

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Pd I Spectrum, Term System, Isotope Shift and Hyperfine Structure – Revised and Extended Analysis Based on FTS Emission Spectroscopy

R. ENGLEMAN, U. LITZÉN, H. LUNDBERG and J.-F. WYART, *Phys. Scr.*, 1998, 57, (3), 345–364

The spectrum of a neutral Pd atom emitted from hollow cathode discharges was studied by Fourier transform spectroscopy in the 1750–55000 Å region. 684 lines were identified as transitions between 67 even and 76 odd levels. Isotope shift and hyperfine structure were seen and interpreted in 24 lines. Forbidden lines caused by Stark-effect mixing were observed. Most Pd I lines below 64000 cm⁻¹ are now known.

Formation of Thin Single-Wall Carbon Nanotubes by Laser Vaporization of Rh/Pd-Graphite Composite Rod

H. KATAURA, A. KIMURA, Y. OHTSUKA, S. SUZUKI, Y. MANTWA, T. HANYU and Y. ACHIBA, *Jpn. J. Appl. Phys.*, 1998, 37, (5B), L616–L618

Single-wall C nanotubes (1) were prepared in high yield by laser vaporisation of a Rh/Pd-graphite composite rod at 1200°C. Lattice constants of the bundle were found to be 1.0–1.5 nm. Nine Raman peaks originating from the breathing modes were observed, and these frequencies and lattice constants indicate the presence of the (1) indexed from (5,5) to (8,8) which are thinner than (1) obtained with a Ni/Co catalyst.

CHEMICAL COMPOUNDS

Facile Synthesis of Isomerically Pure *cis*-Dichlorodiammineplatinum(II), *Cisplatin*

V. YU. KUKUSHKIN, Å. OSKARSSON, L. I. ELDING and N. FARRELL, *Inorg. Synth.*, 1998, 32, 141–144

The rapid and facile one-step synthesis of isomerically pure *cis*-[PtCl₂(NH₃)₂] (*cisplatin*), an important anticancer agent, is described. This involves heating a mixture of K₂[PtCl₄], NH₄CO₂CH₃, and KCl in H₂O under reflux.

Pd(II) and Pt(II) Complexes with Chalcogenide Derivatized Phosphathia Ligands

J. CONNOLLY, A. R. J. GENGE, S. J. A. POPE and G. REID, *Polyhedron*, 1998, 17, (13–14), 2331–2336

The mixed phosphine sulfide/thioether and phosphine selenide/thioether ligands L¹–L³ react with PdCl₂ or PtCl₂ in the presence of TIPF₄ in MeNO₂ solution to give the distorted square planar complexes [Pd(L)](PF₆)₂ or [Pt(L)](PF₆)₂. The complexes are characterised by IR spectroscopy and ¹⁹⁵Pt NMR studies and the X-ray crystal structure of L¹ is reported.

Face-Coordinated C₆₀ Complexes with Carbido-Pentaruthenium Cluster Cores Including a Bimetallic Platinum-Pentaruthenium Complex

K. LEE and J. R. SHAPLEY, *Organometallics*, 1998, 17, (14), 3020–3026

The interaction of C₆₀ with Ru₅C(CO)₁₅ or PtRu₅C(CO)₁₅(COD) in hot chlorobenzene, followed by treatment with solubilising phosphines, gave compounds with a hexahapto co-ordination of C₆₀ to a Ru₅ face of the square pyramidal Ru₅C or octahedral PtRu₅C cluster framework. The C₆₀-cluster bond is robust.

Convergent and Divergent Noncovalent Synthesis of Metallodendrimers

W. T. S. HUCK, L. J. PRINS, R. H. FORKENS, N. M. M. NIBBERING, F. C. J. M. VAN VEGGEL and D. N. REINHOUDT, *J. Am. Chem. Soc.*, 1998, 120, (25), 6240–6246

A new building block, with one pyridine and two kinetically inert complexed Pd(II) ions, is reported for controlling the assembly of metallodendrimers by a convergent or a divergent route. A double pincer ligand was cyclopalladated with Pd[CH(CN)₂](BF₄)₂ and converted to a neutral *bis*-Pd chloride complex (1). The pyridine moiety of (1), covalently attached to the spacer bridging the two pincer complexes, co-ordinates to activated Pd centres. Via pyridine- and cyano-based building blocks, dendrons up to the third generation were assembled and characterised, by divergent and convergent routes, respectively.

Preparation and Structure of [Ru(CO)₂(PPh₃)(η-C₅Me₅)] [Fe₃(μ₃-C₂Bu')₂(CO)₉]

M. I. BRUCE, N. N. ZAITSEVA, B. W. SKELTON and A. H. WHITE, *Aust. J. Chem.*, 1998, 51, (5), 433–435

The reaction between RuCl(C=CHBu')(PPh₃)(η-C₅Me₅) and Fe₂(CO)₉ produced the Ru salt [Ru(CO)₂(PPh₃)(η-C₅Me₅)] [Fe₃(μ₃-C₂Bu')₂(CO)₉]. X-ray structure studies showed a piano-stool structure for the cation while the anion contained a CCBu' ligand sitting on a triangular Fe₃ cluster.

A Simple and Convenient Synthesis of *cis/trans*-RuH₂(Ph₂PCH₂PPh₂)₂ and of *trans*-RuHCl(Ph₂PCH₂PPh₂)₂

G. S. HILL, D. G. HOLAH, A. N. HUGHES and E. M. PROKOPCHUK, *Inorg. Chim. Acta*, 1998, 278, (2), 226–228

Treatment of a suspension of *cis*-RuCl₂(Ph₂PCH₂Ph₂)₂ (*cis*-1) in EtOH or 2-propanol with a large excess of KOH, gave *cis/trans*-RuH₂(Ph₂PCH₂PPh₂)₂ (2) in ≤ 90% yields, with the reaction taking < 2 min in EtOH. A similar reaction with a small excess of KOH gives *trans*-RuHCl(Ph₂PCH₂PPh₂)₂ in 64% yield, which can be converted into (2) in moderate yields. Under these conditions, (*trans*-1) is unreactive.

Ruthenium Nitrosyl Complexes with N-Heterocyclic Ligands

S. DA S. BORGES, C. U. DAVANZO, E. E. CASTELLANO, J. Z-SCHPECTOR, S. C. SILVA and D. W. FRANCO, *Inorg. Chem.*, 1998, 37, (11), 2670–2677

The synthesis of a series of Ru nitrosyl complexes of formula $trans-[Ru(NH_3)_2L(NO)](BF_4)_3$, where L = imidazole, L-histidine, pyridine or nicotinamide, is described. The compounds have relatively high $\nu(NO)$ stretching frequencies showing that a high degree of positive charge resides on the co-ordinated nitrosyl group. The nitrosyl complexes react with OH^- . The crystal structure of $trans-[Ru(NH_3)_2nicNO]_2(SiF_6)_3$ confirms the presence of a $Ru^{II}-NO^+$ moiety.

Reaction of $\{Ru(PPh_3)_2Cp\}_2(\mu-C_4)$ with Tetracyanoethene: Macrocycle Formation by Inter-molecular CN Coordination

M. I. BRUCE, P. J. LOW, B. W. SKELTON and A. H. WHITE, *New J. Chem.*, 1998, 22, (5), 419–422

Reactions between $\{Ru(PPh_3)_2Cp\}_2(\mu-C_4)$ and $C_2(CN)_4$ add the cyanocarbon to one of the $C\equiv C$ bonds forming the allylic complex $Ru\{\eta^1-C(CN)_2C[C\equiv C\{Ru(PPh_3)_2Cp\}]C=C(CN)_2\}(PPh_3)Cp$ (1). In solution, (1) is in equilibrium with its dimer (2). Structural studies of (2) show the presence of a ten-membered macrocyclic ring formed by displacement of the co-ordinated double bond in one molecule of (1) by a CN group from a second molecule.

Enhancement of Molecular Quadratic Hyperpolarizabilities in Ruthenium(II) 4,4'-Bipyridinium Complexes by N-Phenylation

B. J. COE, J. A. HARRIS, L. J. HARRINGTON, J. C. JEFFERY, L. H. REES, S. HOUBRECHTS and A. PERSOONS, *Inorg. Chem.*, 1998, 37, (13), 3391–3399

Dipolar Ru(II) tetra- or pentaammine complexes of N-substituted 4,4'-bipyridinium ligands show static first hyperpolarisabilities, β_0 , among the largest reported for transition metal complexes. The d^8 , 18-electron Ru(II) centres function as powerful π -electron donors, and the nonlinear optical properties are readily tuned by ligand changes. N-phenylation of 4,4'-bipyridinium ligands is shown as an effective means to increase β_0 in MLCT-based chromophores.

ELECTROCHEMISTRY

Electrocatalytic Dehalogenation of Chloroaromatics on Palladium-Loaded Carbon Felt Cathode in Aqueous Medium

A. I. TSYGANOK, I. YAMANAKA and K. OTSUKA, *Chem. Lett. Jpn.*, 1998, (4), 303–304

The selective dechlorination of highly toxic chloroaromatic herbicides based on phenoxyacetic acid is reported. This was achieved under mild conditions in H_2O by electrocatalytic reduction using a Teflon membrane-separated flow-through cell with a 5 wt.% Pd/C felt cathode and a Pt foil anode. After 4 hours, all the compounds underwent > 90% conversion giving 80–93% yield of Cl-free phenoxyacetic acid. This method is also applicable to other chloroaromatics.

A Catalytic Hydrogen Wave of the Osmium-Cysteine System

M. KAWASAKI, T. KAKIZAKI, W. HU, K. TOYOTA and K. HASEBE, *Electroanalysis*, 1998, 10, (4), 276–278

$Os(VIII)O_3$, in the presence of cysteine in HCl, exhibits a well-defined maximum wave at -0.85 V (vs. SCE). The effects of the Os valence states and the coexisting anions on the reduction wave have been studied polarographically in acidic solution. The high, as opposed to low, oxidation states ($Os(VIII)$ and (VI)), greatly influence the height of the H_2 wave.

PHOTOCONVERSION

Photocatalytic Degradation of Trichlorobenzene using Immobilized TiO_2 Films Containing Poly(tetrafluoroethylene) and Platinum Metal Catalyst

H. UCHIDA, S. KATOH and M. WATANABE, *Electrochim. Acta*, 1998, 43, (14–15), 2111–2116

A new photocatalyst film is described which has Pt-loaded TiO_2 and poly(tetrafluoroethylene) particles immobilised on an In-Sn oxide glass substrate. This gives rapid and complete degradation of trichlorobenzene in dilute aqueous solutions under illumination, with higher catalytic activity than Pt- TiO_2 or TiO_2/Ni -PTFE films. The decomposition rate was enhanced by the efficient consumption of photogenerated electrons and holes in the reduction of O_2 and oxidative degradation of trichlorobenzene, respectively.

Large Enhancement in Photocurrent Efficiency Caused by UV Illumination of the Dye-Sensitized Heterojunction $TiO_2/RuLL'NCS/CuSCN$: Initiation and Potential Mechanisms

B. O'REGAN and D. T. SCHWARTZ, *Chem. Mater.*, 1998, 10, (5), 1501–1509

When subjected to low-power UV illumination for 10–30 min, the wide band-gap, dye-sensitised heterojunctions, $n-TiO_2/Ru-dye/p-CuSCN$ (Ru-dye = Ru polypyridyl dyes) undergo a dramatic increase in efficiency. The UV illumination increases the incident photon-to-current efficiency for light absorbed by the dye by a factor of 5–10 and increases the open circuit voltage by 100–300 mV. This effect is stable for months after the UV illumination has ceased.

Photocatalytic Activity of RuS_2/SiO_2 for Water Decomposition

K. HARA, K. SAYAMA and H. ARAKAWA, *Chem. Lett. Jpn.*, 1998, (5), 387–388

H_2 and O_2 were produced from the photocatalytic decomposition of H_2O using a RuS_2 powder catalyst (1) in the presence of sacrificial agents. The activity towards H_2 production was greatly improved by supporting (1) on SiO_2 , with a 1 wt.% RuS_2/SiO_2 catalyst giving 213 μmol of H_2 after 46 hours. No O_2 was formed over a non-supported (1), but O_2 was produced over 1 wt.% RuS_2/SiO_2 (121 μmol O_2 after 25 hours) and 0.2 wt.% Pt/1 wt.% RuS_2/SiO_2 with the yields increasing with increasing irradiation time.

Fine-Tuning the Electronic Properties of Binuclear Bis(terpyridyl)ruthenium(II) Complexes

M. HISSLER, A. EL-GHAYOURY, A. HARRIMAN and R. ZIESSEL, *Angew. Chem. Int. Ed.*, 1998, 37, (12), 1717–1720

Two Ru(terpy)-based binuclear chromophores with vastly improved photophysical properties are described in which the butadiynylene bridge is interspersed with either a 1,4-phenylene or a 5,5'-(2,2'-bipyridylene) spacer. Further improvement in the photoproperties was achieved by complexation of cations, such as Zn^{2+} , Cd^{2+} or Ba^{2+} , to vacant co-ordination sites of the aromatic nucleus in the central unit, due to a better blending of the respective LUMO levels.

APPARATUS AND TECHNIQUE

Sulphur Dioxide Gas Detection by Reversible η^1 -SO₂-Pt Bond Formation as a Novel Application for Periphery Functionalised Metallo-Dendrimers

M. ALBRECHT, R. A. GOSSAGE, A. L. SPEK and G. VAN KOTEN, *Chem. Commun.*, 1998, (9), 1003–1004

Multimetallc dendrimers, functionalised at their periphery with square planar Pt(II) metal centres, reversibly absorb SO₂ to yield macromolecules with significantly enhanced solubility. Drastic colour changes from colourless to bright orange occur in the presence of traces of SO₂ as low as 10 mg dm⁻³, giving highly active sensors for toxic SO₂ gas detection.

Pd-Doped SnO₂ Thin Films Deposited by Assisted Ultrasonic Spraying CVD for Gas Sensing: Selectivity and Effect of Annealing

D. BRIAND, M. LABEAU, J. F. CURRIE and G. DELABOULISE, *Sens. Actuators B: Chem.*, 1998, 48, (1–3), 395–402

Polycrystalline Pd-doped SnO₂ thin films (1) (0.25–1.75 μm) have been deposited on Si nitride by spray pyrolysis at 460–540°C. The gas sensitivity of (1) was tested in air for CO (300 ppm), EtOH (100 ppm) and CH₄ (1000 ppm). Those synthesised at 460–500°C are most sensitive to CO and, in the steady state, sensitivities ≤ 4500 were obtained for the thinnest films at 100°C. Cross-sensitivity to EtOH and CH₄ was observed. Annealing under air at 500°C for 12 hours stabilises the microstructure and gives a 2–10 fold increase in CO sensitivity.

Effect of Plasticizer Viscosity on the Sensitivity of an [Ru(bpy)₃]²⁺(Ph₄B⁻)₂]-Based Optical Oxygen Sensor

A. MILLS and M. D. THOMAS, *Analyst*, 1998, 123, (5), 1135–1140

The quenching of the electronically-excited, lumiphoric state of [Ru(bpy)₃]²⁺(Ph₄B⁻)₂ by O₂ was studied in various neat plasticisers. The compatibility of the polymer-plasticiser combination is the dominant factor in determining the O₂ sensitivity. For highly compatible combinations, such as TPP-PMMA, the plasticiser with the lowest viscosity, TPP, produces films of the highest O₂ sensitivity.

Electrochemiluminescence Oxalic Acid Sensor Having a Platinum Electrode Coated with Chitosan Modified with a Ruthenium (II) Complex

C.-Z. ZHAO, N. EGASHIRA, Y. KURAUCHI and K. OHGA, *Electrochim. Acta*, 1998, 43, (14–15), 2167–2173

An electrochemiluminescence (ECL) sensor containing a Pt electrode coated with a tris(2,2'-bipyridine)Ru(II)-modified chitosan responded to oxalic acid (1) more strongly than to other substrates, including trialkylamines. The ECL response to (1) was reproducible within 5% over 10 runs and the calibration curve gave a straight line in the concentration range 0.1–10 mM with a detection limit of 3×10^{-7} M.

HETEROGENEOUS CATALYSIS

Mechanistic Considerations for the Reduction of NO_x over Pt/Al₂O₃ and Al₂O₃ Catalysts under Lean-Burn Conditions

R. BURCH, J. A. SULLIVAN and T. C. WATLING, *Catal. Today*, 1998, 42, (1–2), 13–23

The reduction of NO_x under lean-burn conditions is compared over a series of catalysts and the reaction mechanisms are divided into 2 classes. In (1), NO_x reduction occurs on the Pt surface (such as C₂H₆-NO-O₂ over Pt/Al₂O₃), and is active at the lowest temperatures and resistant to S poisoning. In (2), DeNO_x reactions occur on Al₂O₃ with a weakly adsorbed reductant (such as C₂H₆-NO-O₂ over Pt/Al₂O₃ and Al₂O₃, and C₃H₈-NO₂-O₂ over Al₂O₃). They are strongly poisoned by S and occur via formation of a surface nitrate species on the Al₂O₃ which activates the reductant.

Pt/MCM-41 Catalyst for Selective Catalytic Reduction of Nitric Oxide with Hydrocarbons in the Presence of Excess Oxygen

R. LONG and R. T. YANG, *Catal. Lett.*, 1998, 52, (1, 2), 91–96

0.5–5 wt.% Pt/MCM-41 (1) catalysts were used for the selective catalytic reduction of NO with CH₄, C₂H₆, C₃H₈ and C₃H₆ in the presence of excess O₂. High activity was seen with C₂H₄ or C₂H₆ as the reductant, with a maximum NO reduction rate of 4.3 mmol g⁻¹ h⁻¹ achieved with 1000 ppm NO, 1000 ppm C₂H₆, 2% O₂ and He as the balance. Little or no activity was observed with CH₄ or C₃H₈. (1) showed good stability and H₂O and SO₂ did not cause deactivation.

Activity and Stability of Two Polymer-Supported Rhodium-Based Catalysts for the Vapour Phase Carbonylation of Methanol

N. DE BLASIO, E. TEMPESTI, A. KADDOURI, C. MAZZOCCHIA and D. J. COLE-HAMILTON, *J. Catal.*, 1998, 176, (1), 253–259

Rh catalysts supported on a diphenylphosphinated copolymer of styrene and divinylbenzene (SDT) or polyvinylpyrrolidone (PVP) were tested for the carbonylation of MeOH at 80 bar and 180–190°C. Rh/PVP catalysts showed excellent activity and selectivity, as well as very high stability, with no Rh leaching during 50 h testing, unlike Rh/SDT catalysts.

Hydroformylation of 1-Octene under Atmospheric Pressure Catalyzed by Rhodium Carbonyl Thiolate Complexes Tethered to Silica

H. GAO and R. J. ANGELICI, *Organometallics*, 1998, 17, (14), 3063–3069

The SiO₂-tethered Rh thiolate complex catalysts Rh-S/SiO₂ and Rh-S-P/SiO₂ were prepared by the condensation of SiO₂ with Rh₂[μ-S(CH₂)₂Si(OCH₃)₃]₂(CO)₄ or Rh₂[μ-S(CH₂)₂Si(OCH₃)₃]₂[Ph₂P(CH₂)₂-Si(OC₂H₅)₂](CO)₂. These catalysts were highly active for the hydroformylation of 1-octene in the presence of phosphine donor ligands at 60°C and 1 atm. The high activity resulted from the stabilisation of Rh(SR)(CO)₂(PR')₂ species on the catalyst surfaces.

Effect of Support on the Conversion of Methane to Synthesis Gas over Supported Iridium Catalysts

K. NAKAGAWA, K. ANZAI, N. MATSUI, N. IKENAGA, T. SUZUKI, Y. TENG, T. KOBAYASHI and M. HARUTA, *Catal. Lett.*, 1998, 51, (3, 4), 163–167

The production of synthesis gas from CH₄ (1) via partial oxidation was studied using Ir catalysts supported on various metal oxides. The reaction proceeded via a two-step process consisting of combustion of (1) to give H₂O and CO₂ followed by the reforming of (1) from CO₂ and steam. The combustion and reforming of (1) from steam was not dependent on the catalyst support, but reforming of (1) from CO₂ with Ir was highly dependent on the support in the order: TiO₂ ≥ ZrO₂ ≥ Y₂O₃ > La₂O₃ > MgO ≥ Al₂O₃ > SiO₂.

HOMOGENEOUS CATALYSIS

Asymmetric Direct α,β-Functionalization of Allenes via Asymmetric Carbopalladation

K. HIROI, F. KATO and A. YAMAGATA, *Chem. Lett. Jpn.*, 1998, (5), 397–398

The asymmetric direct α,β-functionalisation of allenenes with chiral phosphine ligands in the presence of Pd(dba)₂ in various solvents is described. The reaction of racemic allenenes with iodobenzene and a nucleophile (malonate carbanion) using chiral phosphines occurred with extremely high enantioselectivity. However, a similar reaction of the chiral allene using an achiral phosphine ligand proceeded with complete enantiospecificity.

Heterocycles via Pd Catalysed Molecular Queuing Processes. Relay Switches and the Maximisation of Molecular Complexity

R. GRIGG and V. SRIDHARAN, *Pure Appl. Chem.*, 1998, 70, (5), 1047–1057

Pd(0) catalysts facilitate the orderly assembly of complex heterocycles and carbocycles containing 3–7 membered rings from diverse building blocks (allenes, CO, alkenes, etc.) by polymolecular queuing. Certain compounds are identified as relay switches because they extend the relay phase of the cyclisation-anion capture cascade while the Pd catalysed cascades switch between inter- and intra-molecular processes.

Palladium-Catalyzed Cross-Coupling Reactions in Supercritical Carbon Dioxide

D. K. MORITA, D. R. PESIRI, S. A. DAVID, W. H. GLAZE and W. TUMAS, *Chem. Commun.*, 1998, (13), 1397–1398

The C–C bond coupling Heck and Stille reactions are reported in supercritical CO₂ (scCO₂) with various phosphines giving rates and selectivities comparable to those in toluene. Fluorinated phosphines, in particular tris[3,5-bis(trifluoromethyl)phenyl]phosphine (1), give high conversions (> 99%) as they enhance the solubility of metal complexes in scCO₂.

A Highly Active Palladium Catalyst System for the Arylation of Anilines

J. P. SADIGHI, M. C. HARRIS and S. L. BUCHWALD, *Tetrahedron Lett.*, 1998, 39, (30), 5327–5330

A 0.5 mol% Pd(OAc)₂/DPEphos system, where DPEphos is bis[2-(diphenylphosphino)phenyl] ether, was a highly active catalyst for the arylation of primary anilines by aryl bromides giving products in ≤ 99% yield. This system is effective for electron-poor anilines and electron-rich aryl bromides.

Palladium-Catalyzed Carbon-Nitrogen Bond Formation: A Novel, Catalytic Approach Towards N-Arylated Sulfoximines

C. BOLM and J. P. HILDEBRAND, *Tetrahedron Lett.*, 1998, 39, (32), 5731–5734

Pd(OAc)₂, in the presence of chelating bisphosphines, catalyses the coupling of sulfoximines with aryl bromides (1), giving N-arylated products. High yields (≤ 96%) were obtained with (1) containing electron-withdrawing groups in the *ortho*- or *para*-positions.

Rhodium Cationic Complexes Using Dithioethers as Chiral Ligands. Application in Styrene Hydroformylation

A. OREJÓN, A. M. MASDEU-BULTÓ, R. ECHARRI, M. DIÉGUEZ, J. FORNÍES-CÁMER, C. CLAVER and C. J. CARDIN, *J. Organomet. Chem.*, 1998, 559, (1–2), 23–29

The dithioethers (–)-DIOSR₂ (R = Me, ⁱPr) (2,3-O-isopropylidene-1,4-dimethyl (and diisopropyl) thioether-L-threitol) react with [Rh(COD)₂]ClO₄ (COD = 1,5-cyclooctadiene) in CH₂Cl₂ to give [Rh(COD)(DIOSR₂)]ClO₄. These were active catalyst precursors for styrene hydroformylation, giving conversions of ≤ 99% at 30 atm and 65°C, with regioselectivity in 2-phenylpropanal as high as 74%.

Transition Metal Catalysis in Fluorous Media: Application of a New Immobilization Principle to Rhodium-Catalyzed Hydrogenation of Alkenes

D. RUTHERFORD, J. J. JULIETTE, C. ROCABOY, I. T. HORVÁTH and J. A. GLADYSZ, *Catal. Today*, 1998, 42, (4), 381–388

Biphase systems comprise toluene solutions of various alkenes and CF₃C₆F₁₁ solutions (1) of the pre-catalyst, ClRh[P(CH₂CH₂(CF₃)₂CF₃)₃] (1.1–0.8 mol%) (1). After 8–26 hours under 1 atm of H₂ at 45°C, hydrogenation products were extracted in 98–87% yields from (1), which could be reused.

New Catalysts and Methods for Highly Enantioselective Metal Carbene Reactions

M. P. DOYLE, *Pure Appl. Chem.*, 1998, 70, (5), 1123–1128

Chiral diRh(II) carboxamidate catalysts, with bridging chiral pyrrolidone, oxazolidinone, azedinone or imidazolidinone ligands, are effective for highly enantio-, diastereo- and regioselective syntheses of lactones and lactams by cyclopropanation, cycloprope-
nation, C-H insertion, and ylide derived reactions of diazoacetates and diazoacetamides. Reactions occur with high turnover numbers and give products in high yield with enantiomeric excesses $\geq 90\%$.

Rhodium Complex-Catalysed Allylic Alkylation of Allylic Acetates

R. TAKEUCHI and N. KITAMURA, *New J. Chem.*, 1998, 22, (7), 659–660

[Rh(COD)Cl]₂-P(OPh)₃ (P:Rh = 2–3) is an efficient catalyst for the allylic alkylation of allylic acetates giving products in $\leq 90\%$ yield. Alkylation at the more substituted allylic terminus is predominant.

Kinetics and Mechanism of Iridium(III) Catalysed Oxidation of Formaldehyde by Cerium(IV) in Aqueous Sulfuric Acid Media

D. KAR, S. K. MONDAL, M. DAS and A. K. DAS, *J. Chem. Res. (S)*, 1998, (7), 394–395

Studies of the kinetics and mechanism of the Ir(III) ($\sim 10^{-6}$ mol dm⁻³) catalysed oxidation of formaldehyde to formic acid by Ce(IV) were performed in aqueous H₂SO₄. An intermediate, involving an association of the catalyst, substrate and oxidant, was formed prior to the electronic transfer step and the Ir(III)/Ir(IV) catalytic cycle.

Cationic Ruthenium Allenylidene Complexes as a New Class of Performing Catalysts for Ring Closing Metathesis

A. FÜRSTNER, M. PICQUET, C. BRUNEAU and P. H. DIXNEUF, *Chem. Commun.*, 1998, (12), 1315–1316

The cationic 18-electron allenylidene Ru complexes [Ru=C=C=CR₂(L)(Cl)(arene)]PF₆ (L = PCy₃, PPr₃), were found to be excellent catalyst precursors for ring closing olefin metathesis. Particularly important are the smooth cyclisations of the conformationally flexible dienes to 16- and 18-membered cycloalkenes.

Catalysis in Aqueous Solution: Hydrogenation of Benzene Derivatives Catalysed by (η^6 -C₆H₆)₂Ru₂Cl₄

E. G. FIDALGO, L. PLASSERAUD and G. SÜSS-FINK, *J. Mol. Catal. A: Chem.*, 1998, 132, (1), 5–12

The catalyst precursor (η^6 -C₆H₆)₂Ru₂Cl₄ was used for the hydrogenation of benzene and various alkyl-benzene derivatives. Under biphasic conditions, cyclohexane derivatives were obtained with turnover rates of 20–2000 cycles per hour. The less active species, [(η^6 -C₆H₆)₂Ru₂H₂]²⁺ and [(η^6 -C₆H₆)₂Ru₂H₂]²⁺, were found in the reaction mixture after the catalytic runs. A more active intermediate, [Ru₂(η^6 -C₆H₆)₂(μ_2 -Cl)(μ_2 -O)(μ_2 -H)₂]⁺ was also detected.

Selective Aerobic Oxidation of Primary Alcohols Catalyzed by a Rh(PPh₃)₃Cl₂/Hydroquinone System

A. HANYU, E. TAKEZAWA, S. SAKAGUCHI and Y. ISHII, *Tetrahedron Lett.*, 1998, 39, (31), 5557–5560

The selective aerobic oxidation of primary alcohols to aldehydes, even in the presence of secondary alcohols, was catalysed by a Ru(PPh₃)₃Cl₂/hydroquinone system under atmospheric O₂ at 60°C. Aliphatic and cyclic primary alcohols gave aldehydes in good yields, while allylic alcohols gave unsaturated aldehydes in high yields without intramolecular H transfer.

Homogeneous Catalysis. Use of a Ruthenium(II) Complex for Catalysing the ene Reaction

W. W. ELLIS, W. ODENKIRK and B. BOSNICH, *Chem. Commun.*, 1998, (12), 1311–1312

The complex *trans*-[Ru(salen)(NO)(H₂O)]⁺ (1) catalyses the ene reaction between activated enophiles and olefins to give homoallylic alcohols by a stepwise process. Using 1 mol% of (1), (+)-citronellal was converted to *l*-isopulegol after 6 h in 80% yield. It may be possible to use chiral analogues of this catalyst for asymmetric catalytic intramolecular ene reactions.

FUEL CELLS

Carbon Supported and Unsupported Pt-Ru Anodes for Liquid Feed Direct Methanol Fuel Cells

L. LIU, C. PU, R. VISWANATHAN, Q. FAN, R. LIU and E. S. SMOTKIN, *Electrochim. Acta*, 1998, 43, (24), 3657–3663

The performance of supported (1) (< 0.8 mg cm⁻², Pt-Ru (1:1)/C) and unsupported (2) (Pt-Ru (1:1)) catalysts was compared in DMFCs having a reversible H reference electrode. The measured specific activities of (1) were ≤ 3 times higher than (2) but membrane electrode assemblies made with (1) showed no improvement with loadings > 0.5 mg cm⁻². Fuel cells with 0.46 mg cm⁻² supported electrodes performed as well as unsupported electrodes with 2 mg cm⁻².

ELECTRICAL AND ELECTRONIC ENGINEERING

Electrical and Structural Properties and Phase Diagram of a Molecular Superconductor β -[(CH₃)₄N][Pd(dmit)₂]₂

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β -[(CH₃)₄N][Pd(dmit)₂]₂ (1) is isomorphous to [(CH₃)₄N][Ni(dmit)₂]₂ which is the first pure π acceptor molecular conductor exhibiting a superconducting transition. The phase diagram of (1) resembles that of typical organic superconductors. The superconducting phase appeared at 6–9 kbar. (1) has a characteristic “pre-superconducting region” at ~ 5.5 kbar, where resistivity decreases very rapidly with lowering temperature. The highest *T*_c was 6.5 K.