

Polymetallic Activation

A REVIEW OF THE INTERNATIONAL SYMPOSIUM

By P. Braunstein

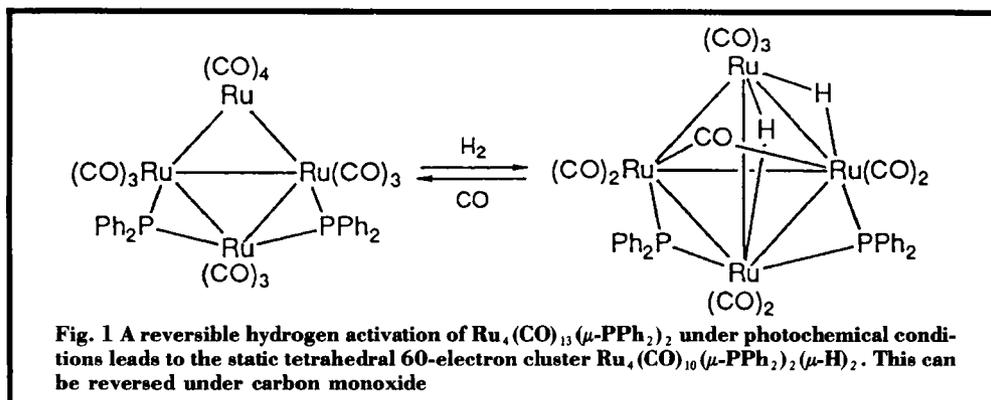
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An International Symposium on Polymetallic Activation was held at the Università di Parma, Italy, from the 13th to 15th September 1990, as part of a collaboration, supported by the European Commission, involving university laboratories at Strasbourg, Freiburg, Torino and Parma which carry out research on diverse aspects of polymetallic activation. An international panel of speakers presented plenary lectures giving the state of the art in their area, discussing and evaluating the results of this initiative and suggesting future actions aimed at developing and strengthening the links between European laboratories performing complementary research.

Polymetallic activation occupies a central position in organometallic and co-ordination chemistry as it has frontiers with the synthesis of new materials, with the study and applications of pure metals and metal particles, and brings an enormous insight into how organic substrates can interact with metal atoms and surfaces and undergo coupling/or decoupling reactions. The dynamics of clusters and of their ligands have also shown how uniquely an ensemble of atoms behave. The development of new catalytic processes requires a fundamental understanding of the elementary steps responsible for molecular activation and transformation. The desired high chemo-, regio- and enantioselectivity, essential for the manufacture of fine chemicals and phar-

maceuticals, necessitates the development of more complex and sophisticated catalysts of a tunable nature. Molecular design and polymetallic activation thus become central themes. They need to be studied in greater depth and in a multidisciplinary manner, using the different techniques which are now available, but the costs of which require optimum utilisation of the equipment and co-operative research.

Professor A. J. Carty of the University of Waterloo, Ontario, Canada, presented the structural chemistry, hydrogen activation and substitution reactions associated with a series of tetranuclear clusters of ruthenium or osmium, such as $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PPh})$ and $\text{Ru}_4(\text{CO})_{13}(\mu\text{-PPh}_2)_2$. The latter undergoes reversible

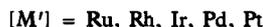
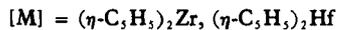
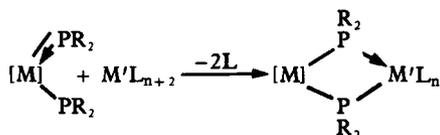


hydrogen activation under photochemical conditions leading to $\text{Ru}_4(\text{CO})_{10}(\mu\text{-PPh}_2)_2(\mu\text{-H})_2$, a static tetrahedral 60-electron cluster, see Figure 1. This net 4-electron change on metal-metal bond formation is reversed under an atmosphere of carbon monoxide (1).

The role of the ligands (carbonyls, phosphido, phosphinidene ...) was shown to be very important for the chemistry of these and related clusters, and the wide variety of structural types encountered in the regime of M_n clusters having a 62-64 electron count was illustrated by X-ray diffraction results.

The theoretical nature of the metal-metal bonding in clusters of low nuclearity was discussed by Dr. C. Mealli, C.N.R., Florence, Italy. A number of systems were presented where the distance between the metal atoms cannot be used as a sufficient criterion for deciding about the bonding between the metals. Valuable pieces of information can however be obtained from the nature and energy levels of the molecular orbitals involved. It was also emphasised that a negative Overlap Population is not always in conflict with the existence of a direct σ bond (2).

The synthesis and co-operative reactivity of unsaturated heterobimetallic complexes containing early and late metals zirconium, hafnium, rhenium, and ruthenium, rhodium, iridium, palladium, platinum, respectively, were described by Dr. R. T. Baker, E.I. Du Pont de Nemours, Wilmington, U.S.A. Their synthesis involves metal complexes containing multiply-bonded terminal $(\text{PR}_2)_2$ ligands which lead to built-in electronic unsaturation at the early metal centre, see below:



Reactivity studies have demonstrated the importance of the bridging ligands in allowing, amongst other things, different core structures (planar, bent, with metal-metal interactions) to be stabilised. For example, the $d^2\text{-}d^8$ complex

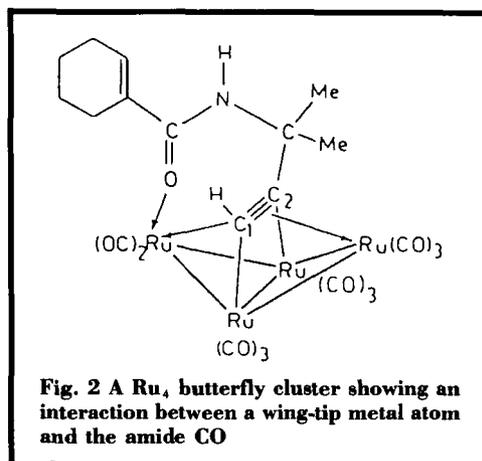


Fig. 2 A Ru_4 butterfly cluster showing an interaction between a wing-tip metal atom and the amide CO

$(\eta\text{-C}_5\text{Me}_5)_2\text{Ta}(\text{PPh}_2)(\mu\text{-PPh}_2)_2\text{Rh}(\text{PMe}_3)_2$ adds hydrogen across the $\text{Ta}=\text{Rh}$ double bond, forming $(\eta\text{-C}_5\text{Me}_5)_2\text{TaH}(\mu\text{-PPh}_2)_3\text{RhH}(\text{PMe}_3)$ (3).

Professor E. Sappa of the Università di Torino, Italy, one of the partners in the European programme, presented reactions of homo- and heterometallic carbonyl clusters of iron, ruthenium and cobalt with functionalised alkynes and dialkynes. The flexibility of the metal core allows unusual bonding modes of the organic fragments to occur and the resulting clusters often display novel features of catalytic relevance (4). For example, the nucleophilic reactivity of acetylides co-ordinated to many metal centres represents a model of related behaviour on metal surfaces, where formation of new carbon-carbon, carbon-nitrogen or carbon-sulphur bonds may occur, see Figure 2. Some clusters have been found to catalyse selectively the homogeneous hydrogenation of dienes and alkynes (5) or represent possible models, isolable in the case of ruthenium, for the intermediates involved in the cobalt mediated co-oligomerisation of functionalised alkynes leading to heterocyclic products.

The construction of new bridging ligands in dinuclear and trinuclear cobalt complexes was presented by Dr. M. J. Mays of the University Chemical Laboratory, Cambridge, U.K. The coupling of small molecules or fragments such as Ph_2P , $\text{RC}=\text{CR}'$, $\text{CH}_2=\text{C}=\text{CH}_2$ and CO may follow different pathways, and a high regio

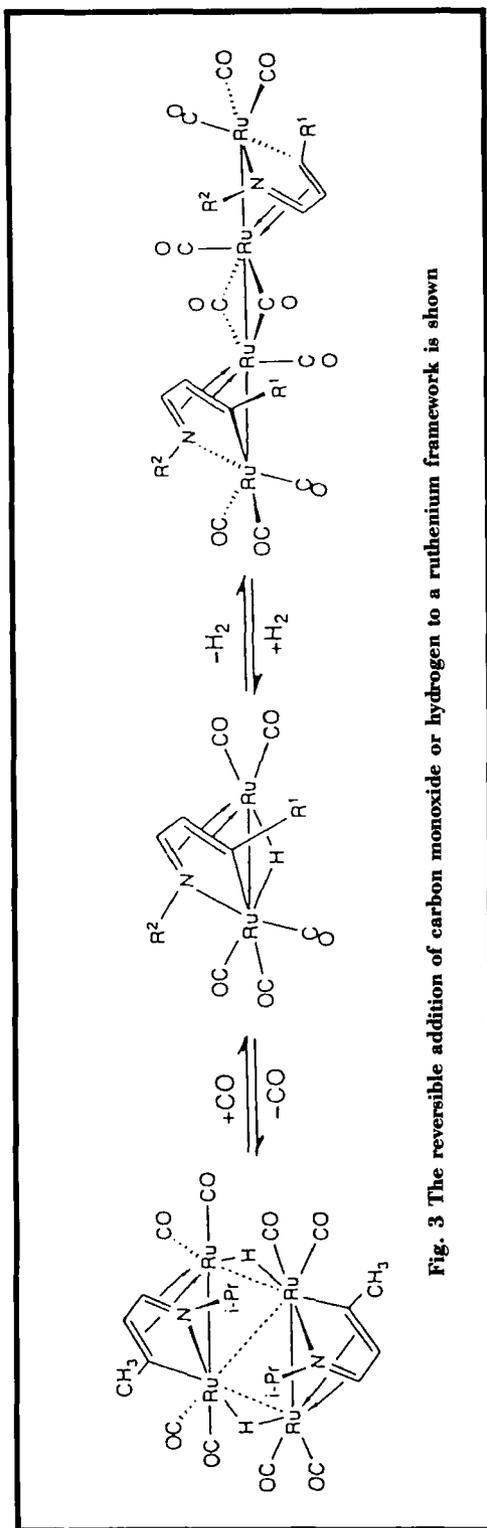


Fig. 3 The reversible addition of carbon monoxide or hydrogen to a ruthenium framework is shown

selectivity has been observed, depending on the nuclearity of the initial cobalt complex, the nature of the R or R' groups and the order of addition of the ligands. Inorganic units may serve as unique templates for the coupling of organic moieties (6a). A different chemistry will take place at a dimolybdenum centre (6b).

Professor K. Vrieze of Van't Hoff Instituut, Amsterdam, The Netherlands, described the activation of metal cluster-co-ordinated enimine by hydrogen and carbon monoxide, see Figure 3. A sequence of isomerisations which took place about a Ru₄ chain of atoms was carefully monitored. The diastereoselectivity of the reactions was emphasised, illustrating the importance of introducing chirality in such molecular systems. Two processes were observed in an unprecedented interconversion between diastereoisomers of a linear tetranuclear ruthenium complex: a radical mechanism and an intramolecular conversion induced by carbon monoxide addition.

The chemistry of carbon-carbon, carbon-nitrogen and nitrogen-nitrogen multiple bonds on clusters was described by Professor H. Vahrenkamp of the Universität Freiburg, Germany, another member of the four-party joint research project. By varying the ligands and the metals in a systematic way (isoelectronic and isolobal relationships) he described the basic aspects of the cluster-surface analogy and various substrate interconversions in the ligand sphere (7), see Figure 4. The key influence of the substrate bonding mode on its reactivity is illustrated, for example, by the fact that the μ_3 - η^2 -C=CH₂ unit is electrophilic at the outer carbon atom, in contrast to vinylidene ligands in mono- or dinuclear complexes. Selected examples illustrated the pathway from the fundamental study of cluster-ligands interactions to cluster-mediated organic synthesis. The reversible and diastereospecific insertion of the prochiral alanine precursor, 2-acetamidoacrylic methyl ester, into the metal-hydrogen function of the chiral clusters HCoMM'(μ_3 -CR)Cp(CO)₃, see Figure 5, (where M = Ru, Os; M' = Mo, W; R = Me, Ph) was shown to be of the Markovnikov-type. The diastereospecificity observed illustrates the

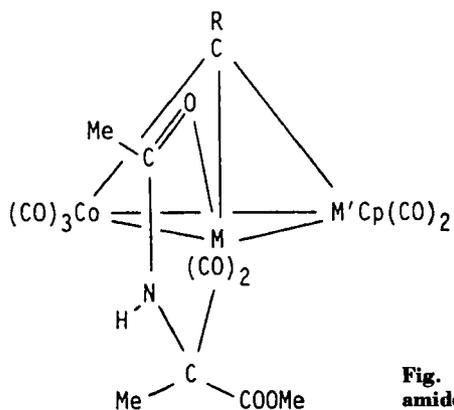
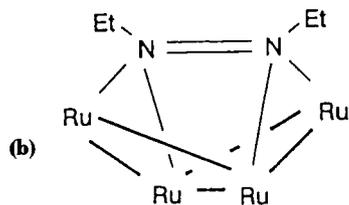
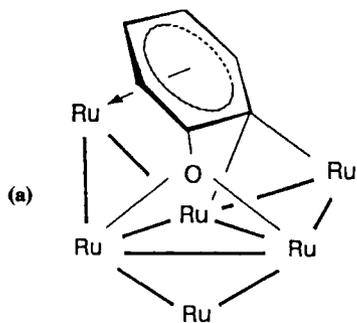


Fig. 4 This cluster-surface analogy shows the core structures of (a) $\text{H}_2\text{Ru}_6(\text{CO})_{16}(\text{C}_6\text{H}_4\text{O})$ and (b) $\text{Ru}_4(\text{CO})_{12}(\text{N}_2\text{Et}_2)$ produced from reactions of $\text{Ru}_3(\text{CO})_{12}$ with (a) phenol and (b) N_2Et_2

transfer of chiral information from a cluster to an organic substrate (8).

The preparation of unusual clusters, organophosphorus and organoboron cage compounds, and organic cyclic addition products of alkynes and alkenes by using the highly reactive intermediates generated in metal vapour reactions was described by U. Zenneck of the Universität Heidelberg, Germany. Mild reaction conditions may thus be used, owing to the enhanced reactivity which characterises bare metal atoms (9).

Professor L. A. Oro of the University of Zaragoza, Spain, presented a number of multinuclear rhodium and iridium complexes whose structures are largely controlled by binucleating $\widehat{\text{N}}\widehat{\text{N}}$, $\widehat{\text{N}}\widehat{\text{O}}$ or $\widehat{\text{N}}\widehat{\text{S}}$ ligands. The stabilisation provided by these ligands enables different arrangements of metal atoms to be characterised. Their flexibility allows, in many cases, the promotion of intra- or intermolecular interactions. A linear tetrairidium complex was

Fig. 5 Insertion of a prochiral substrate 2-acetamidoacrylic methyl ester into the M-H bond of a chiral cobalt cluster

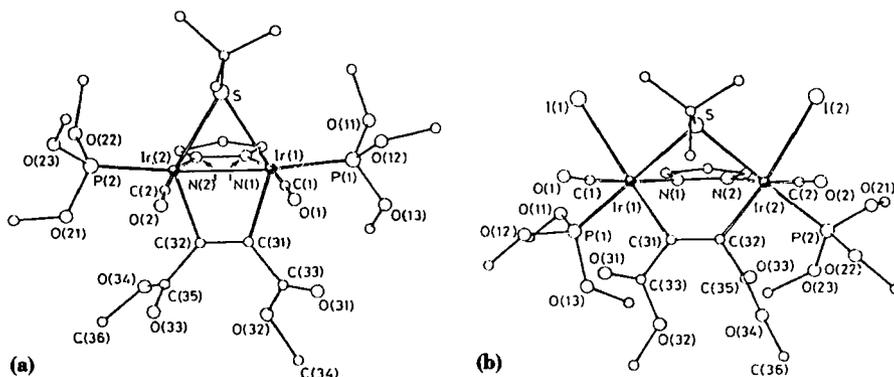


Fig. 6 The flexible framework of binuclear iridium complex $[\text{Ir}_2(\mu\text{-pz})(\mu\text{-SBU})(\mu\text{-MeO}_2\text{CC}=\text{CCO}_2\text{Me})(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ (a) before and (b) after oxidative addition of I_2

Platinum Group Metals-Based Bimetallic Couples Used in Heterogeneous Catalysis	
Catalysed reaction	Bimetallic couples
Hydrocarbon skeletal rearrangements	Cr-Pd W-Ir, W-Pd Re-Pt Fe-Ru, Fe-Pt Ru-Ni, Ru-Pt Co-Rh, Co-Pt Rh-Ir, Rh-Pt Ir-Pt
Hydrogenation/isomerisation of carbon-carbon multiple bonds	Ru-Os, Ru-Ni Os-Ni
Hydrogenation of CO and CO ₂	Mo-Fe, Mo-Os, Mo-Co W-Os Mn-Co, Mn-Fe Fe-Ru, Fe-Os, Fe-Co Ru-Co, Ru-Os Os-Rh, Os-Ni Co-Rh
Hydrogenation of ketones	Os-Ni
Hydroformylation of olefins	Fe-Rh Ru-Co Co-Rh
Reductive carbonylation of nitro derivatives	Mo-Pd Fe-Pd
Hydrodesulphurisation	Mo-Fe, Mo-Co

shown to be an intermediate in the transannular oxidative addition of I₂ to an Ir₂ complex (10). Oxidative addition of I₂ to the triply heterobridged complex [Ir₂(μ-pz)(μ-SBu⁺)(μ-MeO₂CC=CCO₂Me)(CO)₂{P(OMe)₃}₂] (pz = pyrazolate), as shown in Figure 6 results in a remarkable change in the Ir-Ir distance from 2.614(2) to 3.626(2) Å (11).

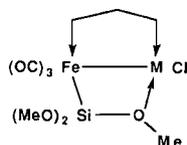
Professor G. Predieri of the Università di Parma, Italy, presented some recent results obtain-

ed during the course of the joint research project on the use of homo- and heterobimetallic carbonyl clusters as precursors of heterogeneous catalysts. This important area of catalysis has been recently reviewed and the Table indicates the major role played by the platinum group metals in such mixed-metal cluster-derived heterogeneous catalysis (12).

The pentanuclear cluster [NiOs₃(η-C₅H₅)(μ-H)₂{μ-Cu(PPh₃)}(CO)₉], supported on

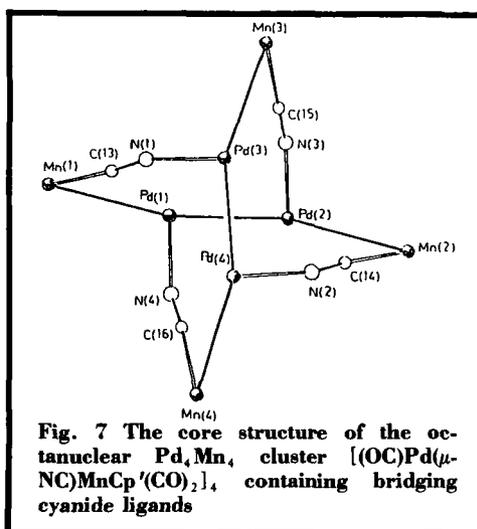
Chromosorb and thermally activated under hydrogen, forms a heterogeneous catalyst for the hydrogenation-dehydrogenation of several substrates, in particular alcohols. It shows higher dehydrogenating ability than the systems derived from the parent cluster $[\text{NiOs}_3(\eta\text{-C}_5\text{H}_5)(\mu\text{-H})_3(\text{CO})_9]$ or from $[\text{NiRu}_3(\eta\text{-C}_5\text{H}_5)(\mu\text{-H})_3(\text{CO})_9]$ (13). The latter cluster has also been supported on alumina in the presence of potassium hydroxide and thermally decomposed, with the aim of preparing catalysts for ammonia synthesis which would work under milder conditions than the current industrial catalysts. Bimetallic particles were generated, as shown by energy-dispersive X-ray analysis. Although it was found that the $\text{Ru}_3(\text{CO})_{12}$ -derived catalyst was more than twice as active as the NiRu_3 -derived catalyst for the same metal loading and at 400°C , the addition of small amounts of cobalt (0.1 per cent) or copper (0.05 per cent) to the 5 per cent ruthenium catalyst resulted in an increased productivity at lower temperature (14). It is known that ruthenium, promoted by alkali metals, is much more active than iron in ammonia synthesis and is less affected than iron by the poisoning effects of water and carbon monoxide but suffers much more from the inhibitory effects of hydrogen.

Finally, Dr. P. Braunstein, the co-ordinator of the European research project, described heterometallic complexes held together by diphosphine or phosphido bridges and which are good candidates for the study of site selectivity in heterometallic systems. The first complexes containing an alkoxysilyl ligand which forms a $\eta^2\text{-}\mu_2\text{-SiO}$ bridge, where M is palladium or



platinum were discussed, where the unexpected interaction between the oxygen donor and the soft metal centre was demonstrated by X-ray analysis and ^1H NMR spectroscopy (15).

The unprecedented structure and topology of an octanuclear Pd_4Mn_4 cluster containing bridging cyanide ligands was discussed. The highly symmetrical structure of this molecule con-



stituted of two helices of opposite chirality (16) prompted its use as the "logo" for the Symposium, Figure 7.

The excellent local organisation by Professor A. Tiripicchio of the Università di Parma, Italy, who is a participant in the joint project and who has determined crystal structures for many of the speakers at this Symposium, and the limited number of participants, facilitated numerous excellent discussions.

The synergy between the different studies performed by the research groups represented at this Symposium was very obvious and was emphasised during the round-table discussion at the end of the meeting. Among the conclusions reached were that concerted European actions, which are also increasingly needed in industry, are essential to successfully perform competitive fundamental research; and that the high-level teaching facilities available in various Centres of Excellence must be optimised by encouraging the mobility of post-graduate and post-doctoral students and staff, and by co-ordinating complementary expertise.

It was felt that the areas covered by this Symposium are more topical than ever, and that continuity in performing such studies and training post-graduate students constitute major priorities. Initiatives were taken to promote these ideas, particularly at the European level.

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Advances in the Study of Platinum Group Elements

Progress in the understanding of the mineralogy of platinum group metals worldwide is reported in *The Canadian Mineralogist*, 1990, **28**, (3). Of the twenty-one papers included, twelve were presented at the annual meeting of the Geological and Mineralogical Associations of Canada (GAC-MAC) which was held in Montreal, in May 1989. The remainder are new papers, all relevant to the theme of the above title.

The section on occurrences consists of nine papers, commencing with the 1990 MAC Presidential address given by J. M. Duke on the implications of magmatic segregation process models for Kambalda-type nickel sulphide deposits. A unifying model of the magmatic mineralisation process in layered intrusions is proposed by A. J. Naldrett, G. E. Brüggmann and A. H. Wilson. This attempts to account for the various platinum group metal concentrations found in different deposits of apparently similar genesis.

As these magmatic processes become better understood, the apparent exceptions to the rule, such as the Alaskan-type Tulameen deposits in British Columbia, attract greater interest. There, as discussed by G. T. Nixon, L. J. Cabri and J. H. G. Laflamme, platinum-

iron-copper alloys and osmium-iridium-ruthenium minerals appear to have crystallised directly from a silicate magma. This paper serves as a link to the next section, which includes discussions on ophiolite deposits containing platinum group metals. It is suggested that sulphur concentration is the factor controlling mineralisation in a silicate matrix.

Hydrothermal processes for the transport and deposition of platinum group metals are also considered, including a study by J. H. Crockett of platinum group metal mineralisation in sulphide-rich deposits near to sub-sea hydrothermal vents on ocean ridges. For surface deposits, the importance of ground water transport involving fulvic acid and simple organic analogues is discussed by S. A. Wood.

A mineralogical study of the system platinum-antimony-tellurium has been carried out by W.-S. Kim and G. Y. Chao, and a new palladium-copper-tellurium-sulphur mineral species, Vasilite, is reported by A. V. Atanasov.

While some of the deposits considered may never be economically viable, either for platinum group metal or base metal exploitation, the implications of the work reported for the overall understanding of the subject cannot be over-estimated.

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