Reactions of (\(\eta^2\)-Allyl)tricarbonylchlororuthenium(II) with Hydrogen and Unsaturation Substrates: Catalytic Hydrogenation and Isomerisation of Alkenes


Studies were made of the reactions of \([\text{RuCl}((\eta^2-C_2H_4)(CO))_3]\), with unsaturated substrates such as acrylonitrile (acn), alkynes, butadiene, and acetylenic esters using i.r. and n.m.r. techniques. The solids \([\text{RuCl}(\sigma-C_2H_4)(CO)]_2(acn)\), \([\text{RuCl}((\sigma-CN).C_2H_4)(CO)]_2\) \((R=R'=H;\ R-H,\ R'-Ph;\ and\ R=R'-Rh)\), and \([\text{RuCl}((\sigma-C_2H_4)(C_2H_5)](CO)]_2\) were isolated. In the case of diethyl acetylenedicarboxylate an alkenyl complex of formula \([\text{RuCl}((\sigma-CH=CHC(OEt)O)(CO)]_2\) was obtained.

G. SBRANA, G. BRACA and E. BENEDETTI, J. thethem.

Asymmetric Synthesis by Chiral Ruthenium Complexes. I: Enantioselective Hydrogenation of Ketones and Ketoximes Catalysed by \(H_2\text{Ru}_8(\text{CO})_8[(-)-\text{DIOP}]_2\)

C. BOTTEGHI, M. BIANCHI, E. BENDETTI and U. MATTEZZI; Chimia, 1975, 29, (6), 256-258

\(H_2\text{Ru}_8(\text{CO})_8[(-)-\text{DIOP}]_2\) catalyses asymmetric hydrogenation of C-O and C-N double bonds at high temperature and pressure. In the case of \(\text{diethyl acetylenedicarboxylate}\) an alkenyl complex of formula \([\text{RuCl}(\sigma-CH=CHC(OEt)O)(CO)]_2\) was obtained.

Acid-dependent Selectivity in the Homogeneous Hydrogenation of Mono- and Dienes by Acetatotriphenylphosphine Complexes of Ruthenium and Rhodium


The hydrogenation of mono- and di-enes by catalysts derived from protonation of \(\text{Ru}(\text{CO})_2\text{Me})_2(\text{PPPh}_3)_2\) and \(\text{Rh}(\text{CO})\text{Me}((\text{PPPh}_3)_2\) in methanolic solution with \(p\)-toluenesulphonic acid was studied. The rate of hydrogenation is highly dependent on the acidity. Rapid highly selective reduction of cyclic dienes to monoenes occurs. This selectivity is attributed principally to the superior coordinating power of the dienes.

CHEMICAL TECHNOLOGY

Interaction of Os (IV) Halogen Complexes with Trialkylphosphine Oxides in Extraction Processes


Extraction of Os in the form of \([\text{OsCl}_2]^2-\) and \([\text{OsBr}_2]^2-\) complexes in HCl medium was carried out using \(\text{tri-}n\text{-butylphosphine oxide and tri-}n\text{-octylphosphine oxide}\). The extent of Os recovery measured in terms of coefficient of distribution D increases with increasing HCl concentration and attains a maximum at \(~4\) mol HCl. The influence of different extracting reagents, ligands and diluents on the recovery process as well as on the structure and properties of the complexes obtained was also investigated.

ELECTRICAL AND ELECTRONIC ENGINEERING

I-V Characteristics of PtSi-Si Contacts Made from CVD Platinum


The use of CVD Pt to make PtSi contacts was studied. With heavily doped Si and sintering at 450-700°C no electrical anomalies appear. With light doping there is still no problem provided a relatively low (~450°C) is used. CVD Pt reliably forms PtSi at this temperature. The effects of higher contact formation temperatures are discussed.

TEMPERATURE MEASUREMENT

Rh-Ir Thermocouples Operate at 2100°C

L. R. THOMAS, MetalProg., 1975, 107, (6), 55

The new Feussner thermocouples, Ir :40% Ir-Rh, are recommended for applications where continuous temperatures exceed 1700°C up to 2100°C. Accuracy is ±10°C. Below 1500°C, Pt is preferred.

NEW PATENTS

CHEMICAL COMPOUNDS

New Rhodium Carbonyl Salts

UNION CARBIDE CORP. U.S. Patent 3,878,290

New salts have the formula \(M\text{Rh}_8(\text{CO})_8\) where \(M\) is divalent Be, Mg, Ca, Sr, Ba, Sc, Y, Mn, Fe, Ru, Re, Co, Ni, Pd, Pt, Zn, Cd, Hg, Ce and Eu.

ELECTROCHEMISTRY

Electrolytic Electrodes

ELECTRONOR CORP. British Patent 1,398,211

Electrolytic electrodes are provided with more stable coatings by depositing a mixture of a Pt-Ir alloy and 2.5-20% of a valve metal oxide on their
surfaces. The preferred coatings consist of a 70% Pt-Ir alloy and TiO₂.

**Electrowinning of Metals**

DIAMOND SHAMROCK CORP.
British Patent 1,398,378

An electrode for the recovery of metals by electrolysis has a surface coating containing 1.0-10% Sb₂O₃, 30-90% SnO₂, 1-50% of one or more Pt group metal oxides and 0.5-30% of Ti or Ta oxide.

**Diaphragm Cells for Electrolysis**

ORONZIO DE NORA IMPIANTI ELETTROCHIMICI S.P.A.
British Patent 1,400,053

Diaphragm cells stacked horizontally for electrolysis have a number of horizontal planar anodes made from a valve metal coated with a catalytic layer containing a Pt group metal or its oxide.

**Electrode Having a Silicide Surface**

P.P.G. INDUSTRIES INC.  U.S. Patent 3,862,023

An electrode with a valve metal substrate has a coating consisting of a Pt group metal silicide chosen from Pd₃Si, Pt₃Si and Ru₃Si₂.

**ELECTRODEPOSITION AND SURFACE COATINGS**

**Ruthenium/Osmium in Cutting Tools**

INTERNATIONAL NICKEL LTD.
British Patent 1,393,115

A new cutting tool, e.g. a carbide tool, has a coating of Ru and/or Os on the surfaces adjacent to the cutting edge. In one example the tips of a tool containing 83% W carbide, 12% Ti carbide and 5% Co is given a flash coating of Au and then is electroplated with Ru.

**Platinum and/or Iridium Electroplating**

RHONE-PROGIL  British Patent 1,399,500

The mechanical and chemical resistance of Pt and/or In deposits are improved by using a bath containing bromoplatinic and/or bromoiridic anions and HNO₃, H₂SO₄, HClO₄ and/or HBrO₃. A typical plating bath contains 0.75 g/l ammonium bromoplatinate in 0.35N HClO₄.

**Siloxane Coating Composition**

IMPERIAL CHEMICAL INDUSTRIES LTD.  British Patent 1,399,885

Organopolysiloxane coatings are cured by the presence of 0.1% of a Pt group metal halide catalyst complexed with a suitable ligand, e.g. cyclooctadiene or tripropyl phosphine complexes of PtCl₃.

**Activator Solution for Chemical Plating**

ENTHONE INC.  U.S. Patent 3,871,889

The solution for activating non-metallic surfaces contains a Au chloride, Pd chloride or other noble metal—Sn salt complex modified with a lower alkanol.

**Metallised Macromolecular Material**

HORCHST A.G.  U.S. Patent 3,871,903

A shaped body consists of a solid support thermally resistant at 250-400°C, a sintered film on the surface of the support of polytetrafluoroethylene having a noble metal salt dispersed in it and a metal coating on the surface of the polytetrafluoroethylene film. The noble metal salt is preferably Pd chloride, Pt chloride or Ag nitrate and the metal of the coating may be Ni or Cu.

**LABORATORY APPARATUS AND TECHNIQUE**

**Gas Concentration Cells**

BAILEY METER CO.  British Patent 1,400,079

A solid electrolyte concentration cell has two electrodes and is used for O₂ detection on a porous Pt electrode. The amount of O₂ is indicated by the electrode temperature which is measured by a Au-Pt thick film thermocouple.

**Potentiometric CO Detector**

EXXON RESEARCH & ENGINEERING CO.  U.S. Patent 3,880,722

In an instrument for the detection and measurement of the CO content of gases, particularly in ICE exhaust gases, CO is reacted with H₂O to form CO₂ and H⁺ and to produce a voltage change which is proportional to the CO content of the gas under suitable conditions. The reaction takes place in an aqueous solution and employs suitable oxidising agents and a Pd salt catalyst.

**JOINING**

**Binder for Carbide Tools**

INTERNATIONAL NICKEL LTD.  British Patent 1,393,116

The carbide particles constituting the tool are held together by a binder containing Co and a lesser or equal amount of Ru and/or Os, e.g. 70% Co-30% Ru.

**HETEROGENEOUS CATALYSIS**

**ICE Exhaust Gas Treatment**

KALI-CHEMIE A.G.  British Patent 1,392,528

In a two bed reduction-oxidation catalyst system, the first bed is used in oxidising conditions during cold starts to generate heat before reverting to the reduction-oxidation operation. The first bed contains a calcined support carrying (a) 0.02-0.1% Rh with 0.05-0.2% Pd or (b) 0.005-0.5% Rh with 0.005-0.5% Ir.
Hydrogenation Processes

DIAMOND SHAMROCK CORP.
British Patent 1,399,453

An unsaturated carboxyclic or heterocyclic compound, such as benzene, pyrindine or especially a 2,5-dialkyl-pyrrole, is converted to a corresponding saturated compound in the presence of a mixture of a H₂O soluble unreacted Ru salt and Al₂O₃. In the examples, Al₂O₃ and Ru chloride are milled together.

Hydrogen Isotope Exchange Catalyst

ATOMIC ENERGY OF CANADA LTD.
British Patent 1,388,569

A longer life Pt group metal catalyst for exchange reactions is obtained by hydrophobing the support, e.g. with a polyolefin or polycarlylate. Thus a Pt/Al₂O₃ catalyst may be replaced by a Pt/polystyrene catalyst.

Platinum Group Metal Catalysts

BRITISH PETROLEUM CO. LTD.
British Patent 1,399,453

Small amounts of an alkali or alkaline earth metal, when added to a C-supported Pt catalyst, give a marked increase in its dehydrocyclisation activity. The additive such as sodium is present in an amount of 5-100 at. % based on the 0.01-5 % Pt on the support.

Platinum-Coated Catalysts

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,399,453

A heterogeneous catalyst for use at high temperatures in reducing or non-oxidising conditions, having a refractory carbide, nitride or silicide support which is coated with magnesia, preferably in a thickness of 0.0004-0.5 inches depending on its intended use, before the Pt group metal or alloy is deposited on it. The magnesia layer acts as a heat barrier, e.g. in ICE exhaust gas catalytic converters.

Hydrocarbon Conversion Catalysts

STE FRANCAISE DES PRODUITS POUR CATALYSE
British Patent 1,400,345

A catalyst for use in hydrocarbon conversion, e.g. naphtha reforming, of long life and improved mechanical properties consists of an Al₂O₃ support carrying Pt, Ir and Nb. Preferably the catalyst contains 0.005-1 % Pt, 0.005-1 % Ir and 0.005-5 % Nb.

Hydrocarbon Reforming Catalyst

AIR PRODUCTS & CHEMICALS INC.
British Patent 1,400,491

A reforming catalyst of improved life consists of an Al₂O₃ support having a surface area of at least 200 m²/g, a content of 25-50 % Al₂O₃, less than 5 % γ type and the balance γ type and a bulk density of less than 0.55 kg/l which carries 0.05-0.5 % Group VB metal oxide and 0.2-1.5 % Pt group metal. Thus Pt may be used with niobium oxide or vanadium oxide.

Hydrocarbon Conversion with a Multimetal Catalyst

UNIVERSAL OIL PRODUCTS CO.
U.S. Patent 3,859,201

In a process for converting a hydrocarbon charge stock, the stock is contacted with a catalytic composite consisting of a porous carrier material containing 0.01-2 % Pt group metal, 0.01-2 % Re, 0.1-3.5 % halogen and Bi in an amount sufficient to result in an atomic ratio of Bi to Pt group metal of about 0.1:1 to about 1:1.

Ruthenium-Promoted Fluorided Alumina

PHILLIPS PETROLEUM CO.
U.S. Patent 3,864,425

A method of isomerising paraffin hydrocarbons containing 4-8 C uses a catalytic composition consisting of a Ru-promoted fluorided Al₂O₃ catalyst containing Sb₂F₆-HF.

Reforming with Promoted Platinum-Iridium Catalysts

EXXON RESEARCH & ENGINEERING CO.
U.S. Patent 3,867,280

A process for improving the octane quality of naphtha consists of contacting the naphtha in an an-oil portion of an operating cycle at reforming conditions with a catalyst composite including a porous inorganic oxide support, 0.1-2 % halogen, 0.05-3 % Pt, 0.05-3 % Ir and 0.5-5 % Fe or Bi based on the total weight of the catalyst, and in a subsequent portion of an operating cycle, burning of deposited coke with an O₂-containing gas.

Nuclear Hydrogenation of N-Aryl Polyamides

UNIROYAL INC.
U.S. Patent 3,867,443

A method for nuclear hydrogenation of an N-aryl polyamide to an N-acylic polyamide consists of contacting the N-aryl polyamide with H₂ in the presence of an acid-treated Rh hydrogenation catalyst at 5-250°C.

Catalyst Production of Nitric Acid

DEUTSCHER GOLD- & SILBER-SCHIEDEENSTALT
U.S. Patent 3,873,675

In a process of forming NOₓ by the gas phase oxidation of NH₃ with air in the presence of a Pt-containing catalyst, an improved catalyst consists of 55-70 % Pd, 1-6 % Rh and/or Ru and the balance Pt.

Platinum-Tin Catalyst Regeneration

CHEVRON RESEARCH CO.
U.S. Patent 3,875,049

Hydrocarbons are hydroconverted over a catalyst consisting of 0.01-5 % Pt group metal, 0.01-5 % Sn and 0.1-3 % of a halogen on a porous solid support, such as SiO₂/Al₂O₃, and the spent catalyst is regenerated by heating it with a gas containing oxygen and a halogen.
Three Metal Hydroconversion Catalyst

UNIVERSAL OIL PRODUCTS CO.

A new hydroconversion catalyst has a spinel, SiO₂, Al₂O₃ or other known support carrying 0.01-2% Pt or Pd, 0.01-2% Ir, Bi in an amount giving an atomic ratio of Bi to Pt or Pd of 0.1-1:1 and 0.1-3.5% halogen.

Support for a Three Metal Conversion Catalyst

UNIVERSAL OIL PRODUCTS CO.

A mixture of Al₂O₃ and a zeolite is used to support a catalytic mixture of Pt or Pd, Ir and a Group IVA metal such as Pb or Ge. Typically 0.1-20% zeolite is used with Al₂O₃ to support 0.01-2% of Pt or Pd, 0.01-2% Ir and 0.01-5% Group IVA metal.

Four Component Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

A dehydrogenation catalyst consists of Al₂O₃ or another support carrying 0.01-2% Pt group metal (Pt or Pd), 0.01-5% Sn, 0.01-5% Ge and 0.01-5% of an alkali or alkaline earth metal. In one example isobutylene is obtained from isobutane using a catalyst containing 0.75% Pt, 0.2% Ge, 0.2% Sn, 0.6% Li and less than 0.15% chloride.

Platinum-Indium-Molybdenum Reforming Catalysts

EXXON RESEARCH & ENGINEERING CO.

The octane quality of naphthas is improved by reforming them over a mixture of 0.01-2% Pt, 0.01-2% Mo and 0.05-2% In on Al₂O₃ or another inorganic oxide support.

Platinum Catalyst for Hydrocarbon Conversion

STE FRANCAISE DES PRODUITS POUR CATALYSE

French Appl. 2,234,922

A new catalyst, for hydrocarbon conversion reactions, has a support, preferably Al₂O₃, carrying 0.005-1.0% Pt, 0.005-1.0% Ru and 0.005-5% Mn or Re.

Platinum-Containing Catalyst

STE FRANCAISE DES PRODUITS POUR CATALYSE

French Appl. 2,234,923

A new catalyst, for hydrocarbon reforming and other conversion reactions, has a support, preferably Al₂O₃, carrying 0.005-1.0% Pt, 0.005-1.0% Ru and 0.005-5.0% of Ge, Sn, Pb, Ti, Zr or Hf.

Iridium-Osmium Catalyst

KALI-CHEMIE A.G.

German Offen. 2,341,363

A hydrazine decomposition catalyst is obtained by repeatedly impregnating an Al₂O₃ support with a solution containing Ir and Os salts and then reducing the salts.

Coated Support for a Catalyst

JOHNSON, MATTHEY & CO. LTD.

German Offen. 2,450,664

A catalyst, e.g. for NOₓ removal in spent gases from a HNO₃ plant, consists of (a) an elongated metal support made from a refractory steel alloy of 3-40% Cr, 1-10% Al, at least 5% Co and/or at least 72% Ni with at least 0.5% Ge, remainder Fe coated with (b) an oxide layer and (c) a Pt group metal, Ag, Au or their alloys in a catalytic layer. Thus Kanthal D foil may be coated with Al₂O₃ and then with Pt.

HOMOGENEOUS CATALYSIS

Production of 2-Methyl-1,4-Butanediol

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,859,369

A process for the production of 2-methyl-1,4-butanediol consists of (1) hydroformylating 1,4-butanediol with CO and H₂ at a H₂/CO molar ratio of at least 0.1, 50-250°C and at an elevated pressure in the presence of a catalytic amount of a phosphine complex of Rh, Co, Ir, or Ru and (2) hydrogenating the hydroformylation reaction product using a conventional hydrogenation procedure. The preferred catalyst for high yields of 2-methyl-1,4-butanediol is a phosphine complex of rhodium, such as RhHCO(PPh₃)₂.

Condensation of Alcohols

CONTINENTAL OIL CO.

U.S. Patent 3,860,664

High molecular weight hydrocarbon alcohols are formed by condensing a reaction mixture consisting of at least one lower molecular weight alkanol having a methylene group adjacent to the hydroxylated C atom, an alkali catalyst and a catalytic amount of a Pd(I) halide or (Y)ₓPd(X), where Y is ammonium or an alkali metal and X is a halogen.

Palladium Catalyst for Condensation of Alcohols

CONTINENTAL OIL CO.

U.S. Patent 3,862,994

A process of producing higher molecular weight hydrocarbon alcohols consists of condensing a reaction mixture consisting of at least one lower molecular weight alkanol having a methylene group adjacent to the hydroxylated C atom, an alkali catalyst and a catalytic amount of a Pd(I) halide or (Y)ₓPd(X), where Y is ammonium or an alkali metal and X is a halogen.
Stereospecific Hydrogenation Process  
DIAMOND SHAMROCK CORP.  
U.S. Patent 3,864,361  
A process for hydrogenating 2,5-dimethylpyrrole to 2,5-dimethylpyrrolidine consists of contacting the dimethylpyrrole at 75-160°C and under pH2 of 200-1,000 p.s.i.g. with 0.2-0.8% of an unsupported RuO2 as the sole hydrogenation catalyst the RuO2 having an average crystallite size up to 1,000Å.

Catalysts for Siloxanes  
IMPERIAL CHEMICAL INDUSTRIES LTD.  
U.S. Patent 3,867,343  
An elastomer composition consists of an organohydrogenpolysiloxane, an α-ω-dihydroxydiorganopolysiloxane and an organic Pt complex catalyst in which the ligand or donor groups are selected from As, P, S or N and olefins, the groups being capable of donating electrons to form a bond with Pt and a N compound selected from NH3 and derivatives of NH3, in which the three valences are satisfied by bonding to an atom selected from, C, H, O, N and Si provided that not more than one O atom is bonded to the ammonia N atom.

Metal Rhodium Carbonyl Salts  
UNION CARBIDE CORP.  
U.S. Patent 3,878,214  
New salts, claimed per se, have the formula M2-xRhIz(CO)x where M is Al, Ga, Ir, Sc, Y or Re in a trivalent state. They may be produced by three different methods from Rh carbonyls and are useful as catalysts in the reaction of CO and H2 to produce methanol, ethylene glycol, glycerol and propylene glycol.

CHEMICAL TECHNOLOGY

Purification of Iridium  
U.S. ATOMIC ENERGY COMMISSION  
U.S. Patent 3,867,137  
A method for purifying Ir consists of oxidising impure Ir to form volatile IrO3, decomposing the IrO3 to condense IrO2 as a solid at a point away from the oxidising step and reducing the IrO2 to Ir metal.

Recovery of Metals from Catalysts  
JOHNSON, MATTHEY & CO. LTD.  
German Offen. 2,443,146  
The metal content of catalysts, e.g. Pt on a cordierite support, is recovered by stripping off a layer containing the metal from the catalyst surface and then processing the product.

Separation and Purification of Metals  
MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD.  
German Offen. 2,457,672  
Pt, Rh and Ir, present as salts in an acidic solution are separated and purified by (a) reducing the Ir(IV) to Ir(III), (b) introducing a secondary or tertiary amine or quaternary ammonium compound, (c) removing Pt as its complex with the amine by organic extraction, (d) reoxidising the Ir(III) to Ir(IV) with the Rh remaining in solution, (e) adding fresh nitrogen compound to complex the iridium present and (f) extracting the iridium complex. General Mills’s Alamine 336 is a suitable amine for both extractions which give a 99%+ purity.

GLASS TECHNOLOGY

Wired Glass Production  
PILKINGTON BROS. LTD.  
British Patent 1,394,428  
As float glass is made, a reinforcing wire, e.g. mild steel wire web, is introduced into the ribbon of glass as it passes under a Pt, Pd, Ru, Ir or other refractory metal flow regulating member which is electrically heated.

ELECTRICAL AND ELECTRONIC ENGINEERING

Copper in Noble Metal Metallisation  
E. I. DU PONT DE NEMOURS & CO.  
British Patent 1,393,646  
A balance between cost and performance is struck in printed circuit production by the use of a glass-free mixture of noble metal and/or noble metal oxide with Cu, Cu2O or their precursors. The noble metal must be at least 50% Pd, and at least 90% of the particles of both components must be 5 μm in size or smaller.

Electrical Connectors  
RAYCHEM CORP.  
British Patent 1,395,601  
A connector consists of a member pressed against a heat recoverable member which may be made of an Au-Cd alloy, ZrPd,Rh,X, etc. The recoverable member is deformed while cold but recovers its shape on heating.

Resistive Glaze and Paste Compositions  
AIRCO INC.  
U.S. Patent 3,868,334  
A composition for firing into a resistive glaze consists of finely divided RuO3, a glass frit consisting of 55-75% PbO, 2-10% ZnO, 2-10% MnO, 5-20% SiO2, 5-20% B2O3 and 0-5% ZrO2 and a temporary liquid binder.

TEMPERATURE MEASUREMENT

Platinum Probe for a Thermometer  
J. M. BRUYERE  
German Offen. 2,459,623  
An amplifying circuit is used with a thermometer having a Pt probe and a recoupling stage is fitted to the amplifier to compensate for the non-linear change of Pt resistance values with temperature.