

Rhodium Complexes of Chiral Phosphines as Catalysts for Asymmetric Homogeneous Hydrogenation

J. D. MORRISON, *Strem Chemiker*, 1973, 1, (1), 3-7

The use of a series of soluble Rh complexes, prepared from chiral tertiary phosphines, as catalysts for asymmetric homogeneous hydrogenation is discussed. These catalysts show nearly complete, enzyme-like stereoselectivity and represent a vast improvement in performance over that of simpler chiral-supported heterogeneous catalysts.

Hydrogenation of Tris(triphenylphosphine)-chlororhodium(I)

J. HALPERN and C. S. WONG, *J. Chem. Soc., Chem. Commun.*, 1973, (17), 629-630

The reactivities of $\text{RhCl}(\text{PPh}_3)_3$, $\text{RhCl}(\text{PPh}_3)_2$ and $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$ towards H_2 , and the contributions of each of these species to the overall rate of hydrogenation of $\text{RhCl}(\text{PPh}_3)_3$ in solution were determined. $\text{RhCl}(\text{PPh}_3)_2$ is at least 10^4 times as reactive as the other two species.

Hydrogenation and Dehydrogenation of Chlorotris(triphenylphosphine)rhodium(I)

G. G. STRATHDEE and R. M. GIVEN, *J. Catalysis*, 1973, 30, (1), 30-39

The amount of H_2 absorbed per mole of $\text{RhCl}(\text{PPh}_3)_3$ differs from that recovered by an inert gas purging technique when using C_6H_6 , CH_2Cl_2 and 50% $\text{C}_2\text{H}_5\text{OH}-\text{CHCl}_3$ solutions. In the last case the reversibly bound H:Rh ratio is only ~ 0.3 at 298K because $\text{RhHCl}(\text{PPh}_3)_2$ has been formed, whereas in C_6H_6 the ratio is 0.85 and in CH_2Cl_2 it is 0.66.

NEW PATENTS

METALS AND ALLOYS

Novel Platinum-Rhodium-Tungsten Alloy

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. Patent 3,737,309

A new alloy composition comprising 25-30% Rh, 6-10% W with the remainder Pt, is useful for encapsulating radioisotope fuels. It has a melting point of 1980-2050°C.

Wrought Dispersion Strengthened Metals by Powder Metallurgy

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,738,817

Powder metallurgy is used to produce Pt-based alloys by dispersion hardening with uniform distribution of the dispersed agent transversely and longitudinally.

Homogeneous Olefin Hydrogenation Catalysed by Dichlorodicarbonyl-bis(triphenylphosphine)ruthenium(II)

D. R. FAHEY, *J. Org. Chem.*, 1973, 38, (19), 3343-3348

The relative hydrogenation rates for a variety of alkenes and alkadienes catalysed by $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ were measured in the presence of added PPh_3 . Reaction rates and the means of obtaining selective hydrogenation are discussed.

GLASS TECHNOLOGY

Observation of Contact Phenomena in Glass/Metal Systems

G. J. COPLEY, A. D. RIVERS and R. SMITH, *J. Mater. Sci.*, 1973, 8, (7), 1049-1051

A study of the glass droplets found near the wetting edge of glass sessile drops on Pt has clarified the deposition process and the influence of the Pt grain structure on their nucleation and growth. The mode of grain boundary movement during grain growth is discussed.

TEMPERATURE MEASUREMENT

A Reciprocal Kelvin Temperature Sensor

L. FOWLER and W. N. TRUMP, *Rev. Sci. Instrum.*, 1973, 44, (9), 1333-1334

A simple bridge circuit using a Pt resistance thermometer is described which generates a signal proportional to $1/T$ with an error $< 0.1\%$ over a wide range. The superiority of Pt over other materials is discussed.

Metal Atomisation

JOHNSON, MATTHEY & CO. LTD.

French Appl. 2,148,349

Metal articles are produced by arc, flame or plasma spraying metal droplets at a cold target to form a coherent layer of individual particles which are then mechanically worked to a mass. The metal is particularly a Pt-group metal or alloy, e.g. an alloy of 49% Pt, 50% Au and 1% Rh.

Alloy for Metering Instruments

F.A. CARL HAAS

German Offen. 2,206,397

Suspension strips for meters are made from Pd and/or Pt containing small amounts of at least one Group III-VI element to increase corrosion resistance and deformability. Au, Ag and Cu may also be present.

CHEMICAL COMPOUNDS

Rhodium Molybdenum Oxide

SOLVAY & CIE. *British Patent* 1,330,589

A new oxide for use as an electrolysis electrode, oxidation catalyst and composite semiconductor is a mixed oxide of formula Rh_2MoO_6 formed from hydrated rhodium trichloride and molybdic oxide.

Silyl Metal Complexes

DOW CORNING CORP. *German Offen.* 2,260,215

Disilanes and hydrosilanes having Cl substituents are reacted with Pd or Pt phosphine complexes to give silyl complexes of the type $Pd(SiPhCl_2)(PBu_3)_2Br$.

ELECTRODEPOSITION AND SURFACE COATINGS

Chemical Plating Process

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

British Patent 1,324,653

Insulators such as glass and plastics are chemically plated by ion bombardment to produce an activated surface which is then contacted with a suitable plating bath. The examples show the use of positive Pd ions for bombardment.

Ruthenium Alloy Electroplating

SEL-REX CORP. *British Patent* 1,328,928

Stress in Ru electroplated coatings may be reduced by the co-deposition of another Pt-group metal and optionally a Group IIIB metal such as Ga, In or Ti. The bath used contains 0.5–50 g/l Ru as $(NH_4)_3(Ru_2Cl_8(H_2O)_2N)$ and 0.5–20 g/l of other Pt-group metal as a water-soluble salt, e.g. Na_2PtCl_6 .

Rhodium Plating

AMERICAN CHEMICAL & REFINING CO. INC.

U.S. Patent 3,729,396

An aqueous acidic Rh plating bath contains Rh ions, Al ions, SO_4 ions and a polycarboxylic organic acid. Optionally PO_4 ions are also present.

Electrolyte for Rhodium Deposition

AMERICAN CHEMICAL & REFINING CO. INC.

French Appl. 2,150,988

An electrolyte for the deposition of Rh, in the manufacture of jewellery and ornaments, comprises 1.0–30.0 g/l Rh ions, 0.05–5.0 g/l Al ions, 50.0–400.0 g/l sulphate ions and 1.0–25.0 g/l of an organic polyacid, e.g. azelaic, oxalic, maleic acids. The pH is within the range 0.1–2.0. The electrolyte may also include 10.0–70.0 g/l PO_4 radicals.

Ruthenium Plating Bath

INTERNATIONAL NICKEL LTD.

German Offen. 2,261,944

Bright flash coatings of Ru are obtained using

baths of pH 4 or lower containing a N-bridged Ru complex and at least 1.5 g/l SO_4 ion. $[Ru_2N(H_2O)_2Cl_8]^{3-}$ is a suitable complex.

HETEROGENEOUS CATALYSIS

Paraffin Hydrocracking and Isomerisation

TEXACO DEVELOPMENT CORP.

British Patent 1,324,480

Control over catalyst activity and selectivity when using fluorided Pt, Pd, Rh, Ru or Re catalysts on Al_2O_3 supports is achieved by adding an oxide of C.

Organosiloxane Composition

DOW CORNING CORP. *British Patent* 1,324,964

Adhesives are produced from a mixture of organosiloxane and vinyl triacetoxysilane in the presence of a Pd catalyst.

NO_x Abatement

JOHNSON, MATTHEY & CO. LTD.

British Patent 1,330,841

Tail gas from HNO_3 plants is mixed with excess CH_4 or other gaseous reducing fuel and passed over a layer of Pt-Rh deposited on a wash-coated ceramic honeycomb. The metallic layer contains 20–50% Rh-Pt.

Oxidation of Methane

JOHNSON, MATTHEY & CO. LTD.

British Patent 1,330,842

A gaseous compound of C is mixed with O_2 and passed over a Pt-Rh alloy deposited on a wash coated ceramic honeycomb. The alloy contains 20–50% Rh-Pt. The feed gases may be C-enriched HNO_3 tail gases or engine exhaust gases.

Azole Derivatives

MERCK PATENT G.M.B.H. *British Patent* 1,331,408

In the synthesis of azole derivatives the hydrogenation of nitro to amine and the hydrogenolysis of benzyl groups may be catalysed by Pd catalysts.

Benzotriazoles

RHEIN-CHEMIE RHEINAU G.M.B.H.

British Patent 1,331,606

Benzotriazoles can be hydrogenated smoothly and rapidly in the presence of Pd, Pt or Rh catalysts to give the hitherto unknown 4, 5, 6, 7-tetrahydrobenzotriazoles in good yields.

Cyclohexanone Production

V.E.B. LEUNA-WERKE WALTER ULBRICHT

British Patent 1,332,211

The hydrogenation of phenol to cyclohexanone is catalysed by an Al_2O_3 -supported mixture of 0.1–5% Pt-group metal and 5–50% alkaline earth metal hydroxide and/or alkaline earth metal oxide. The catalyst must have a specific area of 110 m^2/g and at least 40% of the pores in the range 100Å–500Å.

Hydrogenation Catalysts

ESSO RESEARCH & ENGINEERING CO.
British Patent 1,332,483

The activity of supported catalysts is increased by treating the supports before impregnation with a Group I-III metal alkyl, aryl, etc. For example 0.6% Pt can be deposited on an alcoholate alumina pretreated with $AlEt_3$.

Hydroformylation

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,332,894

Catalysts suitable for hydrogenation, hydroformylation and carbonylation may be prepared by absorbing into the pores of a solid porous support solutions of hydrido carbonyl complexes of Rh such as $RhH(CO)(PR_3)_3$, $RhH(CO)(PR_3)_2$ or $RhH(CO)_2(PR_3)_2$ where R is an organic substituent.

Methane Production

CLARKE CHAPMAN-JOHN THOMPSON LTD.
British Patent 1,333,251

CH_4 is produced from CO and H_2 in the presence of a Ru, Pt, Co or Ni catalyst, stripped of H_2O and then the reaction is repeated to increase the yield.

Paraffin Hydrocracking and/or Isomerisation

TEXACO DEVELOPMENT CORP.
British Patent 1,324,209

Control over temperature and reaction during hydrocracking and/or isomerisation over a Pt/Al_2O_3 catalyst containing Cl_2 is achieved by introducing CO during the reaction.

Lubricating Oils

SHELL OIL CO. *U.S. Patent 3,730,877*

Lubricating oils are produced by the treatment of paraffinic-naphthenic oils with hydrogen over a Pt/Al_2O_3 catalyst containing up to 4% alkali or alkaline earth metal.

Palladium-Gold Catalyst

KNAPSACK A.G. *U.S. Patent 3,743,607*

An improved catalyst for the catalytic vapour phase production of $CH_3COOCHCH_3$ from C_2H_4 , CH_3COOH and O_2 is disclosed. A catalyst for the synthesis reaction is metallic Pd and an alkali metal acetate or formate supported on a carrier activated by metallic Au.

Ammonia Oxidation Catalyst

JOHNSON, MATTHEY & CO. LTD.
French Appl. 2,148,525

Gas reactions, e.g. NH_3 oxidation for HNO_3 production, are catalysed by two sets of gauzes. The reactant gases first come into contact with noble metal gauzes (e.g. 10% Rh-Pt alloy, and then with less volatile catalytic gauzes such as austenitic 21% Ni, 23% Cr stainless steel or a Pt-Ni-Cr alloy.

Ring Hydrogenation of Arylamides

UNIROYAL INC. *Dutch Appl. 73,02459*

N-alicyclic polyamides are produced from N-aryl polyamides by hydrogenation in the presence of a catalyst such as Rh, Ru, Pd, Os, Ir, Ni or Co.

Hydrocarbon Conversion Catalyst

SHELL INTERNATIONALE RESEARCH MIJ. N.V.
Dutch Appl. 73,07241

Petrols containing straight chain paraffins are treated to raise the octane number by selective hydrocracking using a catalyst, e.g. Pt deposited on a porous support with a pore diameter of 0.42-0.58 μ and a C content of at least 2.5%, especially a zeolite.

HOMOGENEOUS CATALYSIS

Nitro Compound Reduction

AMERICAN CYANAMID CO. *U.S. Patent 3,729,512*
Nitro compounds are reduced to amines with CO/H_2 in the presence of Ru carbonyls or their precursors.

Rhodium Based Catalysts for Diene Synthesis

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,742,080

Improved catalysts are provided for the synthesis of 1,4-dienes from α -monoolefins and conjugated dienes. The catalysts are Rh(III) salts in combination with amides, phosphoramides, phosphine oxides, or water. The improved catalysts allow control of the *trans-cis* ratio of the 1,4-diene formed and are operable at useful rates in a wide range of solvent systems, both protonic and aprotic.

Carboxylic Acid or Anhydride Production

MONSANTO CO. *Dutch Appl. 73,02968*

Carboxylic acids are produced by the reaction of olefins and CO in the presence of an Ir complex of an arsine, phosphine and/or stibine, e.g. $HRh(CO)(PPH_3)_3$.

FUEL CELLS

Electrochemical Cells

NATIONAL RESEARCH DEVELOPMENT CORP.
British Patent 1,332,295

A cell for operating a cardiac pacemaker or the like uses Pt-black in an O_2 proof seal as one electrode.

CHEMICAL TECHNOLOGY

Noble Metal Image Stabilisation

POLAROID CORP. *U.S. Patent 3,730,716*

Noble metals below Ag in the electromotive series, e.g. Pt-group metal, are used to enhance Ag halide image stability.

Chemical Plating of Fibres

COPPERTECH INC. *U.S. Patent 3,733,213*
Fibres or fabric are degreased with solvent, oxidised and then sensitised using Pd and Sn solutions.

Silver Halide Grains Sensitised with a Rhodium Salt

EASTMAN KODAK CO. *U.S. Patent 3,737,313*
Rh salts are used to sensitise Ag-halide emulsions used in non-destructive testing.

Sensitising Composition

NAUCHNO-ISSLEDOVATELSKI TECHNOCHIMICHESKII INSTITUT *German Offen. 2,206,150*
Photographic compositions are sensitised with a mixture of organic dyestuff, a water-soluble Pt or Pd salt and a complexing agent.

GLASS TECHNOLOGY

Coating Refractory Metals

JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,736,109

Articles for use at high temperature, for example in the glass industry, have a refractory core made from Nb, Ta, Cr, Zr, V, Hf, Re or their alloys, a barrier layer of MgO and a sheath of a Pt-group metal. The oxides of the core metal or alloy are chosen to be less volatile than the oxides of Mo at operating temperature within the range 1100° to 1500°C.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electric Lamps

THORN ELECTRICAL INDUSTRY LTD.
British Patent 1,327,363
Heat is conducted away from a lamp seal by the use of a contact cap arrangement having a high thermal conductivity. A Cu sleeve is brazed to Pt-clad Mo conductors by a high Ag-content Cu brazing alloy, which also serves to protect the embedded ends of the conductors from oxidation.

Monolithic Capacitors

N.L. INDUSTRIES INC. *British Patent 1,327,902*
A fired capacitor has stacked alternating layers of Bi-containing barium titanite and electrode layers, inert to bismuth, consisting of up to 90% Pd with the remainder Au and/or Pt.

Memory Discs

PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD.
British Patent 1,328,016
Improved performance memory discs have a Co-P layer applied to a disc over an intermediate layer of Pt.

Electrical Lead Structures

INTERNATIONAL STANDARD ELECTRIC CORP.
British Patent 1,329,050
External leads on vidicon tubes are eliminated by placing the leads, e.g. of Pt, in grooves formed internally in the envelope and then sealing with a melted glass frit.

Circuit Patterns

WESTERN ELECTRIC CO. INC.
British Patent 1,329,287
A layer between a circuit pattern and the substrate has a discontinuous, etch resistant portion of Pd which is highly adherent to the base. A thicker layer of easily etched material, such as Au, Cu or Ni is then applied. The resulting composite has good adhesion and can be easily etched.

Electroless Deposition

R.C.A. CORPORATION *British Patent 1,332,000*
An apertured colour TV selection mask is produced by first depositing a pattern of catalytic material such as Pd and then depositing enough metal chemically on the pattern to form the opaque pattern required.

Sandwiched Eutectic Reaction Anticompromise Circuits

U.S. SECRETARY OF THE NAVY
U.S. Patent 3,745,227
An anticompromise circuit has a thin film circuit sandwiched between two eutectic reaction films separated by electrical insulating films. The eutectic reaction films consist of a mixture of Pd and Al and are adapted to be coupled to a switched electrical source to produce a eutectic reaction to destroy the thin film circuit.

Schottky Diode

SIGNETICS CORP. *German Offen. 2,264,322*
A Schottky diode is produced by the application of a Pt-Ni-Si alloy layer to a Si block.

Grid Electrodes

BROWN, BOVERI & CIE. *Dutch Appl. 72.17592*
Grid electrodes for discharge tubes have an intermetallic layer, such as ZrPt₃, coated with a noble metal layer such as Pt.

TEMPERATURE MEASUREMENT

Platinum Resistance Temperature Sensors

ROSEMOUNT ENG. CO. LTD.
British Patent 1,325,451
A Pt resistance temperature sensor is described which does not deteriorate in stability, provided that the pressure is prevented from rising substantially within the sheath.