Further Studies on the Homogeneous Hydroformylation of Alkenes by Use of Ruthenium Complex Catalysts

R. A. SANCHEZ-DELGADO, J. S. BRADLEY and G. WILKINSON, *J. Chem. Soc., Dalton Trans.*, 1976, (5), 399–404

Studies of the use of tertiary-phosphine-Ru complexes in the catalytic hydroformylation of alkenes have been carried out and are described. Under the conditions required for the reaction to take place $Ru(CO)_3(PPh_3)_2$ is recovered from all the effective mononuclear complexes and may be used repeatedly without apparent loss of catalytic activity. The results suggest the reaction involves $Ru(H)_2(CO)_2(PPh_3)$ as the principal active catalytic species. $Ru(CO)_3(PPh_3)_2$ is also active for the hydrogenation of alkenes and aldehydes, and mechanisms are proposed.

Transfer Hydrogenation and Transfer Hydrogenolysis. IX. Hydrogen Transfer from Organic Compounds to Aldehydes and Ketones Catalysed by Dihydridotetrakis (triphenylphosphine)ruthenium(II)

H. IMAI, T. NISHIGUCHI and K. FUKUZUMI, *J. Org. Chem.*, 1976, **41**, (4), 665–671

Studies have shown that even under mild conditions $RuH_2(PPh_3)_4$ has excellent catalytic activity for the transfer of hydrogen from ethers, hydroaromatic compounds, tertiary amines and alcohols to aldehydes and ketones. The mechanism of the hydrogen transfer from alcohols to the aldehydes was also studied and data suggest that the rate of reaction is determined by the coordination of the alcohols to the complex.

ELECTRICAL AND ELECTRONIC ENGINEERING

Schottky Barrier Heights of Nickel-Platinum Silicide Contacts on *n*-type Si

L. E. TERRY and J. SALTICH, *Appl. Phys. Lett.*, 1976, **28**, (4), 229–231

Studies of the barrier heights of NiPt silicide-*n*-type Si, and the saturation current density of the diodes, for various concentrations of Ni and Pt showed them to change smoothly from that of NiSi-Si to PtSi-Si with increasing amounts of Pt in the NiPt films. The barrier is 0.69eV for 19 wt.% Pt and the height is 0.78eV for 67 wt.%Pt.

MEDICAL USES

Studies of Rhodium(II) Carboxylates as Anti-tumour Agents

L. C. RAINEN, *Diss. Abstr. B*, 1976, **36**, (7), 3299-B

Studies of interactions of Rh(II) carboxylates with synthetic and natural macromolecules showed that they differ in anti-tumour, toxic and inhibitory properties when applied to either *in vivo* or *in vitro* systems. The more potent drugs formed more stable complexes, but the more lipophilic drugs were more effective as anti-tumour agents because of increased permeability into the cell and enzyme active centres.

NEW PATENTS

METALS AND ALLOYS

Platinum Group Metal Alloys

JOHNSON, MATTHEY & CO. LTD.

German Offen. 2,530,245

Alloys suitable for withstanding high temperatures in glassmaking and aircraft consist of at least 40% Ni or Co, up to 30% Cr and up to 15% of one or more of the six Pt group metals. Small amounts of Ti, Al, Mo and W may also be present.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Ductile Palladium

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 3,920,526

An aqueous electrodeposition bath for electrodepositing non-porous, ductile Pd consists of 16–32 g/l $Pd(NH_3)_2Cl_2$ and 65–250 g/l of NH_4Cl and aqueous NH_3 to provide a pH $\geqslant$8.8.

Electroplating a Gold-Platinum Alloy

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION *U.S. Patent* 3,923,612

An aqueous electrolyte solution for the electrodeposition of Pt-Au alloys consists of an alkali metal hexahydroxyplatinate and an alkali metal aurate where the pH of the solution is above 11.0. A typical solution containing 21 g/l Pt as $K_2Pt(OH)_6$ and 2.8 g/l Au as $KAuO_2$ was used to plate clean brass parts. The bath was operated at 65°C using a 0.2A current. The composition of the final deposit was 30%Pt-70%Au and the deposit was of high quality.

Bright Palladium Electrodeposits

AMERICAN CHEMICAL & REFINING CO. INC.

U.S. Patent 3,925,170

A bright plating bath contains 0.02–0.25g mole/l Pd, 0.9–3.6g mole/l NH_4OH, 0.1–0.7g mole/l alkali metal or NH_4 salt electrolyte, a Co and/or Ni brightener and a small amount of cetyl trimethyl NH_4Br.

Palladium Electroplating Bath

OXY METAL INDUSTRIES CORP. *U.S. Patent* 3,933,602

The bath, which is free of CN, NO_3 and NO_2 contains the sulphite ion, Pd in the form of a Pd(II) tetracoordinated complex, specifically $Pd(SO_3)(NH_3)_3$ and can also contain other metals, including Au, Ag, Pt, Rh, Ru, Ir and Os.

LABORATORY APPARATUS AND TECHNIQUE

Explosive Gas Detectors

SECRETARY OF STATE FOR TRADE AND INDUSTRY *British Patent* 1,427,515

The detector has a reaction chamber containing a Pd/ThO_2 catalyst, means for admitting and retaining a discrete sample of gas in the chamber, and integrating measuring means for determining the entire effect of the gas on the catalyst body.

JOINING

Joining a Thermoplastic Part to a Mesh Part

JOSEPH LUCAS LTD. *British Patent* 1,425,030

In the joining of a thermoplastic synthetic resin material part to a mesh part in a metal-air battery cell, a Pt, Pd or Ag on C catalyst layer is arranged to form the air electrode of the cell.

Metallised Isotropic Boron Nitride Body

RAYTHEON CO. *U.S. Patent* 3,926,571

An isotropic boron nitride body is metallised with an alloy or intimate mixture formed from an active metal, Zr, Ti or Hf, dissolved in a solder metal, such as Ni, Pt, Cu, Au or Ag, the remainder of the alloy being Mo. The solder metal has a lower melting point than the active metal hydride, and the Mo is selectively added for increasing craze resistance.

Bonded Silver Article

ELECTRO OXIDE CORP. *U.S. Patent* 3,929,491

A metallising composition consists of an intimate mixture of 0.5–5.0% of an initial mixture of CdO powder and at least one Cu oxide powder, 0.25–2.0% of Pt, Ir, Rh and/or Os powder, 0.50–4.0% of Ru oxide and the balance Ag and/or Ag oxide. The metallising composition further includes about 10.0–95.0% of the intimate mixture of an organic binder.

HETEROGENEOUS CATALYSIS

Catalysts for Synthesis of Methane and Steam, etc. and Reforming of Hydrocarbons

BRITISH GAS CORP. *British Patent* 1,422,327

A catalyst is composed of 1–20% Ru or a Ru compound, 30–50% ZnO or a Zn compound, calculated as ZnO, and 65–35% catalyst carrier.

Ruthenium Catalyst

FORD MOTOR CO. LTD. *British Patent* 1,424,629

In the preparation of an I.C.E. exhaust catalyst, Ru is reacted with O_2 and a compound based on an alkaline earth, a rare earth or mixed rare earths to form a ruthenate compound, and the compound is powdered, slurried with a γ-Al_2O_3 containing substance, deposited on a support, dried and calcined.

NO_x Removal with Stabilised-Ruthenium Catalysts

EXXON RESEARCH & ENGINEERING CO. *U.S. Patent* 3,922,235

A stabilised supported Ru catalyst consists of Ru metal in combination with an oxide support selected from Zr titanate and Zr titanate mixed with TiO_2, the Ru is present in an amount $\leq$0.003g Ru/g of oxide support.

Production of Secondary Alkyl Primary Amines

TEXACO INC. *U.S. Patent* 3,923,893

The amine is separated from a mixture of unreacted paraffin and by-products by catalytic hydrogenation of the mixture in the presence of a Pt/Al_2O_3 catalyst at 600–700°F, and recycling the hydrogenated product for nitration with an *n*-paraffin.

Reaction of Chlorosilanes with Unsaturated Organic Compounds

UNION CARBIDE CORP. *U.S. Patent* 3,925,434

The Pt-catalysed addition reaction of a chlorosilane, containing at least one H bonded to Si, with an olefinically unsaturated hydrocarbon other than acrylonitrile, is accelerated by 0.001–10% of a promoter selected from phenothiazine, diphenylamine, N,N-diphenyl-p-phenylenediamine or phenoxazine.

High Octane Motor Fuel Production

UNIVERSAL OIL PRODUCTS CO. *U.S. Patent* 3,930,986

The process consists of a new form of low severity hydrocracking followed by catalytic reforming. Hydrocracking is carried out in the presence of a 0.01–2% Pd catalyst, and reforming is carried out in the presence of a Pt catalyst.

I.C.E. Exhaust Catalysts

W. R. GRACE & CO. *U.S. Patent* 3,932,309

An I.C.E. exhaust gas conversion catalyst is prepared from a solution of a Pt, Pd or Pt-Pd complex salt having the formula $M_6(Z)(SO_3)_4$ or $M_2(Z)(SO_3)_2$ where M is Na, NH_4 or H ion and Z is Pt and/or Pd, then impregnating Al_2O_3, SiO_2-Al_2O_3, mullite, cordierite or ZrO_2 with the solution, drying in air at 800–1400°F for 1 to 4 h or in a reducing environment at 600–800°F for 0.5 to 2 h and recovering the catalyst product.

Process for Preparation of Naphthol

SUMITOMO CHEMICAL CO. LTD.

U.S. Patent 3,935,282

Alpha-naphthol is produced by dehydrogenating ketotetrahydronaphthalene in the presence of Pt, chloroplatinic acid or a chloroplatinate, a Na sulphate, carbonate, acetate, chloride or chloroplatinate and a Mn salt and/or a Cr compound on an Al_2O_3 support.

Hydrocarbon Hydrotreatment Catalysts

COMPAGNIE FRANCAISE DE RAFFINAGE

French Appl. 2,260,382

The catalyst consists of a mineral oxide support including a combined halogen, and a combination of 0.02–2%, preferably 0.1–0.7%, Pt group metals; 0.02–2%, preferably 0.02–0.6%, of at least one of Mo, Cr and Mn; 0.02–2%, preferably 0.05–1.0%, Sn and optionally 0.05–0.5% S.

Hydrodealkylation of Aromatic Alkyl Hydrocarbons

INSTITUT FRANCAIS DU PETROLE

French Appl. 2,262,654

The process is carried out in the presence of a catalyst consisting of Al_2O_3 support, 0.05–5% of at least one metal chosen from Ni, Ru, Os, Pd, Rh, Ir, Pt and 0.05–5% of at least one metal chosen from Zn, Cd, Ga, In, Tl and Ge.

Partial Hydrogenation Catalyst

B.A.S.F. A.G. *German Offen.* 2,431,929

The partial hydrogenation of acetylenes to olefins is catalysed by a supported mixture of Pd, Zn, and/or Cd and Bi or Te. Butynediol is hydrogenated using an Al_2O_3 catalyst supporting 0.5% Pd, 0.1% Te and 0.1% Zn.

HOMOGENEOUS CATALYSIS

Aromatic Isocyanates

OLIN CORP. *U.S. Patent* 3,923,850

In processes for preparing an organic isocyanate by reacting an organic nitro compound with CO in the presence of a catalyst, improved recovery of the isocyanate is obtained when the reaction is carried out in the presence of a hydroxyl-substituted hydrocarbon. Preferred catalysts are prepared from halides and oxides of Pd, Rh, Ir and Ru (mixtures) with a hydroxyl-substituted hydrocarbon, e.g., $Pd(py)_2Cl_2$, py is pyridine.

Alcohol Carbonylation Catalyst

B.P. CHEMICALS INTERNATIONAL LTD.

U.S. Patent 3,923,880

Alcohols and alcohol derivatives are carboxylated to carboxylic acids using as catalyst a cationic complex of Rh or Ir in which the anion is not halide. A typical complex has the formula $(ML_m(CO)_nS_1)_kA$ in which M is Rh or Ir, L is a stabilising ligand, e.g. acetonitrile, S is a solvent ligand, e.g. benzene, and m, n, etc. are 0–5.

Production of Aromatic Isocyanates

SUMITOMO CHEMICAL CO. LTD.

U.S. Patent 3,925,436

Aromatic isocyanates are produced by reacting an aromatic nitro compound with CO in the presence of a catalyst at an elevated temperature under an elevated pressure. The catalyst is a product obtained by contacting halides, carbonyl halides, complexes and complex salts of Pd, Rh, Ir, Ru, Pt and Os with a copolymer of styrene, vinylpyridine and divinylbenzene.

Ruthenium Complexes as Catalysts for Reduction of Polyenes

PHILLIPS PETROLEUM CO. *U.S. Patent* 3,925,494

A catalyst for the partial hydrogenation of 1,5,9-cyclododecatriene to cyclododecene is a Ru ligand complex catalyst consisting essentially of $(Ph_3P)_2(CO)_3Ru$ or $[Ru(CO)_4]_3$.

Selective Hydrocarboxylation of Unsaturated Fatty Compounds

U.S. SECRETARY OF AGRICULTURE

U.S. Patent 3,928,231

Carboxy acids are prepared in high yields by reacting without isomerisation unsaturated vegetable oil with CO and H_2O in the presence of a highly selective catalyst system consisting of $PdCl_2$ mixed with a trisubstituted phosphine chosen from triphenylphosphine and trialkylphosphine.

CHEMICAL TECHNOLOGY

Preparing Super-High Purity Hydrogen

URALSKY ORDENA TRUDOROGO KRASNOGO ZNAMENI POLITEKHNICHESKY INSTITUT IMENI S. M. KIROVA

British Patent 1,426,644

Water vapour is added to a gaseous flow containing H_2O-free H_2 to form a gaseous mixture in which the partial pressure of H_2O vapour is not less than 5 mm Hg, bringing the gaseous mixture into contact with a diaphragm made of Pd, or its alloys, to diffuse H_2 through it, and maintaining the partial pressure of the diffused H_2 less than that of the H_2 in the gaseous mixture.

Colour Photographic Materials

FUJI PHOTO FILM CO. *British Patent* 1,428,296

Pt group metals and Au may be used to sensitise a colour photographic material which includes a light sensitive silver halide emulsion layer containing a coupler having in its molecule an aryloxyalkoxycarbonyl arylene group, such as β-(2,4-di-tert-butylphenoxy)ethoxycarbonyl.

Recovering Osmium from Glycol Solutions

ATLANTIC RICHFIELD CO. *U.S. Patent* 3,927,168

Ozone is passed through the crude oxidation reaction mixture obtained during the Os catalysed oxidation of an organic compound, e.g. an olefin,

to recover Os by distillation from the reaction product, e.g. glycol, and avoid the formation of insoluble deposits, principally OsO_2.

Refining Platinum Group Metals

MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD. *French Appl.* 2,264,880

A particulate mineral concentrate is contacted with a gas containing a halogen at a temperature sufficiently high for the non-noble metals and Ag to be transformed into halides which are separated from the concentrate by volatilisation, then the volatilised halides are separated from the solid mixture containing the remaining precious metals.

ELECTRICAL AND ELECTRONIC ENGINEERING

Clad Wire Electric Conductors

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD. *British Patent* 1,432,906

The conductors are made by providing a strip including at least a base metal and at least a surface layer of a noble metal chosen from Au, Ag, Pt, Pd (alloys) bonded to the base metal, forming the strip into a transversely arcuate form with the noble metal on the convex surface and drawing the strip through a die.

Nickel Oxide Metallisation

E. I. DU PONT DE NEMOURS & CO. *U.S. Patent* 3,922,387

Electrical conductors on a ceramic substrate consist of finely divided powders of noble metals and 0.1–10% nickel oxide. The noble metal is selected from Pd, Pt, Au and Ag, preferably Pd-Ag and the conductors are metallised on dielectric substrates.

Dry Plasma Process for Etching Noble Metal

INTERNATIONAL PLASMA CORP. *U.S. Patent* 3,923,568

An electrically conductive pattern is produced on an electrically non-conductive substrate by forming a film of electrically conductive Au, Pt, Pd or Ag on the substrate, providing a film of resist over the film of noble metal covering those areas where the noble metal is to remain, and contacting the exposed noble metal with a plasma consisting essentially of F_2, Cl_2 and not more than 25% O_2 by volume for a time sufficient to remove the exposed noble metal.

Platinum Oxide Lithographic Masks

BELL TELEPHONE LABORATORIES INC. *U.S. Patent* 3,925,677

A lithographic mask consisting of a rigid transparent substrate and a selectively applied pattern of thin Pt oxide formed on the substrate, the pattern having microscopic features suitable for microcircuit lithography, is described.

Solid Sensor Electrode

OWENS-ILLINOIS INC. *U.S. Patent* 3,929,609

A noble metal, particularly a Au, Ag, Pt or Pd (mixture)-glass composite, is screen printed on an inert substrate such as low alkali glass and fired to provide a solid sensor electrode.

Palladium Alloy for Relay Contacts

WESTFALISCHE METALL INDUSTRIE KG, HUECK & CO. *German Offen.* 2,439,315

Contacts of longer life in d.c. relays, especially flasher circuits, are produced from alloys of Pd with up to about 40% Cu (anodes) and Ag or Ag alloys (cathodes).

TEMPERATURE MEASUREMENT

Thermosensor for I.C.E. Conversion Catalysts

NIPPON TOKUSHU TOGYO K.K. *British Patent* 1,428,267

A thermosensor for use in an I.C.E. exhaust purifier consists of a thermally sensitive element with a pair of lead wires connected to it, a ceramic tube with two lengthwise holes, a ceramic coating surrounding the element, and a catalyst layer to promote oxidation of the unburnt components of the exhaust gas deposited on the ceramic coating. The electrodes in the tube holes are of Pt wire and/or a Pt-Rh alloy wire, and the catalyst is Pt.

MEDICAL USES

Chemotherapeutic Agents for Cancer (Cyclopropylamines)

RUSTENBURG PLATINUM MINES LTD. *British Patent* 1,432,562

A *cis* coordination compound of platinum for the treatment of cancer has the formula (A)-(B)-Pt-(X)-(Y) in which (X) and (Y) are the same or different and are halogen or pseudohalogen and (A) and (B) are the same or different alicyclic amines coordinated to the Pt through their N atoms. Each amine itself has the general formula cyclo-$C_nR_{2n-1}NH_2$, in which n is 3–7 and the R's are the same or different and are preferably H, lower alkyls or solubilising groups, for example sulphonic or carboxylic acid or their salts.

Palladium Alloys for Ceramic Bonding

J. M. NEY CO. *U.S. Patent* 3,928,913

A dental casting alloy consists of 40–60% Pd or mixtures of Pd with 12–25% Pt, 20–59% of a base metal component selected from 20–50% Co and Co-Ni mixtures and a modifier selected from 1–8% In, 1–3% Sn and 1–8% of mixtures of Sn and In where the Sn does not exceed 3%, also optionally, 0–5% Zn, 0–5% Fe, 0–5% W, 0–2% Ru, 0–2% Rh and 0–10% Mo.