

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Theoretical Investigation of Isomer Stability in Platinum–Palladium Nanoalloy Clusters

L. D. LLOYD, R. L. JOHNSTON, S. SALHI and N. T. WILSON, *J. Mater. Chem.*, 2004, 14, (11), 1691–1704

The interatomic interactions of Pt–Pd nanoalloy clusters (1) were modelled by the Gupta many-body potential. For 18–20 atom clusters, a general algorithm was used to establish the lowest energy structures for each size and for all possible compositions. In the lowest energy isotopes (homotops), the Pd atoms are mainly at the surface, with the Pt atoms preferentially occupying interior sites.

### Dendrimer-Templated Ag–Pd Bimetallic Nanoparticles

Y.-M. CHUNG and H.-K. RHEE, *J. Colloid Interface Sci.*, 2004, 271, (1), 131–135

Ultrafine amine-terminated fourth-generation starburst poly(amidoamine) dendrimer-templated Ag–Pd bimetallic nanoparticles (1) were prepared from silver(I)-bis(oxalato)palladate(II) (2). The use of (2), in which two metal ions exist in one complex, prevented Ag halide formation. The particle size distributions of (1) were all in the narrow range of 2–5 nm, but were dependent upon the Ag/Pd ratio.

## CHEMICAL COMPOUNDS

### The Construction of P-O/P-N Ligands on Platinum and Palladium

P. BERGAMINI, V. BERTOLASI and F. MILANI, *Eur. J. Inorg. Chem.*, 2004, (6), 1277–1284

Pt<sup>II</sup> and Pd<sup>II</sup> diphenyldiphosphinites were prepared by adding diols to a solution containing *cis*-[MCl<sub>2</sub>(PPh<sub>2</sub>Cl<sub>2</sub>)] (M = Pt or Pd) preformed *in situ* from *cis*-[MCl<sub>2</sub>(1,5-COD)] and PPh<sub>2</sub>Cl. As for the P-O bond, the P-N bond can be formed via nucleophilic attack of an amine group on coordinated PPh<sub>2</sub>Cl in the presence of base to give aminophosphine-phosphinite and N,N'-bis(antipyril-4-methyl)-piperazine complexes of Pt<sup>II</sup> and Pd<sup>II</sup>.

### C–H and N–H Activation by Pt(0) in N- and O-Heteroaromatic Compounds

J. T. CHANTSON and S. LOTZ, *J. Organomet. Chem.*, 2004, 689, (7), 1315–1324

[Pt(PEt<sub>3</sub>)<sub>4</sub>] reacts with azoles to give Pt(II) hydride complexes, *trans*-[PtH(1-azolyl)(PEt<sub>3</sub>)<sub>2</sub>] (azolyl = indolyl, imidazolyl, benzimidazolyl, pyrazolyl, indazolyl), by oxidative insertion of the Pt centre into the N–H bonds of the respective azoles. Pyrrole was much less reactive. The *trans*-[PtH(R)(PEt<sub>3</sub>)<sub>2</sub>] complexes (R = 2-furyl, 2-benzoxazolyl, 2-benzothiazolyl) were prepared via C–H bond activation.

## ELECTROCHEMISTRY

### The Electrochemical Formation and Properties of Bilayers Composed of Polypyrrole and C<sub>60</sub>Pd Films

M. WYSOCKA, K. WINKLER and A. L. BALCH, *J. Mater. Chem.*, 2004, 14, (6), 1036–1042

Bilayers of polypyrrole and C<sub>60</sub>Pd were prepared by sequential electropolymerisation of the parent monomers and investigated by cyclic voltammetry. For the electrode/polypyrrole/C<sub>60</sub>Pd bilayer, the high permeability of the C<sub>60</sub>Pd film for the supporting electrolyte ions allowed the oxidation of the polypyrrole inner layer. For the electrode/C<sub>60</sub>Pd/polypyrrole bilayer, the outer polypyrrole layer inhibited the reduction of the inner C<sub>60</sub>Pd layer.

## PHOTOCONVERSION

### Effects of Chlorine Gas Exposure on the Optical Properties of Rhodium Phthalocyanine Films

L. GAFFO, O. D. D. COUTO, R. GIRO, M. J. S. P. BRASIL, D. S. GALVÃO, F. CERDEIRA, O. N. DE OLIVEIRA and K. WOHNDRATH, *Solid State Commun.*, 2004, 131, (1), 53–56

Rh phthalocyanine films (1) were deposited on glass by the Langmuir-Blodgett technique. On exposure to Cl<sub>2</sub> (1) changed from blue to transparent. Incorporation of Cl<sub>2</sub> caused quenching of the characteristic triplet centred around the Q-absorption band at 662 nm. Leaving prior Cl<sub>2</sub> exposed (1) in air for several hours resulted in a slow partial recovery of the optical spectra.

### A Synthesis and Luminescence Study of Ir(ppz)<sub>3</sub> for Organic Light-Emitting Devices

E. J. NAM, J. H. KIM, B.-O. KIM, S. M. KIM, N. G. PARK, Y. S. KIM, Y. K. KIM and Y. HA, *Bull. Chem. Soc. Jpn.*, 2004, 77, (4), 751–755

OLEDs were fabricated with doped films of tris(1-phenyl-κC<sup>1</sup>-pyrazolato-κN<sup>2</sup>)iridium (1) in several hosts. The electroluminescence peak occurred at 450 nm. The luminance of the OLEDs was pure blue, but luminous efficiencies were low since the LUMO of (1) was higher than those of the hosts.

### Photobleaching and Single Molecule Detection of a Phosphorescent Organometallic Iridium(III) Complex

M. VACHA, Y. KOIDE, M. KOTANI and H. SATO, *J. Luminesc.*, 2004, 107, (1–4), 51–56

The photostability of bulk samples of Ir(ppy)<sub>3</sub> (1) (ppy = 2-phenylpyridine) in polymer films was examined by measuring the photobleaching kinetics under intense laser irradiation. On a single molecule level, (1) was characterised by phosphorescence time traces, distribution of phosphorescence intensity levels and by polarisation modulated excitation.

## Synthesis and Characterization of Naphthyridine and Acridinedione Ligands Coordinated Ruthenium(II) Complexes and Their Applications in Dye-Sensitized Solar Cells

S. ANANDAN, J. MADHAVAN, P. MARUTHAMUTHU, V. RAGHUKUMAR and V. T. RAMAKRISHNAN, *Sol. Energy Mater. Sol. Cells*, 2004, 81, (4), 419–428

The title complexes were synthesised and characterised, and then used in dye-sensitised solar cells. From the  $I$ - $V$  curves, the short-circuit photocurrent ( $I_{sc}$ ) and the open-circuit photovoltage ( $V_{oc}$ ) were measured. A maximum current conversion efficiency of  $\sim 7.7\%$  was achieved by the 5-amino-4-phenyl-2-(4-methylphenyl)-7-(pyrrolidin-1-yl)-1,6-naphthyridine-8-carbonitrile coordinated Ru(II) complex.

## ELECTRODEPOSITION AND SURFACE COATINGS

**Mesoporous Microspheres Composed of PtRu Alloy**  
J. JIANG and A. KUCERNAK, *Chem. Mater.*, 2004, 16, (7), 1362–1367

Electrochemical co-reduction of  $H_2PtCl_6$  and  $RuCl_3$  dissolved in the aqueous domains of the liquid crystalline phase of an oligoethylene oxide surfactant ( $C_{16}EO_8$ ) gave the title microspheres (1) ( $0.5$ – $1 \mu m$ ). The ordered mesoporous internal structure of (1) involves periodic pores of  $\sim 2.4$  nm in diameter separated by walls of  $\sim 2.4$  nm thick. (1) have high specific surface area.

## Synthesis of PtN<sub>x</sub> Films by Reactive Laser Ablation

G. SOTO, *Mater. Lett.*, 2004, 58, (16), 2178–2180

Thin films of Pt (1) with  $\sim 14$  at.% N were prepared by reactive laser ablation in molecular  $N_2$  ambient. AES, XPS and electron energy loss spectroscopy were used to characterise (1). The existence of chemisorbed N was supported by the  $N_{1s}$  binding energy of 398.4 eV. The  $+0.2$  eV shift of the  $Pt_{4f}$  peak position indicated charge transfer from Pt to N. The Pt formed an incipient nitride phase with composition near to  $Pt_6N$ .

## APPARATUS AND TECHNIQUE

### Calorimetric Hydrocarbon Sensor for Automotive Exhaust Applications

M.-C. WU and A. L. MICHELL, *Sens. Actuators B: Chem.*, 2004, 100, (3), 291–297

The title sensor (1) is a thermoelectric device supported on a planar  $Al_2O_3$  substrate. A non-selective Pt catalyst was used in (1) to detect hydrocarbons with high selectivity. For CO detection (1) uses a CO oxidation catalyst of Pb-modified Pt, which exhibits excellent CO selectivity at  $200$ – $400^\circ C$ . (1) gave a linear output of  $0$ – $2.75$  mV over  $0$ – $1000$  ppm of propylene (at  $350^\circ C$ ). Engine dynamometer evaluation showed that the response of (1) paralleled the change in concentration of the CO and hydrocarbons when the engine air:fuel ratio was varied.

## Chemiresistor Coatings from Pt- and Au-Nanoparticle/Nonanedithiol Films: Sensitivity to Gases and Solvent Vapors

Y. JOSEPH, B. GUSE, A. YASUDA and T. VOSSMEYER, *Sens. Actuators B: Chem.*, 2004, 98, (2–3), 188–195

Layer-by-layer self-assembly using 1,9-nonanedithiol and dodecylamine-stabilised nanoparticles of Pt or Au gave films (1) of thickness,  $66 \pm 2$  and  $31 \pm 1$  nm, respectively. The sensitivity of (1) was investigated by dosing them with  $NH_3$ , CO and vapours of  $H_2O$  and toluene (300 ppb–5000 ppm). (1) have a high signal:noise ratio. A detection limit for  $NH_3 < 100$  ppb was achieved.  $NH_3$  and CO bind to vacant sites on the metal nanoparticle cores.

## HETEROGENEOUS CATALYSIS

### Palladium(II) Chloride Catalyzed Selective Acetylation of Alcohols with Vinyl Acetate

J. W. J. BOSCO and A. K. SAIKIA, *Chem. Commun.*, 2004, (9), 1116–1117

$PdCl_2$  with  $CuCl_2$  can be used for the catalytic acetylation of primary and secondary alcohols with vinyl acetate. The reaction is carried out in dry toluene at room temperature. The catalyst system can be recovered by filtration. The acetaldehyde byproduct can be removed by evaporation along with the toluene solvent. This mild reaction proceeds more rapidly with primary alcohols.

### Assembled Catalyst of Palladium and Non-Cross-Linked Amphiphilic Polymer Ligand for the Efficient Heterogeneous Heck Reaction

Y. M. A. YAMADA, K. TAKEDA, H. TAKAHASHI and S. IKEGAMI, *Tetrahedron*, 2004, 60, (18), 4097–4105

An insoluble catalyst (1) was prepared from self-assembly of  $(NH_4)_2PdCl_4$  and a non-cross-linked amphiphilic phosphine polymer. (1) in only  $5.0 \times 10^{-5}$  mol equiv. concentration was effective for the heterogeneous Heck reaction of aryl iodides with acrylates, styrenes and acrylic acid. (1) could be recycled five times. (1) showed good stability in toluene and  $H_2O$  and so efficiently catalysed the Heck reaction in these media. (1) can be used for the synthesis of resveratrol, a cyclooxygenase-II inhibitor.

### Effect of Activated Carbon and Its Surface Property on the Activity of Ru/AC Catalyst

W. HAN, B. ZHAO, C. HUO and H. LIU, *Chin. J. Catal.*, 2004, 25, (3), 194–198

Activated C was pretreated by washing with  $HNO_3$  and then calcined before the preparation of Ru/activated C catalysts (1) for  $NH_3$  synthesis. The  $HNO_3$  treatment increased the catalytic activity from 17.4 to 18.4%, due to the reduction of S and ash. Gas phase oxidation of the C caused the Ru to be more dispersed in (1) by changing the texture and surface groups of the support. Overall, the Ru dispersion and catalytic activity were improved from 43 to 62% and 17.4 to 19%, respectively.

## HOMOGENEOUS CATALYSIS

### The First Platinum-Catalyzed Hydroamination of Ethylene

J.-J. BRUNET, M. CADENA, N. C. CHU, O. DIALLO, K. JACOB and E. MOTHE, *Organometallics*, 2004, 23, (6), 1264–1268

The hydroamination of ethylene with aniline, using  $\text{PtBr}_2$  as a catalyst precursor in *n*-Bu<sub>4</sub>PBr under 25 bar of ethylene pressure, gave *N*-ethylaniline with 80 turnovers after 10 h at 150°C. 2-Methylquinoline was simultaneously produced in ~ 10 cycles. Additions of  $\text{P}(\text{OMe})_3$  (2 equiv./ $\text{PtBr}_2$ ) or of a proton source (3 equiv./ $\text{PtBr}_2$ ) were beneficial. A TON of 145 after 10 h at 150°C was achieved with a biphasic system (*n*-Bu<sub>4</sub>PBr/decane) in the presence of  $\text{C}_6\text{H}_5\text{NH}_3^+$  (3 equiv./ $\text{PtBr}_2$ ). The lower the basicity of the arylamine, the higher the TON.

### Important Consequences for Gas Chromatographic Analysis of the Sonogashira Cross-Coupling Reaction

E. H. NIEMELÄ, A. F. LEE and I. J. S. FAIRLAMB, *Tetrahedron Lett.*, 2004, 45, (18), 3593–3595

Typical quenching procedures for GC analysis of the Sonogashira reaction for 4-bromo-6-methyl-2-pyrone with phenylacetylene (catalysed by  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ ) cannot be used. Turnover continues to occur in sample vials even after quenching by commonly used  $\text{SiO}_2$  adsorption and product elution with  $\text{CH}_2\text{Cl}_2$ . Trace amounts of Pd are carried through the  $\text{SiO}_2$  plug. Addition of 1,2-bis(diphenylphosphino)ethane to the sample inhibited any further reaction.

### Role of Base in Palladium-Catalyzed Arylation of Carbanions

A. V. MITIN, A. N. KASHIN and I. P. BELETSKAYA, *J. Organomet. Chem.*, 2004, 689, (6), 1085–1090

The arylation of carbanions, derived from various sulfones, cyanoacetic ester and malononitrile, with aryl bromides using  $\text{Pd}_2\text{dba}_3/3\text{L}$ ,  $\text{L} = \text{PPh}_3$ ,  $\text{P}^t\text{Bu}_3$ , as well as the reaction of the carbanions with 1 equiv. of 4- $\text{CF}_3\text{C}_6\text{H}_4$ ,  $\text{Pd}(\text{PPh}_3)_2\text{Br}$  were carried out. A base stronger than the initial carbanion was required. The reaction mechanism includes the acceleration of the reductive elimination due to the deprotonation of the intermediate  $\text{ArPdL}_2\text{CHXY}$ .

### New Chiral Bis(oxazoline) Rh(I)-, Ir(I)- and Ru(II)-Complexes for Asymmetric Transfer Hydrogenations of Ketones

N. DEBONO, M. BESSON, C. PINEL and L. DJAKOVITCH, *Tetrahedron Lett.*, 2004, 45, (10), 2235–2238

The transfer hydrogenation of acetophenone in 2-propanol was used to examine the title complexes. The Ru(II)-based catalyst exhibited good activity with 50% conversion and high enantioselectivity (89%), whereas the Rh(I)- and Ir(I)-complexes gave low conversions (~ 20%) and poor enantioselectivities (16–20%). A free hydroxyl group on the ligand was a prerequisite for high enantioselectivity. The stronger the base present, the higher the conversion.

## FUEL CELLS

### Effect of Preparation Conditions of Pt/C Catalysts on Oxygen Electrode Performance in Proton Exchange Membrane Fuel Cells

J. H. TIAN, F. B. WANG, ZH. Q. SHAN, R. J. WANG and J. Y. ZHANG, *J. Appl. Electrochem.*, 2004, 34, (5), 461–467

Pt/C catalysts with 3.2 nm Pt crystallites were prepared by the impregnation-reduction method, varying conditions such as the reaction temperature, the concentration of  $\text{H}_2\text{PtCl}_6$  and different reducing agents. Heat treatment in  $\text{N}_2$  of the C black support improved Pt dispersion and increased the relative content of Pt (111) orientation. This benefited the acceleration of the oxygen reduction reaction in the PEMFC.

### Preparation and Performance of Pt-Co/C Catalyst for PEMFC

Y. ZHANG, X. LI, X. WU, M. XU and L. DENG, *Precious Met. (Chin.)*, 2004, 25, (1), 19–23

Pt-Co/C electrocatalysts (1) were prepared by the liquid deposition and high temperature alloying method. The Pt and Pt-Co have f.c.c. structure, with small particle size and high dispersity. The Co addition shortened the length of the Pt–Pt bond. (1) showed better performance than Pt/C in PEMFCs. The Co addition exhibited high catalytic activity.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Microstructure and Magnetic Properties of Bamboo-Like CoPt/Pt Multilayered Nanowire Arrays

Y.-K. SU, D.-H. QIN, H.-L. ZHANG, H. LI and H.-L. LI, *Chem. Phys. Lett.*, 2004, 388, (4–6), 406–410

Double-pulse electrodeposition into the pores of a porous anodic Al oxide template gave highly ordered CoPt/Pt multilayered nanowire arrays (1). The nanowires had a bamboo-like structure. The section lengths could be adjusted by varying the pulse width and pulse intensity. (1) exhibited in-plane anisotropy. High coercivity ( $H_c = 1.8$  kOe) and squareness ( $M_r/M_s$ ) ~ 0.35 were obtained in (1) when the field was applied perpendicular to the wire axis of (1). This is attributed to the disordered f.c.c. CoPt formation.

### Effects of Post-Annealing on the Dielectric Properties of Au/BaTiO<sub>3</sub>/Pt Thin Film Capacitors

E. J. H. LEE, F. M. PONTES, E. R. LEITE, E. LONGO, R. MAGNANI, P. S. PIZANI and J. A. VARELA, *Mater. Lett.*, 2004, 58, (11), 1715–1721

BaTiO<sub>3</sub> thin films (1) were prepared by the polymeric precursor method and deposited onto Pt/Ti/SiO<sub>2</sub>/Si. The BaTiO<sub>3</sub> perovskite phase formation was investigated. (1) were post-annealed in O<sub>2</sub> and N<sub>2</sub> at 300°C for 2 h. Post-annealing in O<sub>2</sub> increased the dielectric relaxation phenomenon, whereas in N<sub>2</sub> a slight dielectric relaxation was produced.