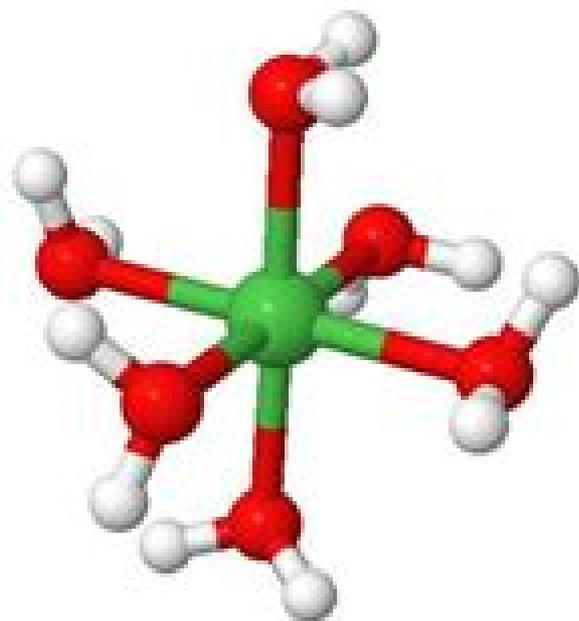
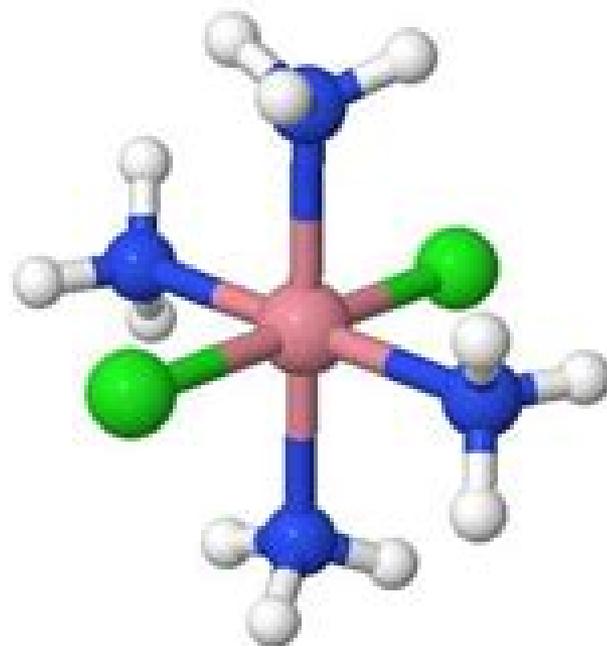


Examples of Metal Complexes



Six H_2O ligands bound
to a Ni^{2+} cation



Four NH_3 ligands and two Cl^-
ligands bound to a Co^{3+} cation

<http://www.3dchem.com/3dinorgmolecule.asp?ID=490>

<http://www.3dchem.com/3dinorgmolecule.asp?ID=196>

Supported Metal Complexes

Enrique Iglesia



Supported Metal Complexes:

Supported Metal Complexes F.R. Hartley, 1985-11-30 It is now 35 years since the first patents in polymer supported metal complex catalysts were taken out In the early days ion exchange resins were used to support ionic metal complexes Soon covalent links were developed and after an initially slow start there was a period of explosive growth in the mid to late 1970s during which virtually every homogeneous metal complex catalyst ever reported was also studied bound to a support Both polymers and inorganic oxides were studied as supports although the great preponderance of workers studied polymeric supports and of these polystyrene was by far the commonest used This period served to show that by very careful design polymer supported metal complex catalysts could have specific advantages over homogeneous metal complex catalysts However the subject was a complicated one Merely immobilising a successful metal complex catalyst to a functionalised support rarely yielded other than an inferior version of the catalyst Amongst the many discouraging results of the 1970s there were more than enough results that were sufficiently encouraging to demonstrate that by careful design supported metal complex catalysts could be prepared in which both the metal complex and the support combined together to produce an active catalyst which due to the combination of support and complex had advantages of activity selectivity and specificity not found in homogeneous catalysts Thus a new generation of catalysts was being developed

Supported Metal Complexes F.R. Hartley, 2012-12-06 It is now 50 years since the first patents in polymer supported metal complex catalysts were taken out In the early days ion exchange resins were used to support ionic metal complexes Soon covalent links were developed and after an initially slow start there was a period of explosive growth in the mid to late 1970s during which virtually every homogeneous metal complex catalyst ever reported was also studied bound to a support Both polymers and inorganic oxides were studied as supports although the great preponderance of workers studied polymeric supports and of these polystyrene was by far the commonest used This period served to show that by very careful design polymer supported metal complex catalysts could have specific advantages over homogeneous metal complex catalysts However the subject was a complicated one Merely immobilising a successful metal complex catalyst to a functionalised support rarely yielded other than an inferior version of the catalyst Amongst the many discouraging results of the 1970s there were more than enough results that were sufficiently encouraging to demonstrate that by careful design supported metal complex catalysts could be prepared in which both the metal complex and the support combined together to produce an active catalyst which due to the combination of support and complex had advantages of activity selectivity and specificity not found in homogeneous catalysts Thus a new generation of catalysts was being developed

Synthesis of Metal Complexes Supported by Ferrocene-based Ligands for Tandem Catalysis and Applications Toward Liquid Cell Quantum Sensing Yi Shen, 2023 Developing methodologies to synthesize high value products efficiently from simple substrates with control over the reactivity and selectivity is highly favored by the chemical industry Employing assisted tandem catalysis where serial reactions can be carried out in one pot to

achieve streamlined complex syntheses significantly reduces the number of steps and waste Harnessing spatial and temporal control in catalysis enables approaches toward one pot transformations and allows the integration of several catalytic processes Ferrocene based ligand supported metal complexes represent a promising class of catalysts that can incorporate redox control over catalytic processes We have developed a redox controlled selective hydroamination reaction catalyzed by thiolfan Zr NEt_2 2 thiolfan 1 1 bis 2 4 di tert butyl 6 thiophenoxy ferrocene In situ switching of the catalyst s state during the reaction enables selectivity toward different substrates Chapter 2 Incorporating the greenhouse gas CO_2 into N carboxyanhydrides NCAs followed by subsequent NCA utilization illustrates the possibility of integrating two synthetic steps in one vessel to afford a valuable material with possible CO_2 recycling To demonstrate the immense potential of integrating multi step transformations in one pot we developed a set of sustainable conditions for NCA synthesis Chapter 3 Moreover several metal catalysts supported by ferrocene based ligands were found to catalyze NCA polymerization in the presence of a co catalyst To establish an integrated system composed of two incompatible processes we aimed to compartmentalize the active reagents for each step The structure of the ferrocene based pro ligand was modified for surface anchoring Our efforts toward immobilizing ferrocene supported metal catalysts onto conductive surfaces pave the way of achieving spatiotemporal control over the processes of NCA synthesis and polymerization Chapter 4 In addition to the redox switchable characteristic ferrocene based compounds provide a unique platform to support lanthanides and engender distinctive optical properties to them We synthesized and characterized a series of ytterbium complexes displaying an ultra narrow absorption in the ultraviolet visible UV Vis region The extraordinarily narrow linewidth observed for thiolfan YbCl THF thiolfan 1 1 bis 2 4 di tert butyl 6 thiomethylenephenoxy ferrocene allows us to investigate its applications toward magnetic field and liquid cell quantum sensing Chapter 5

Supported Mono- and Bimetallic Complexes and Clusters Joseph David Kistler,2014 Site isolated solid supported metal catalysts are important in industry and technology due to the cost efficiency to make and to recover and reuse them These types of materials have catalytic properties similar to molecular complexes in solution while being easy to separate in heterogeneous catalytic reactions The goal of this work was to synthesize supported metal complex catalysts while maintaining uniform catalytic sites The syntheses were performed using precise glovebox and Schlenk techniques to achieve these highly uniform structures These materials were then used to understand the relationship between structure of a catalytic site and the activity of the catalyst This fundamental understanding of catalysts is important in advancing the field of catalysis The structure of the catalysts were characterized using infrared IR extended X ray absorption fine structure EXAFS and X ray absorption near edge structure XANES spectroscopies along with high angle annular dark field scanning transmission electron microscopy HAADF STEM with the HAADF STEM work carried out by colleagues in other research groups The catalytic activity of the catalysts was examined with gas chromatography GC and mass spectrometry MS The samples characterized in this work include complexes and clusters of second and third row

transition metals supported on highly crystalline metal oxides. Specifically, there is a large focus in this work on supported rhodium complexes prepared from the organometallic precursor $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ and a pre-calcined magnesium oxide (MgO). This specific catalyst is important as not only is it active for olefin hydrogenation at mild temperatures but also there are reports of a unique surface-mediated synthesis of uniform rhodium dimers which are ideal for catalytic comparison of structures with different nuclearities. Reactivities of the MgO-supported rhodium complexes and dimers for carbon monoxide oxidation were investigated with the results showing the dimers were significantly more active for the reaction at 353 K. The stability of the dimers was tested in different reactive conditions with the results showing that under conditions with excess oxygen the dimers are less stable and less active than under conditions with excess carbon monoxide. A bimetallic catalyst was synthesized on MgO incorporating rhodium and osmium using $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$ and $\text{Os}_3(\text{CO})_{12}$ as precursors. A unique synthesis method was developed to create a site-isolated, segregated bimetallic catalyst with the osmium and rhodium sites acting independently of each other for ethylene hydrogenation at 298 K. The metals remained structurally segregated and catalytically independent even following reduction in H_2 at 393 K. Zeolites, another class of highly crystalline supports, were studied to gain information on the support effects in catalysts. The analogous rhodium complexes as were synthesized on the MgO were synthesized on zeolite HY. These catalysts were tested to determine structural and catalytic stability under hydrogen, a reducing gas, and CO, a catalyst poison, with the results showing that as compared to the complexes on zeolite HY, MgO-supported rhodium complexes form more uniform, stable clusters under H_2 and develop unique catalytic properties, selectivity for partial hydrogenation of dienes when exposed to CO. Another zeolite, KLTL, was studied with supported platinum complexes synthesized from the salt precursor $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$. This catalyst was oxidized at 633 K to form supported single-atom platinum complexes. Both the as-prepared $\text{Pt}(\text{NH}_3)_4$ and oxidized PtOx complexes were analyzed structurally and studied as catalysts for CO oxidation. The oxidized platinum complexes proved to have significantly higher activity for CO oxidation at 423 K. Furthermore, HAADF-STEM was used to directly identify the locations of the platinum atoms in the pores of the zeolite before and after oxidative treatment, providing a method of ex situ tracking of supported metal atoms.

Late Transition-metal Complexes Supported by Pincer Ligands Wilson D. Bailey, 2016. Late transition metal pincer complexes of primarily palladium(II) and platinum(II) have been investigated for their application as catalysts in partial oxidation reactions. The epoxidation of higher olefins using molecular oxygen as the oxidant has been targeted, and the individual reaction steps needed to accomplish this overall transformation are described herein, including 1) hydrogenolysis of a metal hydroxide (M-OH) species to yield a metal hydride (M-H), 2) insertion of O_2 into the M-H bond to form a metal hydroperoxide (M-OOH), and 3) O-atom transfer from the M-OOH to epoxides, yielding a M-OH and completing the catalytic cycle. Previous results from our group on these individual transformations using tBuPCP-Pd and tBuPCO-Pd fragments are also reviewed. The requirements for O_2 insertion into Pd(II) and Pt(II) hydrides are discussed. An array of cationic, neutral, and

anionic Pd H and Pt H complexes supported by a tBuPNP backbone were synthesized and evaluated for O₂ insertion tBuPNP 2,6-bis(di-*t*-butylphosphinomethyl)pyridine Metal ligand cooperation was observed in the activation of H₂ to form neutral hydride complexes The effect of ligand protonation/deprotonation on the trans influence experienced by the hydride ligand was investigated No reaction with O₂ was observed with the cationic hydrides while the neutral and anionic forms reacted with O₂ at the tBuPNP backbone The synthesis and characterization of mono and dinuclear Pd OH complexes supported by a PCNR pincer ligand PCNR 1,3-bis(di-*t*-butylphosphino)methylphenyl 1H-5R-pyrazole R H Me is presented When R H ligand pyrazole rollover C H activation was observed forming a mixed ligand PCNH Pd OH Pd PCC dinuclear structure This rollover was investigated using DFT computations The mono and dinuclear hydroxide species were evaluated for hydrogenolysis The dinuclear compounds PCNR Pd 2 OH OTf reacted under an H₂ atmosphere to yield the corresponding dinuclear hydrides PCNR Pd 2 H OTf A mechanistic study on the hydrogenolysis of the bridged hydroxide PCNMe Pd 2 OH OTf revealed first order kinetics in both Pd and H₂ Terminal hydrides were not detected and reduction of the mononuclear hydroxide complexes PCNR Pd OH to Pd⁰ was observed under H₂ The reduction was proposed to proceed through displacement of the pyrazole arm and was examined by DFT computations Lastly a new strategy to promote O atom transfer from M OOH to epoxides the final step in the targeted catalytic cycle is proposed Preliminary studies on NNNPyz NNNEt and NNMe ligated PdII and PtII are discussed NNNPyz 2,6-bis(5-*t*-butyl-1H-pyrazol-3-yl)pyridine NNNEt 2,5-*t*-butyl-1H-pyrazol-3,6-diethylaminomethylpyridine NNMe 2,5-*t*-Bu-1H-pyrazol-3,6-dimethylpyridine The NNNPyz ligand containing two acidic sites in proximity to the fourth site in the square plane was found to protonate M O₂ complexes chelate to the metal center and oxidize phosphine substrates Similar reactivity was observed with NNNEt and NNMe however hemilability of these ligands resulted in undesired coordination modes

Encyclopedia of Catalysis István T. Horváth, 2003 Catalysis the speeding up of a chemical reaction by a substance which itself does not react is vital not only to the chemical process industry but also to life itself The six volume Encyclopedia of Catalysis is the definitive A to Z reference work covering the most significant aspects of homogenous heterogeneous asymmetric biomimetic and biological catalysis Available both on line and in print the state of the art Encyclopedia encompasses the principles of catalysis the scope of catalytic reactions the preparation characterization and use of catalysts including catalytic technology the modeling of catalytic processes and related reaction engineering techniques The logical organization of this seminal work renders the text easily accessible to both process personnel and those involved in basic and applied research and development For more information regarding the online edition please visit Wiley InterScience at www.mrw.interscience.wiley.com/encat

Comprehensive Coordination Chemistry II J. A. McCleverty, T.J. Meyer, 2003-12-17 Comprehensive Coordination Chemistry II CCC II is the sequel to what has become a classic in the field Comprehensive Coordination Chemistry published in 1987 CCC II builds on the first and surveys new developments authoritatively in over 200 newly commissioned chapters with an emphasis on current trends in biology

materials science and other areas of contemporary scientific interest **Metal-support Bonds in Supported Metal Catalysts** ,1990 This research project now in its third year is an investigation of the synthesis structure and bonding of a family of metal complexes clusters and particles on the surfaces of high area metal oxide supports The focus is the structure of the metal support interface Surface species have been prepared by synthetic organometallic chemistry on the support surfaces The organometallic precursors are complexes of W Re Os Ir and Pt including W CO 6 HRe CO 5 Re2 CO 10 H3Re3 CO 12 H2Os CO 4 Ir eta 3 C3H5 3 and Pt eta 3 C3H5 2 The supports are primarily MgO and gamma Al2O3 The surface species have been characterized by infrared and EXAFS spectroscopies among other techniques 7 refs 5 figs 4 tabs

Chemical Abstracts ,1921 *Catalysis by Polymer-Immobilized Metal Complexes* Anatoly D. Pomogailo,2020-08-18 Deals with a new and promising field developed during the last two decades on the boundary between homogeneous and heterogeneous catalysis This book presents general information on catalysis for a wide range of organic reactions e g hydrogenation and oxidation reactions and polymerization transformations Special attention is paid to electro and photochemical stimulation of catalytic processes in the presence of immobilized metal complexes Other topics covered are the quantitative data on the comparison of catalyses by mobile and immobilized metal complexes main factors affecting the activity of these catalytic systems and methods of optimizing their control and specific problems of catalysis by fixed complexes e g ligand exchange and electron transfer in metal polymer systems macromolecular effects and polyfunctional catalysis **Synthesis of Group 9 and 10 Metal Complexes Supported by Chelating Nitrogen-based Ligands and Mechanistic Studies of Their Role in Catalytic Transformations** Jennifer Lauren McBee,2009 Catalysis by Supported Complexes Iñaki Ivanovich Ermakov,Boris Nikolaevich Kuznetsov,Vladimir A. Zakharov,1981

Government Reports Announcements & Index ,1988 Catalysis by Supported Complexes Y. I. Yermakov,B. N. Kuznetsov,V. A. Zakharov,1981 Theoretical Chemical Engineering Abstracts ,1980 **Revue Roumaine de Chimie** ,2007 NMR and Molecular Modeling of the Heavy-metal Complexes of Phytochelatins and the Cis/Trans Isomerization Kinetics of Proline-containing Peptides Stephen Micheal Spain,2003 Synthesis and Properties of Advanced Catalytic Materials Enrique Iglesia,1995 *Pandex Current Index to Scientific and Technical Literature* ,1971 Metals Abstracts ,1992

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