

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Theoretical Study of the Interaction of Molecular Hydrogen with PdCu(111) Bimetallic Surfaces

C. SOUSA, V. BERTIN and F. ILLAS, *J. Phys. Chem. B*, 2001, 105, (9), 1817–1822

A density functional cluster model approach was applied to the interaction of H<sub>2</sub> with two different cluster models of PdCu(111). Despite the similar surface morphology of the two bimetallic clusters, Pd<sub>4</sub>Cu<sub>6</sub> and PdCu<sub>12</sub>, they exhibit different reactivity towards H<sub>2</sub>. A single surface Pd atom coordinated to other Pd atoms in the second layer is able to trap and dissociate H<sub>2</sub> at a very low energy cost, so is a potential active site for catalysis. Thus, electronic or ligand effects are important in this activity towards H<sub>2</sub>.

### Crystallization of Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> Bulk Glass under Pressure

J. Z. JIANG, Y. X. ZHUANG, H. RASMUSSEN, N. NISHIYAMA, A. INOUE and C. LATHE, *Europhys. Lett.*, 2001, 54, (2), 182–186

The effect of pressure on the crystallisation behaviour of Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> bulk glass having a wide supercooled liquid region was investigated by *in situ* high-pressure and high-temperature X-ray powder diffraction using synchrotron radiation. At 0–4 GPa, the crystallisation temperature increases with pressure and has a slope of 11 K GPa<sup>-1</sup>.

### Effect of Heat Treatment of Pure and Carbon-Polluted Rhodium Samples on the Low-Temperature Resistivity

K. LEFMAN, T. A. KNUUTTILA, J. E. MARTIKAINEN, L. T. KUHN and K. K. NUMMILA, *J. Mater. Sci.*, 2001, 36, (4), 839–844

The maximal value of the residual resistivity ratio (RRR) for a 25 μm thick Rh foil was 1050 at > 1400°C and ~ 1 μbar pure O<sub>2</sub>. Another batch of foils, containing less magnetic impurities, showed a RRR of only 600. A 0.4 mm thick single crystal was heat treated to a RRR value of 740. C impurities from oil were found to be quite detrimental to the resistivity.

## CHEMICAL COMPOUNDS

### Selective Formation of Integrated Stacks of (α-Diimine)(ethylenediamine)platinum(II) and Neutral π Systems of the Phenanthrene Type

M. KATO, J. TAKAHASHI, Y. SUGIMOTO, C. KOSUGE, S. KISHI and S. YANO, *J. Chem. Soc., Dalton Trans.*, 2001, (5), 747–752

[Pt(en)L]<sup>2+</sup> complexes (1) (L = bipy, phen) with a planar α-diimine ligand and a non-planar diamine ligand form 1:1 integrated stacks taking up free phen and phenanthrene selectively. The composite crystals with PF<sub>6</sub><sup>-</sup> exhibit emission spectra which originate from the <sup>3</sup>ππ\*(L) state of (1) in the integrated stack.

### Metallacyclic Platinum(II) Bis(sulfonamides)

C. EVANS, W. HENDERSON and B. K. NICHOLSON, *Inorg. Chim. Acta*, 2001, 314, (1–2), 42–48

Metallacyclic Pt(II) bis(sulfonamido) complexes (1) were prepared by the reaction of *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = PPh<sub>3</sub>; L<sub>2</sub> = cod) with RSO<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHSO<sub>2</sub>R, RSO<sub>2</sub>NHCH<sub>2</sub>CHMeNHSO<sub>2</sub>R or RSO<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>NHSO<sub>2</sub>R (R = Ph, *p*-C<sub>6</sub>H<sub>4</sub>Me) and Ag<sub>2</sub>O. The only significant bands in the IR spectra of (1) are those associated with the sulfonyl groups. (1) give strong [M + H]<sup>+</sup> ions in their positive ion electrospray mass spectra.

### Pd(en) as a Sequence-Selective Molecular Pinch for α-Helical Peptides

I. HAMACHI, N. KASAGI, S. KIYONAKA, T. NAGASE, Y. MITO-OKA and S. SHINKAI, *Chem. Lett. Jpn.*, 2001, (1), 16–17

Pd(II)(ethylenediamine) (1) was found to selectively stabilise an α-helix conformation of peptides having two histidine (His) residues at *i* and *i* + (3 or 4) positions. Helix conformations of the other peptides having one or two His at different positions are destabilised. The interactions between (1) and peptides were monitored by circular dichroism spectroscopy.

### Ship-in-Bottle Synthesis of Anionic Rh Carbonyls in Faujasites

L. BRABEC and J. NOVÁKOVÁ, *J. Mol. Catal. A: Chem.*, 2001, 166, (2), 283–292

Direct carbonylation of [Rh(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> ion exchanged in Na and K faujasites gives carbonyls, such as [Rh(CO)<sub>2</sub>]<sup>-</sup> and [Rh<sub>6</sub>(CO)<sub>15</sub>]<sup>2-</sup>. Polynuclear anionic Rh carbonyls are formed at 25–100°C, if H<sub>2</sub>O is present in sufficient amount. Higher carbonylation temperature as well as higher zeolite dehydration prior to carbonylation give [Rh(CO)<sub>2</sub>]<sup>-</sup>; this complex can be changed to polynuclear Rh carbonyls at lower temperature and in the presence of H<sub>2</sub>O. These changes proceed reversibly.

### Osmium Dithiophosphates. Synthesis, X-Ray Crystal Structure, Spectroscopic and Electrochemical Properties

P. U. JAIN, H. PAUL, P. MUNSHI, M. G. WALAWALKAR and G. K. LAHIRI, *Polyhedron*, 2001, 20, (3–4), 245–252

(RO)<sub>2</sub>PS<sub>2</sub>NH<sub>4</sub><sup>+</sup> (R = Me, Et) reacts with (NH<sub>4</sub>)<sub>2</sub>Os<sup>IV</sup>Br<sub>6</sub> in MeOH under N<sub>2</sub> to give one-electron paramagnetic complexes [Os<sup>III</sup>{(RO)<sub>2</sub>PS<sub>2</sub>}<sub>3</sub>] (1) in the solid state. However, in the solution state, (1) are transformed selectively into the diamagnetic complexes [(RO)<sub>2</sub>PS<sub>2</sub>}<sub>3</sub>Os<sup>III</sup>–Os<sup>III</sup>{S<sub>2</sub>P(RO)<sub>2</sub>}<sub>3</sub>] (2) where the paramagnetic Os(III) centres are antiferromagnetically coupled. (2) are susceptible to undergo stereoretentive electrochemical oxidations and reductions to [(RO)<sub>2</sub>PS<sub>2</sub>}<sub>3</sub>Os<sup>IV</sup>–Os<sup>IV</sup>{S<sub>2</sub>P(RO)<sub>2</sub>}<sub>3</sub>]<sup>2+</sup> and [(RO)<sub>2</sub>PS<sub>2</sub>}<sub>3</sub>Os<sup>II</sup>–Os<sup>II</sup>{S<sub>2</sub>P(RO)<sub>2</sub>}<sub>3</sub>]<sup>2-</sup>, respectively.

## ELECTROCHEMISTRY

### Effect of Power Ultrasound on the Electrochemical Platinum | HCOOH Interface

C. LE NAOUR, PH. MOISY, J. M. LÉGER, C. PETRIER and C. MADIC, *J. Electroanal. Chem.*, 2001, 501, (1–2), 215–221

Investigation of HCOOH oxidation on a Pt electrode showed that low-intensity ultrasound ( $\sim I_{\text{us}} = 2 \text{ W cm}^{-2}$ ) increases the potential oxidation zone and the current intensity. The catalytic activity of the newly reduced Pt was also seen to increase significantly under ultrasound, depending upon the upper potential investigated during Pt oxidation.

### Commensurate Water Monolayer at the RuO<sub>2</sub>(110)/Water Interface

Y. S. CHU, T. E. LISTER, W. G. CULLEN, H. YOU and Z. NAGY, *Phys. Rev. Lett.*, 2001, 86, (15), 3364–3367

Molecular level details of surface redox processes occurring on the RuO<sub>2</sub>(110) surface under H<sub>2</sub>O were established by utilising the measurement of selected surface X-ray scattering rods which are extremely sensitive to the position of surface O atoms. At anodic potentials (close to O<sub>2</sub> evolution), the extraneous H<sub>2</sub>O layer and surface OH layer form a bilayer with a O–H–O bond distance similar to that of ice X. At cathodic potentials, the H<sub>2</sub>O molecules converted from the bridging OH molecules to form a low-density H<sub>2</sub>O layer.

## PHOTOCONVERSION

### Spectroscopy and Photochemical Reactivity of Cyclooctadiene Platinum Complexes

A. KLEIN, J. VAN SLAGEREN and S. ZÁLIŠ, *J. Organomet. Chem.*, 2001, 620, (1–2), 202–210

The optical transitions of [(COD)Pt(R)<sub>2</sub>] (1) (R = alkyl, alkynyl, phenyl) were determined by absorption spectroscopy, spectral deconvolution and quantum-chemical calculations. The observed photoreactivity is wavelength dependent and observed reaction rates correlate with the donor strength of R. The photochemical reactivity of (1) was greatly increased by the replacement of methyl by stronger donating R groups, such as benzyl, adamantylmethyl or *iso*-propyl.

### Synthesis and Structural Characterisation of Luminescent Di- and Tri-Nuclear Palladium(II) Acetylide Complexes as Building Blocks for Metallodendrimers

V. W.-W. YAM, L. ZHANG, C.-H. TAO, K. M.-C. WONG and K.-K. CHEUNG, *J. Chem. Soc., Dalton Trans.*, 2001, (7), 1111–1116  
*trans*-Pd(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> reacts with 1,3,5-triethynylbenzene and 1,3-diethynyl-5-triisopropylsilylethynylbenzene, in the presence of HNEt<sub>2</sub> and a Cu(I) catalyst, to give luminescent 1,3,5-[Cl(Et<sub>3</sub>P)<sub>2</sub>PdC≡C]<sub>3</sub>C<sub>6</sub>H<sub>3</sub> (1) and 1,3-[Cl(Et<sub>3</sub>P)<sub>2</sub>PdC≡C]<sub>2</sub>-5-[('Pr)<sub>3</sub>SiC≡C]C<sub>6</sub>H<sub>3</sub> (2), respectively. (1) and (2) can be used as building blocks for the construction of metallodendrimers. (1) and (2) are emissive in EtOH–MeOH glass at 77 K.

### A New Bridging Ligand for the Synthesis of Luminescent Polynuclear Ru(II) and Os(II) Polypyridine Complexes

A. BÖRJE, O. KÖTHE and A. JURIS, *New J. Chem.*, 2001, 25, (2), 191–193

[Ru(bpy)<sub>2</sub>(bpy-O-bpy)]<sup>2+</sup> (1) (bpy-O-bpy = bis[4-(2,2'-bipyridinyl)] ether) has been synthesised by reacting 4-hydroxy-2,2'-bipyridine with a Ru(II)-coordinated 4-bromo-2,2'-bipyridine [Ru(bpy)<sub>2</sub>(Br-bpy)]<sup>2+</sup>. (1) reacts with [Os(bpy)<sub>2</sub>Cl<sub>2</sub>] to give [(bpy)<sub>2</sub>Ru(μ-bpy-O-bpy)Os(bpy)<sub>2</sub>]<sup>4+</sup> (2). (1) reacts with [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] to give [(bpy)<sub>2</sub>Ru(μ-bpy-O-bpy)Ru(bpy)<sub>2</sub>]<sup>4+</sup> (3). The polynuclear complexes (2) and (3) display similar luminescence properties as [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.

### Spectroscopic Studies of Colloidal Solutions of Nanocrystalline Ru(bpy)<sub>3</sub><sup>2+</sup>-Zeolite Y

N. B. CASTAGNOLA and P. K. DUTTA, *J. Phys. Chem. B*, 2001, 105, (8), 1537–1542

Ru(bpy)<sub>3</sub><sup>2+</sup>-zeolite Y (1) dispersed in toluene to yield a transparent solution was studied by transmission spectroscopic techniques. For (1) in suspension at  $\leq 1 \text{ mg}/10 \text{ cm}^3$ , scattering is sufficiently low so that all the Ru(bpy)<sub>3</sub><sup>2+</sup> trapped in the zeolite is measured by optical spectroscopy. In the Ru(bpy)<sub>3</sub><sup>2+</sup>-zeolite Y system, intrazeolitic electron transfer from the photogenerated viologen radical to Ru(bpy)<sub>3</sub><sup>2+</sup> was followed by flash photolysis to obtain information about the electron-transfer process.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Preparation and Electrocatalytic Activity of Pt/Ti Nanostructured Electrodes

L.-B. LAI, D.-H. CHEN and T.-C. HUANG, *J. Mater. Chem.*, 2001, 11, (5), 1491–1494

Pt/Ti nanostructured electrodes (1) were prepared, first by the electrophoretic deposition of Pt nanoparticles on a Ti support, followed by heat treatment. The electrocatalytic activity of (1) for the oxidation of HCOOH was much higher than that of a bulk Pt electrode. With increases in the temperature of heat-treatment and size of the Pt nanoparticles, the electrocatalytic activity of (1) decreased due to sintering and reduction of the specific surface area.

### Effects of Electroless Plating Chemistry on the Synthesis of Palladium Membranes

Y. S. CHENG and K. L. YEUNG, *J. Membrane Sci.*, 2001, 182, (1–2), 195–203

The effects of plating chemistry on plating efficiency and on the membrane microstructure of Pd deposits on porous glass and stainless steel supports are reported for PdCl<sub>2</sub>/Na<sub>2</sub>EDTA/NH<sub>4</sub>OH/N<sub>2</sub>H<sub>4</sub> (1) and PdCl<sub>2</sub>/NH<sub>4</sub>Cl/NH<sub>4</sub>OH/Na<sub>2</sub>H<sub>2</sub>PO<sub>2</sub> (2) plating baths. (2) has a slower plating rate, but provides better plating efficiency than (1). The oxidation of hypophosphite in (2) produces H<sub>2</sub>, which has a detrimental effect on the deposited Pd film.

## APPARATUS AND TECHNIQUE

### Determination of Methane and Other Small Hydrocarbons with a Platinum–Nafion Electrode by Stripping Voltammetry

P. JACQUINOT, B. MÜLLER, B. WEHRLI and P. C. HAUSER, *Anal. Chim. Acta*, 2001, 432, (1), 1–10

CH<sub>4</sub> in the gas phase can be determined via pre-adsorption on a dispersed Pt electrode backed by Nafion which is in contact with 10 M H<sub>2</sub>SO<sub>4</sub>. The adsorption process is strongly temperature dependent with an activation energy of 8.7 kcal mol<sup>-1</sup>. During the anodic sweep the adsorbed CH<sub>4</sub> is oxidised at the potential of the onset of formation of the Pt oxide monolayer. A linear calibration curve was obtained at 0.1–5% CH<sub>4</sub> in N<sub>2</sub>, with a detection limit of 130 ppm (*S/N* = 3).

### Ammonia-Sensing Characteristics of Pt and SiO<sub>2</sub> Doped SnO<sub>2</sub> Materials

Y.-D. WANG, X.-H. WU, Q. SU, Y.-F. LI and Z.-L. ZHOU, *Solid-State Electron.*, 2001, 45, (2), 347–350

Pt and SiO<sub>2</sub> doped SnO<sub>2</sub> material was found to exhibit a high sensitivity and good stability to NH<sub>3</sub> gas. The assistant catalyst SiO<sub>2</sub> has no catalytic activity when used alone. However, when it is used with Pt, it improved remarkably the activity of the Pt catalyst and extended the life of the catalyst. The sensing mechanism of the sensor was analysed.

### Combinatorial Discovery of Alloy Electrocatalysts for Amperometric Glucose Sensors

Y. SUN, H. BUCK and T. E. MALLOW, *Anal. Chem.*, 2001, 73, (7), 1599–1604

Combinatorial methods were employed to search for active alloy electrocatalysts for use in enzyme-free amperometric glucose sensors. Electrode arrays (715-member) containing combinations of Pt, Pb, Au, Pd and Rh were prepared and screened by converting anodic current to visible fluorescence. The most active compositions contained both Pt and Pb. A range of binary, ternary and higher Pt-Pb alloy compositions were found to resist poisoning in glucose solution and allowed glucose to be sensed amperometrically at potentials negative of the oxidation of common interfering agents.

### The Fabrication of Reproducible Superconducting Scanning Tunneling Microscope Tips

O. NAAMAN, W. TEIZER and R. C. DYNES, *Rev. Sci. Instrum.*, 2001, 72, (3), 1688–1690

Superconducting scanning tunnelling microscope tips have been fabricated by sequential deposition of superconducting Pb and a proximity-coupled Ag capping layer onto a Pt<sub>0.8</sub>/Ir<sub>0.2</sub> tip. The tips were characterised by tunnelling into both normal-metal and superconducting films. The observed tunnelling characteristics in both superconductor/insulator/normal-metal (S/I/N) and S/I/S configurations and their temperature dependence were as expected.

## HETEROGENEOUS CATALYSIS

### Strong Promotional Effects of Li, K, Rb and Cs on the Pt-Catalysed Reduction of NO by Propene

M. KONSOLAKIS and I. V. YENTEKAKIS, *Appl. Catal. B: Environ.*, 2001, 29, (2), 103–113

The catalytic reduction of NO by propene over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibits strong promotion by alkalis such as Li, K, Rb and Cs at ~ 450–800 K. The best promotion is with Rb, when rate increases, by as much as 420-, 280- and 25-fold, are obtained for the formation rates of N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O, respectively, in comparison with the unpromoted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The selectivity towards N<sub>2</sub> is improved, from ~ 20% using the alkali-free unpromoted Pt catalyst, to > 90% for the optimally alkali-promoted Pt catalyst. Promotion is due to the effects of alkalis on the relative adsorption strengths of reactant species.

### Single-Event Rate Parameters for the Hydrocracking of Cycloalkanes on Pt/US-Y Zeolites

G. G. MARTENS, J. W. THYBAUT and G. B. MARIN, *Ind. Eng. Chem. Res.*, 2001, 40, (8), 1832–1844

A single-event kinetic model is applied to the hydrocracking of cycloalkane model components on two bifunctional Pt/US-Y zeolites at 493–573 K, 10–50 bar and molar H<sub>2</sub>:hydrocarbon ratio of 50–300. Kinetic parameters were determined for the reaction families typical for cycloalkane hydrocracking such as intra-ring alkyl shift, protonated cyclopropane branching, and exo- and endocyclic  $\beta$ -scission.

### Gold-Platinum Alloy Nanoparticle Assembly as Catalyst for Methanol Electrooxidation

Y. LOU, M. M. MAYE, L. HAN, J. LUO and C.-J. ZHONG, *Chem. Commun.*, 2001, (5), 473–474

The preparation of a thiolate-capped Au-Pt alloy nanoparticle assembly (1) (metallic core and organic shell) involved Schiffrin's two-phase synthesis. A 5:1 feed ratio (Au:Pt) of H<sub>2</sub>AuCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>6</sub> was employed. The average core size of (1) was ~ 2.5 ± 0.4 nm. (1) was shown to be a novel catalyst for electrooxidation of MeOH. The MeOH oxidation is mediated by surface oxide redox species.

### Supported Palladium as Catalyst for Carbon–Carbon Bond Construction (Heck Reaction) in Organic Synthesis

K. KÖHLER, M. WAGNER and L. DJAKOVITCH, *Catal. Today*, 2001, 66, (1), 105–114

Pd/MO<sub>x</sub> and Pd/zeolite catalysts exhibit high activity and selectivity in C-C coupling reactions of aryl bromides with olefins (Heck reaction). The supported Pd particles and entrapped Pd complexes exhibit high activity towards the Heck reaction at very small Pd concentrations (0.1 mol%). Catalytic activity is determined by the nature of the support and the Pd dispersion. The catalysts can be recycled and reused without loss in activity.

### Suzuki Coupling with Ligandless Palladium and Potassium Fluoride

G. W. KABALKA, V. NAMBOODIRI and L. WANG, *Chem. Commun.*, 2001, (8), 775

A ligandless Pd catalysed Suzuki coupling reaction has been established. Aromatic iodides readily couple with arylboronic acids in the presence of Pd powder and KF when the reactions are carried out in MeOH. The reaction can also be utilised to couple benzyl bromides with arylboronic acids, but aryl bromides and chlorides are ineffective substrates. Aliphatic boronic acids are also not reactive. The Pd metal can be recovered and recycled by a simple decantation of the reaction solution.

### Pd(II)-Hydrotalcite-Catalyzed Selective Oxidation of Alcohols Using Molecular Oxygen

N. KAKIUCHI, T. NISHIMURA, M. INOUE and S. UEMURA, *Bull. Chem. Soc. Jpn.*, 2001, 74, (1), 165–172

Pd(II)/hydrotalcite (1) was prepared by mixing Pd(OAc)<sub>2</sub>, pyridine and hydrotalcite in toluene at 80°C for 1 h, followed by filtration, washing, and drying under vacuum at room temperature. (1) is effective for the oxidation of alcohols using O<sub>2</sub> as sole oxidant. Various alcohols are readily converted to the corresponding aldehydes or ketones selectively in high to excellent yields. (1) is also suitable for the oxidation of unsaturated alcohols, such as geraniol and nerol, without any isomerisation of an alkenic part. (1) could be reused several times without losing its catalytic activity.

## HOMOGENEOUS CATALYSIS

### Preparation of a New FerroPHOS Derivative for Palladium-Catalyzed Asymmetric Allylic Alkylations

J. KANG, J. H. LEE and J. S. CHOI, *Tetrahedron: Asymmetry*, 2001, 12, (1), 33–35

A new C<sub>2</sub>-symmetric only cylindrically chiral FerroPHOS derivative having (1-methoxy-1-methyl)ethyl substituents was synthesised and tested in the [Pd( $\pi$ -allyl)Cl]<sub>2</sub>-catalysed asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate. High catalytic activity ( $\leq$  500 turnovers) and enantioselectivity (ee  $\geq$  96.3%) were achieved.

### Nature of the Interaction between $\beta$ -Substituents and the Allyl Moiety in ( $\eta^3$ -Allyl)palladium Complexes

K. J. SZABÓ, *Chem. Soc. Rev.*, 2001, 30, (2), 136–143

$\beta$ -Substituted ( $\eta^3$ -allyl)Pd complexes (1) are key intermediates in synthetically important highly selective Pd-catalysed transformations. The electronic interactions occurring between the  $\beta$ -substituents (Cl, OR, OAc and SiR<sub>3</sub>) and the allyl-metal moiety in (1) have been shown to influence: the structure of (1); the kinetic and thermodynamic stability of (1); and the regiochemistry of the nucleophilic attack on the allyl moiety. (44 Refs.)

### Computational Study of a New Heck Reaction Mechanism Catalyzed by Palladium(II/IV) Species

A. SUNDERMANN, O. UZAN and J. M. L. MARTIN, *Chem. Eur. J.*, 2001, 7, (8), 1703–1711

Quantum chemical calculations using density functional theory on a model system (diphosphinoethane; ethylene and phenyl iodide) show that the major steps of a Pd<sup>II</sup>/Pd<sup>IV</sup> and a Pd<sup>0</sup>/Pd<sup>II</sup> pathway in the Heck reaction are structurally similar. A major difference is found for the oxidative addition step of the C–I bond to the Pd centre. This is a rate determining step for the Pd<sup>II</sup>/Pd<sup>IV</sup> mechanism, which is facile for a Pd<sup>0</sup> catalyst. The Pd<sup>II</sup>/Pd<sup>IV</sup> mechanism is feasible only with a weakly coordinating ligand present.

### Palladium-Tetraphosphine Catalysed Allylic Substitution in Water

M. FEUERSTEIN, D. LAURENTI, H. DOUCET and M. SANTELLI, *Tetrahedron Lett.*, 2001, 42, (12), 2313–2315

*cis,cis,cis*-1,2,3,4-Tetrakis(diphenylphosphinomethyl)cyclopentane/[PdCl(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (1) catalyses allylic amination in H<sub>2</sub>O with very high substrate:catalyst ratio in good yields. A turnover number of 980,000 was achieved for the addition of dipropylamine to allyl acetate with (1). (1) is stable in H<sub>2</sub>O. This is probably due to the four diphenylphosphinoalkyl groups stereospecifically bound to the same face of the cyclopentane ring. All four phosphines probably cannot bind to the same Pd centre at the same time, but these phosphines, along with steric factors, increase the coordination of the ligand to the Pd complex.

### Water-Soluble Cyclopalladated Aryl Oxime: A Potent 'Green' Catalyst

E. YU. BEZSOUDNOVA and A. D. RYABOV, *J. Organomet. Chem.*, 2001, 622, (1–2), 38–42

Orthopalladated aryloxime (1) with a 15-crown-5 motif was prepared in 72% yield by the exchange of cyclopalladated ligands from the oxime of 4'-acetylbenzo-15-crown-5 and orthometalated N,N-dimethylbenzylamine, [Pd( $\sigma$ -C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)Cl]<sub>2</sub>. The H<sub>2</sub>O solubility of (1) is more than ten times higher than that of the related complex without the crown fragment and increases further in the presence of Mg(II). (1) was used as a catalyst for the biomimetic hydrolysis of 4-nitrophenyl 2,3-dihydroxybenzoate.

### A Simple Synthesis of Fluoroalkyl Substituted Dihydrofurans by Rhodium(II)-Catalyzed 1,3-Dipolar Reactions

Y. WANG and S. ZHU, *Tetrahedron*, 2001, 57, (16), 3383–3387

The Rh<sub>2</sub>(OAc)<sub>4</sub> catalysed reactions of ethyl 2-diazo-fluoroalkylacetoacetate with vinyl ethers were investigated. Fluoroalkyl-substituted 2-diazo-1,3-dicarbonyls with isobutyl vinyl ethers gave dihydrofuroates in good to excellent yields. Ethyl 2-fluoroalkyl-3-furoates were readily obtained by an acid-catalysed alcohol elimination. Similarly, stable diazo compounds reacted with cyclic vinyl ethers to give 1,3-dipolar cycloaddition products.

## Utility of Osmium(II) in the Catalysis of Asymmetric Diels–Alder Reactions

J. W. FALLER and J. PARR, *Organometallics*, 2001, 20, (4), 697–699

Lewis acid complexes  $[(\eta^6\text{-Cy})\text{OsCl}(\text{L})](\text{SbF}_6)$  ( $\text{L} = (\text{S})\text{-BINAP}$ ,  $(\text{S})\text{-BINPO}$ ) were synthesised and used to prepare the formally dipositive 16-electron Lewis acid species  $[(\eta^6\text{-Cy})\text{Os}(\text{L})](\text{SbF}_6)_2$  (1). (1) catalyse the Diels–Alder condensation of methacrolein or ethylacrolein with cyclopentadiene in high ee ( $> 90\%$ ). (1) with the non- $C_2$ -symmetric bisphosphine monoxide was much more effective than with the  $C_2$ -symmetric bisphosphine.

## In Situ <sup>1</sup>H-PHIP-NMR Studies of the Stereoselective Hydrogenation of Alkynes to (*E*)-Alkenes Catalyzed by a Homogeneous [Cp\*Ru]<sup>+</sup> Catalyst

D. SCHLEYER, H. G. NIESSEN and J. BARGON, *New J. Chem.*, 2001, 25, (3), 423–426

$[\text{Cp}^*\text{Ru}(\text{alkene})]^+$  (1) *trans*-hydrogenates internal alkynes directly and stereoselectively to (*E*)-alkenes (2). Stereoselectivity was studied by *in situ* PHIP-NMR (PHIP = *para*-hydrogen induced polarisation). Different alkyne substrates were used to demonstrate the universal applicability of (1). However, (1) does not exhibit any hydrogenation activity towards 1-alkynes. A mechanism proceeding via a binuclear complex is proposed to explain the formation of (2).

## FUEL CELLS

### A Novel Ni-CERMET Electrode Based on a Proton Conducting Electrode

L. N. VAN RIJ, J. LE, R. C. VAN LANSCHOOT and J. SCHOONMAN, *J. Mater. Sci.*, 2001, 36, (5), 1069–1076

A catalytic  $\text{CH}_4$  sensor has been developed based on  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  or  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  electrolytes. A  $\text{Ru}/\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}/\text{Pt}$  cell has sensor stability of the order of only one day. Long term stability of the sensor (at least 40 days) is achieved using a  $\text{Ni-CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$  CERMET (Ni-CZI10) electrode. The sensor response of a  $\text{Ni-CZI10}/\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}/\text{Pt}$  cell (1) is linear at 600°C and 700°C. The power output of (1) is 0.01 mW  $\text{cm}^{-2}$ .

### Size Effects of Ultrafine Pt–Ru Particles on the Electrocatalytic Oxidation of Methanol

Y. TAKASU, H. ITAYA, T. IWAZAKI, R. MIYOSHI, T. OHNUMA, W. SUGIMOTO and Y. MURAKAMI, *Chem. Commun.*, 2001, (4), 341–342

Cl-free  $\text{Pt}_{50}\text{-Ru}_{50}/\text{C}$  powders were prepared by an impregnation method using C black and ethanolic solutions of  $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$  and  $\text{RuNO}(\text{NO}_3)_x$ . The specific activity,  $i_{\text{sp}}/\text{A m}^{-2}$  (current density per real surface area), of the  $\text{Pt}_{50}\text{-Ru}_{50}/\text{C}$  powders at 25 and 60°C in aqueous acidic solutions decreases as the size of the Pt–Ru alloy particles decreases. The mass activity,  $i_{\text{mass}}/\text{A g}^{-1}$  (current density per mass of catalyst metal loaded), had the same dependency when the size of the alloy particles was  $< \sim 3$  nm in diameter.

## Platinum-Based Alloys as Oxygen–Reduction Catalysts for Solid–Polymer–Electrolyte Direct Methanol Fuel Cells

M. NEERGAT, A. K. SHUKLA and K. S. GANDHI, *J. Appl. Electrochem.*, 2001, 31, (4), 373–378

Electrocatalytic activities of binary: Pt–Co/C (1), Pt–Cr/C and Pt–Ni/C, and ternary: Pt–Co–Cr/C and Pt–Co–Ni/C, alloy catalysts towards  $\text{O}_2$  reduction in SPE-DMFCs were investigated at 70 and 90°C, both at ambient and 2 bar  $\text{O}_2$  pressures. (1) exhibits superior activity relative to Pt/C and other alloy catalysts. (1) improves the performance of SPE-DMFCs.

## H<sub>2</sub> and H<sub>2</sub>/CO Oxidation Mechanism on Pt/C, Ru/C and Pt–Ru/C Electrocatalysts

L. GIORGI, A. POZIO, C. BRACCHINI, R. GIORGI and S. TURTÙ, *J. Appl. Electrochem.*, 2001, 31, (3), 325–334

The oxidation kinetics of  $\text{H}_2$  and  $\text{H}_2 + 100$  ppm CO were investigated on Pt/, Ru/ and Pt–Ru/high surface area C electrocatalysts. The atomic ratios of Pt:Ru were 3, 1 and 0.33. Impedance measurements in  $\text{H}_2\text{SO}_4$ , at open circuit potential, indicated different mechanisms for  $\text{H}_2$  oxidation on Pt/C (Tafel–Volmer path) and Pt–Ru/C (Heyrovsky–Volmer path). These mechanisms also occur in the presence of CO. The best performances were achieved with Pt:Ru of 1.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Microstructural and Interfacial Properties of the Ru/p-InP(100) Heterostructures

T. W. KIM, D. U. LEE, M. JUNG, J. H. LEE, H. J. KIM, D. C. CHOO, J. Y. KIM and Y. S. YOON, *J. Phys. Chem. Solids*, 2001, 62, (4), 711–715

Thin Ru layers (1) were grown on p-InP(100) substrates by ion-beam deposition at room temperature. AES and Rutherford backscattering measurements showed that (1) have a uniform composition throughout the layers and relatively sharp Ru/InP heterointerfaces without significant interdiffusion problems. TEM measurements showed that an interfacial layer is formed between the polycrystalline Ru layer and the InP substrates.

### Conducting Polymer with Metal Oxide for Electrochemical Capacitor:

Poly(3,4-ethylenedioxythiophene)  $\text{RuO}_x$  Electrode  
J. HONG, I.-H. YEO and W. PAIK, *J. Electrochem. Soc.*, 2001, 148, (2), A156–A163

In acidic electrolytes, electrodes made by depositing  $\text{RuO}_x$  on poly(3,4-ethylenedioxythiophene) (PEDT), exhibited large capacitance due to contributions from the double-layer capacitance and the faradaic capacitance. The specific capacitance based on the combined mass of PEDT– $\text{RuO}_x$  was 420  $\text{F g}^{-1}$  and the specific capacitance based on the mass of  $\text{RuO}_2$  was 930  $\text{F g}^{-1}$ . Energy storage density of a capacitance cell with a pair of PEDT– $\text{RuO}_x$  electrodes reached 27.5  $\text{Wh kg}^{-1}$  when the cell was charged to 1.0 V.