligand (cover *Chem. Comm*. 2012, *48*, 8281).


ChemComm

Chemical Communications

Palladium

C_5H_5

C_5H_5

C_5H_5

RSC Publishing

K. Yu. Monakhov, C. Gourlaouen, P. Braunstein
Stabilisation of a Triply-Bridging Cyclopentadienyl Ligand in a Tetrapalladium Cluster
Chem. Commun. **2012**, *48*, 8317-8319.

Our group has successfully created bridges between a priori unrelated areas of chemistry by combining new concepts and synthetic achievements. For example, we predicted in 1989 that phosphines could behave as bridging ligands in dinuclear complexes or clusters, which was achieved in 2000 by H. Werner in Germany (see also “Alkyl, Silyl, and Phosphane Ligands - Classical Ligands in Nonclassical Bonding Modes” *Angew. Chem. Int. Ed*. 2001, *40*, 2427-2433).