

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Enhancement of Surface Self-Diffusion of Platinum Atoms by Adsorbed Hydrogen

S. HORCH, H. T. LORENSEN, S. HELVEG, E. LÆGSGAARD, I. STENSGAARD, K. W. JACOBSEN, J. K. NØRSKOV and F. BESENBACHER, *Nature*, 1999, **398**, (6723), 134–136  
STM of H<sub>2</sub>-promoted self-diffusion of Pt on the Pt(110)-(1×2) surface has been carried out. An activated intermediate Pt-H complex (1) with diffusivity enhanced by a factor of 500 at room temperature, relative to the other Pt adatoms was observed. Density-functional calculations indicated that (1) consists of a H atom trapped on top of a Pt atom, and that the bound H atom decreases the diffusion barrier.

### Polymerization and Decomposition of C<sub>60</sub> on Pt(111) Surfaces

N. SWAMI, H. HE and B. E. KOEL, *Phys. Rev. B*, 1999, **59**, (12), 8283–8291

The interaction of C<sub>60</sub> with Pt(111) was studied by AES, XPS, UPS, HREELS and LEED. At submonolayer coverages, C<sub>60</sub> is polymerised on Pt(111) at ≥ 300 K. Annealing multilayer C<sub>60</sub> films on Pt(111) to ≥ 600 K leads to a C<sub>60</sub> adlayer that is quite different from 1 monolayer C<sub>60</sub>/Pt(111). On annealing C<sub>60</sub> films on Pt(111) to 900 K, graphite domains appear on the surface, and total fragmentation occurs at 1050 K.

### Temperature-Dependent Segregation on Pt<sub>25</sub>Rh<sub>75</sub>(111) and (100)

E. PLATZGUMMER, M. SPORN, R. KOLLER, S. FORSTHUBER, M. SCHMID, W. HOFER and P. VARGA, *Surf. Sci.*, 1999, **419**, (2–3), 236–248

Surface segregation was studied on Pt<sub>25</sub>Rh<sub>75</sub>(111) (1) and Pt<sub>25</sub>Rh<sub>75</sub>(100) (2) by LEED and LEIS. The Pt concentration grew continuously on (1) until 1000°C, whereas it reached a maximum enrichment at ~ 500°C on (2) and decreased thereafter. This contrasting behaviour resulted solely from the kinetic limitations in the low temperature regime.

### Superconductivity Mediated by Spin Fluctuations in the Heavy-Fermion Compound UPd<sub>2</sub>Al<sub>3</sub>

M. JOURDAN, M. HUTH and H. ADRIAN, *Nature*, 1999, **398**, (6722), 47–49

Tunnelling spectroscopy has been used to investigate the superconducting order parameter of a heavy-fermion superconductor: epitaxial thin films of UPd<sub>2</sub>Al<sub>3</sub>. A strong-coupling feature in the tunnelling conductivity was observed, and when combined with inelastic neutron scattering data suggested a pairing interaction mediated by antiferromagnetic spin fluctuations. These induce a presumably *d*-wave order parameter without any unconventional symmetry reduction.

## CHEMICAL COMPOUNDS

### The First Experimental Evidence for the *cis-trans* Isomerism of Metal Chelates with Oxyazo Ligands

V. A. KOGAN, S. G. KOCHIN, A. S. ANTSYSHKINA, G. G. SADIKOV and A. D. GARNOVSKII, *Mendeleev Commun.*, 1999, (2), 82–83

The *cis*- and *trans*-isomers of bis(2-hydroxy-4'-methylazobenzenato)Pt(II) have been isolated and identified for the first time. A special feature of the separation of the isomers is that the *cis* form needs to be rapidly removed from solutions because it spontaneously converts into the *trans* form. The existence of the *cis* structure was proved by XRD analysis.

### Synthesis, Structure, Chemical Bonding, and Properties of CaTIn<sub>2</sub> (T = Pd, Pt, Au)

R.-D. HOFFMANN, R. PÖTTGEN, G. A. LANDRUM, R. DRONSKOWSKI, B. KÜNNEN and G. KOTZYBA, *Z. Anorg. Allg. Chem.*, 1999, **625**, (5), 789–798

CaTIn<sub>2</sub> (T = Pd, Pt, Au) (1) were prepared by reacting the elements in glassy C crucibles under Ar. (1) crystallise with the MgCuAl<sub>2</sub> structure type (space group *Cmcm*). Magnetic susceptibility measurements of compact polycrystalline samples of (1) indicate weak Pauli paramagnetism. (1) are metallic conductors.

### Synthesis and Characterization of Allyl(β-ketoiminato)palladium(II) Complexes: New Precursors for Chemical Vapor Deposition of Palladium Thin Films

Y.-L. TUNG, W.-C. TSENG, C.-Y. LEE, P.-F. HSU, Y. CHI, S.-M. PENG and G.-H. LEE, *Organometallics*, 1999, **18**, (5), 864–869

Treatment of β-ketoiminates with [(allyl)Pd(μ-Cl)]<sub>2</sub> afforded volatile, air-stable allyl(β-ketoiminato)Pd(II) complexes, which are excellent precursors for the CVD of Pd thin films. In solution <sup>1</sup>H NMR analyses indicate either a direct rotation of a planar allyl ligand about the allyl-Pd axis or a solvent-assisted exchange process involving the transient formation of a monodentate ketoiminato ligand.

### Synthesis of Poly(oxyethylene)-Grafted Palladium Clusters

K. NAKA, M. YAGUCHI and Y. CHUJO, *Chem. Mater.*, 1999, **11**, (4), 849–851

A polymer-grafted Pd cluster (3–5 nm) was prepared by stirring an acetic acid solution of Pd(II) acetate and bipyridyl-terminated poly(oxyethylene) (bpy-POE<sub>2000</sub>) under 1 atm H<sub>2</sub> at room temperature. The cluster was soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, MeOH, acetone and H<sub>2</sub>O. <sup>1</sup>H NMR spectra indicated the terminal bpy ligand is fixed at the surface of the Pd cluster. The calculated formula is Pd<sub>2057</sub>(bpy-POE<sub>2000</sub>)<sub>428</sub>O<sub>~2000</sub>.

## PHOTOCONVERSION

### Self-Assembly of Pre-designed Trimetallic Macrocycles Based on Benzimidazole as Nonlinear Bridging Motifs: Crystal Structure of a Luminescent Platinum(II) Cyclic Trimer

S.-W. LAI, M. C.-W. CHAN, S.-M. PENG and C.-M. CHE, *Angew. Chem. Int. Ed.*, 1999, **38**, (5), 669–671

Nonlinear *N*-deprotonated benzimidazole on reaction with square-planar cyclometalated Pt(II) precursors gave cyclic trimers with metal vertices, related to calixarenes. [Pt(thpy)(bzim)]<sub>3</sub> (1) was formed from [Pt(thpy)(Hthpy)Cl] (Hthpy = 2-(2-thienyl)pyridine) on treatment with Na benzimidazolate. (1) photo-luminesces in solution at room temperature.

### Phosphate Anion Binding and Luminescent Sensing in Aqueous Solution by Ruthenium(II) Bipyridyl Polyaza Receptors

P. D. BEER and J. CADMAN, *New J. Chem.*, 1999, **23**, (4), 347–349

A new class of anion luminescent sensor consisting of a series of new Ru(II) bipyridyl polyaza receptors was prepared and can bind and detect phosphate and ATP anions in aqueous solution via MLCT luminescent emission quenching. The receptors were prepared by refluxing bipyridyl substituted amine compounds with (bipy)<sub>2</sub>RuCl<sub>2</sub>·2H<sub>2</sub>O in aqueous EtOH then by HCl addition.

### Electronic and Light-Emitting Properties of Some Polyimides Based on Bis(2,2':6',2''-terpyridine) Ruthenium(II) Complex

W. Y. NG, X. GONG and W. K. CHAN, *Chem. Mater.*, 1999, **11**, (4), 1165–1170

Novel polyimides that contain the bis(2,2':6',2''-terpyridine) Ru(II) complex were synthesised, and their optoelectronic properties were studied. The absorption of the polymers at 500 nm was strongly enhanced by the Ru complex. The polyimides exhibited electroluminescent behaviour when the polymer films were fabricated into single-layered LEDs. The external quantum efficiency and maximum luminance of the devices were 0.1% and 120 cd m<sup>-2</sup>, respectively.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Structure and Electrochemical Properties of Pt/C Catalytic Electrodes Manufactured by Ion Beam Sputtering

B. YANG, S. XU, Y. ZHANG, Y. ZHAO and Y. YU, *Precious Met. (Chin.)*, 1999, **20**, (1), 14–19

Pt/C catalytic electrodes (1) have been prepared by ion beam sputtering. The consumption of Pt in (1) was reduced to 0.19 mg cm<sup>-2</sup>. It was established that the Pt films in (1) have f.c.c. structure, and that the catalytic activities of Pt coatings on graphite cloths is better than that on C papers. Application of high beam voltages and high beam current during ion beam sputtering further improved the catalytic activity of (1) with no degradation after 1000 h working.

### On-Site Characterization of Electrocrystallized Platinum Nanoparticles on Carbon and Sol-Gel Thin Film Modified Carbon Surfaces

Y. GUO and A. R. GUADALUPE, *Langmuir*, 1999, **15**, (3), 759–762

Pt nanoparticles were electrocrystallized on amorphous C film and on sol-gel modified C film deposited on Au mesh grids. These Pt-modified surfaces were characterised by TEM and energy dispersive spectroscopy. The particles deposited on bare C surfaces exhibited polytetrahedral crystallographic morphology. Subsequently, laterally dendritic growth of Pt formed by aggregation of primary particles (3 to 5 nm) was found on the sol-gel modified C surfaces. This was reported to be a new type of morphology for electrodeposited Pt with a high surface area.

### Fabrication of Poly(diphenylsilylenemethylene) and Poly(diphenylsiloxane) Thin Films Using Fine Metal Particles

F. ROSSIGNOL, Y. NAKATA, H. NAGAI, T. OKUTANI, M. SUZUKI, N. KUSHIBIKI and M. MURAKAMI, *Chem. Mater.*, 1999, **11**, (2), 358–366

A new technique for the ring-opening polymerisation of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (1) has been developed. (1) was first evaporated on Si substrates and then exposed to metal particle deposition by sputtering prior to heat treatment. Catalytic activities of Pt, Pt/Pd, Au, Cu and Ag particles were examined; the metal had no effect on the chemical structure of the film; but the polymerisation efficiency and film crystallinity depended greatly on the kind of metal, for identical sputtering and heating conditions.

### Chemical Fluid Deposition: Reactive Deposition of Platinum Metal from Carbon Dioxide Solution

J. J. WATKINS, J. M. BLACKBURN and T. J. MCCARTHY, *Chem Mater.*, 1999, **11**, (2), 213–215

Chemical fluid deposition was validated for the deposition of CVD-quality Pt metal films on Si wafers and polymer substrates via hydrogenolysis of the complex dimethyl(cyclooctadiene)Pt(II) in supercritical CO<sub>2</sub> at 80°C. This reduction yields continuous metal films on solid substrates and discreet metal clusters within the 200 nm pores of an Al<sub>2</sub>O<sub>3</sub> membrane.

### The Electrodeposition & Material Properties of Palladium-Cobalt

J. A. ABYS, G. F. BRECK, H. K. STRASCHIL, I. BOGUSLAVSKY and G. HOLMBOM, *Plat. Surf. Finish.*, 1999, **86**, (1), 108–115

Mechanically stable, mirror-like Pd-Co films with 10–30% Co were produced at current densities of < 50 to > 700 mA cm<sup>-2</sup>. In addition, any desired composition can be maintained within ± 5% over a wide range of operating conditions and plating bath ageing. The material properties of the Pd-Co deposits compared well with Hard-Gold and Pd-Ni finishes, but the Pd-Co alloy was harder and had superior durability. Thus, it proved to be an excellent material for contact finish applications.

### Reactive Pulsed Laser Deposition of Iridium Oxide Thin Films

M. A. EL KHAKANI and M. CHAKER, *Thin Solid Films*, 1998, **335**, (1, 2), 6–12

Highly conductive IrO<sub>2</sub> thin films have been deposited on Si(100) substrates by reactive pulsed laser ablation from an Ir target in an O<sub>2</sub> atmosphere. At 200 mTorr of O<sub>2</sub> ambient pressure, IrO<sub>2</sub> films deposited at substrate temperatures in the 400–550°C range are polycrystalline and exhibit a granular morphology with average feature size increasing (from ~90 to 170 nm) with the substrate temperature. The room temperature resistivities,  $39 \pm 4 \mu\Omega \text{ cm}$ , of these IrO<sub>2</sub> films compare well with those of bulk single-crystal IrO<sub>2</sub>.

### Properties and Application Feasibility of an Osmium-Oxygen Thin Film Prepared by DC-Glow-Discharge Deposition from Osmium Tetraoxide

H. INOUE and K. SATOH, *Bull. Chem. Soc. Jpn.*, 1999, **72**, (1), 121–126

An Os-O thin film (OsO<sub>2</sub>) was deposited by d.c.-glow-discharge from OsO<sub>4</sub>. The prepared films had a homogeneous amorphous structure and  $10^{-3} \Omega \text{ cm}$  order of resistivity. Since the transparency of a 20 nm thick film was ~80% for visible light, a transparent conductive film could be obtained on glass or plastic substrates. Fundamental properties are reported.

## APPARATUS AND TECHNIQUE

### Gas Sensor Materials Based on Metallo dendrimers

M. ALBRECHT and G. VAN KOTEN, *Adv. Mater.*, 1999, **11**, (2), 171–174

Pt complexes (1) containing a terdentate “pincer” ligand [C<sub>n</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6] were synthesised. When coupled to a dendrimer core consisting of a benzene centre substituted with acid chloride functionalities as rigid linkage units, trimetallic macromolecules with 3 diagnostic Pt centres were obtained. Alternatively, coupling of (1) to an appropriate AB<sub>2</sub> branching point containing a protected phenol and 2 acid chloride groups prior to the attachment to the core unit yielded a periphery-functionalised metallo dendrimer containing 6-adsorption-active metal sites. These metallo dendrimers had selectivity towards SO<sub>2</sub>.

### Probing Organometallic Structure and Reactivity by Transition Metal NMR Spectroscopy

W. VON PHILIPSBORN, *Chem. Soc. Rev.*, 1999, **28**, (2), 95–105

Transition metal NMR chemical shifts are readily measured and serve as a probe into electronic and steric effects of ligands and substituents in complexes. Quantitative correlations of metal chemical activities, both experimental and as a result of quantum chemical calculations, are reported to give new mechanistic insights and permit reactivity predictions and a screening of homogeneous catalysts. Examples involving the spin-1/2 nuclei <sup>103</sup>Rh and <sup>187</sup>Os are discussed.

### Electrochemical Detection of Single-Stranded DNA Using Polymer-Modified Electrodes

A. C. ONTKO, P. M. ARMISTEAD, S. R. KIRCUS and H. H. THORP, *Inorg. Chem.*, 1999, **38**, (8), 1842–1846

Glassy C electrodes modified by reductive electropolymerisation of a thin film of poly[Ru(vbpy)<sub>3</sub><sup>2+</sup>] or poly[Ru(vbpy)<sub>3</sub><sup>2+</sup>/vba] (vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine; vba = *p*-vinylbenzoic acid) were prepared. The modified electrodes were active towards the oxidation of guanine in solution in both a mononucleotide and a polymer.

## HETEROGENEOUS CATALYSIS

### High-Throughput Synthesis and Screening of Combinatorial Heterogeneous Catalyst Libraries

R. CONG, R. D. DOOLEN, Q. FAN, D. M. GIAQUINTA, S. GUAN, E. W. MCFARLAND, D. M. POOJARY, K. SELF, H. W. TURNER and W. H. WEINBERG, *Angew. Chem. Int. Ed.*, 1999, **38**, (4), 484–488

The catalytic activity and selectivity of 120 catalysts were measured, in < 1 minute, in combinatorial triangular libraries of Rh-Pt-Cu and Rh-Pd-Cu alloys, via the catalytic oxidation of CO and the reduction of NO, by scanning mass spectrometry. The elements of the libraries (~2 to 4 μg of material) were sputter-deposited in an array, annealed, then heated for test.

### Ethyl Acetate Production from Water-Containing Ethanol Catalyzed by Supported Pd Catalysts: Advantages and Disadvantages of Hydrophobic Supports

T.-B. LIN, D.-L. CHUNG and J.-R. CHANG, *Ind. Eng. Chem. Res.*, 1999, **38**, (4), 1271–1276

Hydrophilic and hydrophobic Pd catalysts were investigated for the selective oxidation of H<sub>2</sub>O-containing EtOH in the presence of excess EtOH, a one-step preparation of ethyl acetate, in a continuous fixed-bed reactor. The conversion of EtOH catalysed by Pd/styrene-divinylbenzene copolymer was found to be 20 times more than that by Pd/γ-Al<sub>2</sub>O<sub>3</sub>. However, it may have been caused by weak metal-support interactions and the formation of Pd(II) acetate.

### Characterization of Model Automotive Exhaust Catalysts: Pd on Ceria and Ceria-Zirconia Supports

H.-W. JEN, G. W. GRAHAM, W. CHUN, R. W. MCCABE, J.-P. CUIF, S. E. DEUTSCH and O. TOURET, *Catal. Today*, 1999, **50**, (2), 309–328

Pure CeO<sub>2</sub>, SiO<sub>2</sub>-CeO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub> solid solutions, and CeO<sub>2</sub>-ZrO<sub>2</sub> solid solutions with partial incorporation of Pr were prepared and used as supports in model Pd automotive three-way catalysts. After ageing, catalysts prepared on the solid solution materials provided much more oxygen storage capacity (OSC) than those based on pure CeO<sub>2</sub> or SiO<sub>2</sub>-CeO<sub>2</sub>. Addition of 5 wt.% Pr as a substitute for CeO<sub>2</sub> improved the thermal stability of the CeO<sub>2</sub>-ZrO<sub>2</sub>, but did not increase the OSC of the model catalysts.

### Combustion of a Trace Amount of CH<sub>4</sub> in the Presence of Water Vapor over ZrO<sub>2</sub>-Supported Pd Catalysts

K. NOMURA, K. NORO, Y. NAKAMURA, H. YOSHIDA, A. SATSUMA and T. HATTORI, *Catal. Lett.*, 1999, **58**, (2, 3), 127–130

Combustion of a trace amount of CH<sub>4</sub> over Pd/ZrO<sub>2</sub> catalyst was studied under nearly exhaust gas conditions (at temperatures 523–773 K) where H<sub>2</sub>O vapour coexists. High catalytic activity was obtained with a ZrO<sub>2</sub> support calcined at 1073 and 1273 K. Durability tests at 673 K for 100 h revealed that the activities of these catalysts hardly decreased, while those of Pd/calcined Al<sub>2</sub>O<sub>3</sub> were much decreased.

### In Situ FT-IR Study of Rh–Al–MCM-41 Catalyst for the Selective Catalytic Reduction of Nitric Oxide with Propylene in the Presence of Excess Oxygen

R. Q. LONG and R. T. YANG, *J. Phys. Chem. B*, 1999, **103**, (12), 2232–2238

Rh/Al-MCM-41(1) was studied for the selective catalytic reduction of NO by C<sub>3</sub>H<sub>6</sub> in the presence of excess O<sub>2</sub>. (1) showed a high activity in converting NO to N<sub>2</sub> and N<sub>2</sub>O at low temperatures. In situ FTIR indicated that a Rh-NO<sup>+</sup> species is formed on (1) in flowing NO/He, NO + O<sub>2</sub>/He and NO + C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>/He at 100–350°C. This species is quite active in reacting with propylene and/or propylene adspecies at 250°C in the presence or absence of O<sub>2</sub>, leading to the formation of isocyanate species, CO and CO<sub>2</sub>.

### Study on Sol-Gel Derived Rh-Based Catalysts for Synthesis of C<sub>2</sub> Oxygenated Compounds Through CO Hydrogenation

Y. WANG, *Chin. J. Catal.*, 1999, **20**, (2), 103–108

Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalysts prepared by a sol-gel process were characterised and studied in CO hydrogenation at 2.0 MPa for the synthesis of C<sub>2</sub> oxygenated compounds. In CO hydrogenation, 2% Rh/SiO<sub>2</sub> mainly catalysed the formation of acetaldehyde. Addition of CeO<sub>2</sub> increased the selectivity for both EtOH and acetaldehyde. CeO<sub>2</sub> decreased the catalytic activity, but increased appreciably the selectivity for MeOH.

### Hydrodenitrogenation of Pyridine over Alumina-Supported Iridium Catalysts

J. CINIBULK and Z. VIT, *Appl. Catal. A: Gen.*, 1999, **180**, (1–2), 15–23

Ir/Al<sub>2</sub>O<sub>3</sub> catalysts obtained from various Ir precursors (Ir(AcAc)<sub>3</sub>, Ir<sub>3</sub>(CO)<sub>12</sub>, H<sub>3</sub>IrCl<sub>6</sub> and (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>6</sub>) were studied in the hydrodenitrogenation (HDN) of pyridine at 320°C and 20 bar of pressure in the absence and presence of a parallel hydrodesulfurisation (HDS) of thiophene. Ir<sub>3</sub>(CO)<sub>12</sub> gave the most active catalyst, due to fewer contaminants in the starting Ir compounds rather than to better Ir dispersion. Ir dispersion was decreased by sintering in air, substantially decreasing the rate of C–N bond hydrogenolysis but with negligible change in the rate of pyridine hydrogenation. Ir/Al<sub>2</sub>O<sub>3</sub> catalysts had much higher HDN activity and HDN/HDS selectivity than NiMo catalysts.

### Supported Ammonia Synthesis Catalysts Based on Potassium Derivatives of Anionic Ruthenium, Osmium and Iron Carbonyl Clusters. The First Catalysts on Carbon Support Exhibiting Activity in Ammonia Synthesis in the Absence of a Specially Added Electron Promoter

S. M. YUNUSOV, E. S. KALYUZHNYAYA, H. MAHAPATRA, V. K. PURI, V. A. LIKHOLOBOV and V. B. SHUR, *J. Mol. Catal. A: Chem.*, 1999, **139**, (2–3), 219–225

K<sub>2</sub>[Ru<sub>n</sub>(CO)<sub>n</sub>], K<sub>2</sub>[Os<sub>n</sub>(CO)<sub>n</sub>] and K<sub>2</sub>[Fe<sub>n</sub>(CO)<sub>n</sub>] catalysts were deposited from THF on graphite-like active C “Sibunit” followed by drying at 20°C in vacuum. The highest efficiency in NH<sub>3</sub> synthesis was displayed by K<sub>2</sub>[Ru<sub>n</sub>(CO)<sub>n</sub>] at ≥ 250°C (1 atm). Replacing “Sibunit” by commercially active C SKT sharply decreases the activity and stability of the catalysts, whereas NH<sub>3</sub> synthesis is greatly accelerated on adding metallic K.

### Novel Supported Catalyst for Hydrodesulfurization Reaction

M. WOJCIECHOWSKA, M. PIETROWSKI and S. LOMNICKI, *Chem. Commun.*, 1999, (5), 463–464

Ru/MgF<sub>2</sub> (1) was highly active in the hydrodesulfurisation (HDS) reaction. (1) was prepared by conventional impregnation with Ru<sub>3</sub>(CO)<sub>12</sub>. The specific properties of MgF<sub>2</sub> of hardness, resistance to calcination in O<sub>2</sub> and well-developed porous structure, contribute to its use as an active support. (1) is more selective for HDS and much less hydrogenation occurs simultaneously with HDS than when using Ru/Al<sub>2</sub>O<sub>3</sub>.

## HOMOGENEOUS CATALYSIS

### Cross-Coupling Reactions of Hypervalent Siloxane Derivatives: An Alternative to Stille and Suzuki Couplings

M. E. MOWERY and P. DESHONG, *J. Org. Chem.*, 1999, **64**, (5), 1684–1688

Bis(dibenzylideneacetone)Pd-catalysed cross-coupling of phenyl, vinyl and allyl siloxane derivatives was found to proceed in good to excellent yield with aryl iodides, electron-deficient aryl bromides, and allylic benzoates. Methyl and 2,2,2-trifluoroethyl siloxanes could be employed in the coupling reaction. Electron-donating and -withdrawing groups were tolerated on the aryl halide without affecting the coupling.

### Use of Fluorinated Palladium Sources for Efficient Pd-Catalysed Coupling Reactions in Supercritical Carbon Dioxide

N. SHEZAD, R. S. OAKES, A. A. CLIFFORD and C. M. RAYNER, *Tetrahedron Lett.*, 1999, **40**, (11), 2221–2224

Pd sources, Pd(OCOCF<sub>3</sub>)<sub>2</sub> and Pd(F<sub>n</sub>-acac)<sub>2</sub>, with fluorinated ligands were shown to be superior to non-fluorinated sources, Pd(OCOCH<sub>3</sub>)<sub>2</sub> and Pd(dba)<sub>3</sub>, for Pd catalysed coupling reactions in supercritical CO<sub>2</sub>. Significantly reduced temperatures and catalyst loadings were possible. The range of phosphine ligands used was increased to include PCy<sub>3</sub> and PBu<sub>3</sub>, often considered to be poor ligands for coupling reactions.

### Biphasic Synthesis of Hydrogen Peroxide from Carbon Monoxide, Water, and Oxygen Catalyzed by Palladium Complexes with Bidentate Nitrogen Ligands

D. BIANCHI, R. BORTOLO, R. D'ALOISIO and M. RICCI, *Angew. Chem. Int. Ed.*, 1999, **38**, (5), 706–708

Effective and stable Pd catalysts for the biphasic synthesis of H<sub>2</sub>O<sub>2</sub> from CO, O<sub>2</sub> and H<sub>2</sub>O are obtained by using a suitable bidentate nitrogen ligand. The best turnover number (578) for this reaction was achieved with a Pd complex with a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand. The reaction was carried out in a biphasic system in which the catalyst is soluble in the organic phase and the produced H<sub>2</sub>O<sub>2</sub> is soluble in the aqueous phase. The biphasic system minimises the ligand oxidation.

### Unprecedented Efficient Hydrogenation of Arenes in Biphasic Liquid-Liquid Catalysis by Re-usable Aqueous Colloidal Suspensions of Rhodium

J. SCHULZ, A. ROUCOUX and H. PATIN, *Chem. Commun.*, 1999, (6), 535–536

A reduced aqueous colloidal suspension of Rh showed efficient activity for the catalytic hydrogenation of benzene derivatives under biphasic conditions at room temperature and atmospheric H<sub>2</sub> pressure. The aqueous phase containing the Rh(0) particles can be reused. The Rh nanoparticles are protected by hydroxyalkylammonium salts containing at least 16C atoms leading to electrosteric stabilisation.

### Homogeneous Hydrogenation of Maleic Anhydride to Succinic Anhydride Catalyzed by Rh Complex Catalyst

L. PU, L. YE and Y. YUANQI, *J. Mol. Catal. A: Chem.*, 1999, **138**, (2–3), 129–133

Hydrogenation of maleic anhydride using various homogeneous transition metal complex catalyst systems was investigated. Typical experimental conditions were: 353–383 K; H<sub>2</sub> pressure 0.5–2.5 MPa; PPh<sub>3</sub>:RhCl(PPh<sub>3</sub>)<sub>3</sub> = 0–16; 0.03 mmol RhCl(PPh<sub>3</sub>)<sub>3</sub>; 20 mmol maleic anhydride; 8 ml of liquid; and 30–360 min reaction time. RhCl(PPh<sub>3</sub>)<sub>3</sub> was the most active catalyst precursor for the hydrogenation of maleic anhydride to succinic anhydride. The optimum ligand and solvent were PPh<sub>3</sub> and ethylene glycol dimethylether, respectively.

### RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> Catalyzed Isomerization of the Baylis-Hillman Adducts

D. BASAVAI AH and K. MUTHUKUMARAN, *Synth. Commun.*, 1999, **29**, (4), 713–719

The RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalysed isomerisation of Baylis-Hillman adducts was investigated. The Baylis-Hillman reaction typically produces functionalised allyl alcohols. Methyl 3-aryl-3-hydroxy-2-methylenepropanoates in the presence of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalysts were converted to methyl 3-aryl-2-methoxy-3-oxopropanoates (~50% yield) by further reaction. This methodology is a new direction for Baylis-Hillman chemistry.

### Homogeneous Dehydrosulfurisation under Ambient Conditions. Harnessing the Facile Polyhedral Rearrangement in the Ruthenium Carbonyl Cluster Ru<sub>5</sub>C(CO)<sub>15</sub>

A. J. BAILEY, S. BASRA and P. J. DYSON, *Green Chem.*, 1999, **1**, (1), 31–32

Reactions of Ru<sub>5</sub>C(CO)<sub>15</sub> (1) with H<sub>2</sub>S affords the bridged butterfly species (μ-H)Ru<sub>5</sub>C(CO)<sub>14</sub>(μ-SH) in which H and SH co-ordinate with simultaneous cleavage of one Ru-Ru bond and displacement of CO. Subsequent reaction with CO regenerates (1) and eliminates S<sub>8</sub> and H<sub>2</sub>. These reactions take place at ambient temperatures and pressures. The Ru-S-Ru bond rupture is quite facile. The CO in the system is not consumed and can be recycled indefinitely.

### Room Temperature Operating Allenylidene Precatalyst [L<sub>n</sub>Ru=C=C=CR<sub>2</sub>]<sup>+</sup>X<sup>-</sup> for Olefin Metathesis: Dramatic Influence of the Counter Anion X<sup>-</sup>

M. PICQUET, D. TOUCHARD, C. BRUNEAU and P. H. DIXNEUF, *New J. Chem.*, 1999, **23**, (2), 141–143

Ru(II) [*p*-cymene(PCy<sub>3</sub>)ClRu=C=C=CPh<sub>3</sub>]<sup>+</sup>X<sup>-</sup> (X = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) (1) was produced from commercial [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>. (1) catalyses the ring-closing metathesis (RCM) of *N,N*-diallyltosylamide at room temperatures whereas (X = BF<sub>4</sub><sup>-</sup>) (2) favours the cyclisation of the 1,6-diene into a 5-membered heterocycle without loss of atoms. The addition of BF<sub>3</sub>·OEt<sub>2</sub> to (2) restores its selectivity in the RCM reaction. (1) also promotes the metathesis of an ene-yne to produce the 3-vinyl-2,5-dihydrofuran.

## FUEL CELLS

### In Situ and Model EXAFS Studies of Electrocatalysts for Methanol Oxidation

R. A. LAMPITT, L. P. L. CARRETTE, M. P. HOGARTH and A. E. RUSSELL, *J. Electroanal. Chem.*, 1999, **460**, (1–2), 80–87

EXAFS of as prepared Pt/C electrocatalysts for the DMFC indicated that the preparation of the dispersed Pt by the oxidation of Pt(SO<sub>3</sub>)<sub>2</sub> forms dispersed PtO<sub>x</sub> species. After reduction by flowing H<sub>2</sub> in the gas treatment cell or potentiostatically in the electrochemical cell, small Pt particles are formed, shown by the presence of Pt neighbours in the first co-ordination shell.

### Improvement in the Diffusion Characteristics of Low Pt-Loaded Electrodes for PEMFCs

F. LUFRANO, E. PASSALACQUA, G. SQUADRITO, A. PATTI and L. GIORGI, *J. Appl. Electrochem.*, 1999, **29**, (4), 445–448

Low Pt loading electrodes were obtained by the direct mixing of electrocatalyst and ionomer (for the catalyst layer) and by the introduction of an intermediate hydrophobic C layer to optimise gas distribution. An optimum content of 20 wt.% PTFE in the C layer at a Pt loading of 0.1 mg cm<sup>-2</sup> gave, for air operation at 5 bar absolute pressure and 95°C, a maximum in the power density of ~450 mW cm<sup>-2</sup>.