ABSTRACTS

of current literature on the platinum metals and their alloys

CHEMICAL COMPOUNDS

Preparation and Reactivity of Penta- and Tetracoordinate Platinum(II) Hydride Complexes with P(OEt)3 and PPh(OEt)2 Phosphite Ligands


Protonating Pt{P(OEt)3}4 gave PtH{P(OEt)3}4 (1) with two Ru(bpy)2(PyCHN) units (PyCHN = fragments of the imino-isomer. (1) is a discrete PdCl4 complex salt (1) that are characteristic of structural study. The orientation technique of solid samples as a liquid crystal suspension, identified IR bands in the title compound. Complexes PtHClP2 (P = P(OEt)3, PPh(OEt)2) were obtained from PtCl2P2 with NaBH4 in MeCN.

Molecular Spectral Analysis and Crystal Structure of the 4-Aminopyridinium Tetrachloropalladate(II) Complex Salt


Linear-dichroic IR spectroscopy, coupled with the orientation technique of solid samples as a liquid crystal suspension, identified IR bands in the title complex salt (1) that are characteristic of structural fragments of the imino-isomer. (1) is a discrete PdCl42– anion with two Npy protonated C5H7N2+ cations.

Syntheses, Crystal Structure and Electrochemical Properties of Dinuclear Ruthenium Complexes Containing Saturated and Unsatuated Spacers


Electrochemical study of dinuclear Ru complexes (1) with two Ru(bpy)(PyCHN) units (PyCHN = N-2- pyridylmethylene) linked together either directly or via spacers, showed that the protonation constant, K+, decreased with an increase in the number of phenyl rings. Inserting an O atom between the two phenyl rings decreased the K+ value, but interruption of saturated CH2 groups increased K+ from 2.7 × 108 to 5.8 × 1010. (1) containing –OCH2CH2O– between the two phenyl groups also gave a large K+ (1.2 × 1010).

PHOTOCONVERSION

Push–Pull Effects and Emission from Ternary Complexes of Platinum(II). Substituted Terpyridines, and the Strong-Field Cyanide Ion


Both [Pt(trpy)(CN)4]2+ (trpy = 2,2′:6′,2″-terpyridine) and [Pt(4′-cyano-trpy)(CN)4]2+ are weakly emissive in CH2Cl2. However, [Pt(4′-dimethylamino-trpy)(CN)4]2+ has an unusually high luminescence quantum yield of Φ = 0.26, and an excited-state lifetime of τ = 22 μs in room temperature, deoxygenated CH2Cl2.

Pressure-Sensitive Paint (PSP): Concentration Quenching of Platinum and Magnesium Porphyrin Dyes in Polymeric Films


Films containing Pt tetra(pentafluorophenyl)porphine (PtTFPP), Pt octaethylporphine (PtOEP) and MgTFPP in polymers were investigated. The emission intensity of all the porphyrins decreased (more for PtOEP than PtTFPP) at higher film concentrations. Response times for O diffusion into the PtTFPP films were faster at higher concentrations of PtTFPP.

Blue-to-Green Electrophosphorescence of Iridium-Based Cyclometalated Materials


The luminescence of Ir complexes (1) were fine-tuned from green to blue by modifying the substituents on the pyridyl ring of the phenylpyridyl ligand. Blue-to green PLEDs using poly(N-vinylcarbazole) containing (1) are reported. The brightness for the bluest (1) is 110 cd m–2 at 18 V and the luminous efficiency at 100 cd m–2 is 0.06 cd A–1.

Improved Turn-on Times of Iridium Electroluminescent Devices by Use of Ionic Liquids


Improved turn-on times of devices based on Ir(ppy)(dip-bpy)PF6 (1) (ppy = 2-phenylpyridine, dip-bpy = 4,4′-di-tert-butyl-2,2′-dipyridine) were obtained by using 1-butyl-3-methylimidazolium hexafluorophosphate (2). Addition of 0.46 mol of (2) per mole of (1) reduced the turn-on time from 5 h to 40 min. However, the lifetime and total emitted energy were each reduced by a factor of 3.

APPARATUS AND TECHNIQUE

Study of Hydrogen-Sensing Characteristics of a Pt-Oxide-AlGaAs Metal-Oxide-Semiconductor High Electron Mobility Transistor


A H sensor, based on the title material, demonstrated remarkable H-sensing properties over a wide temperature range. Based on the transistor amplification action, the device shows significant drain current variation (~ 0.12 mA), even at an extremely low H2 concentration of 14 ppm H2/air.

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Fabrication of Palladium Nanotubes and Their Application in Hydrogen Sensing

A new one-step direct electroless plating procedure was used to deposit Pd nanotubes (1) in the pores of track-etched polycarbonate membranes. (1) are granular and have a large expanded surface area ideal for this application. (1) have high sensitivity, a low detection limit (500 ppm), and fast response times for H2 sensing compared to a sputtered Pd thin film on glass.

Development of Fiber Optic Hydrogen Sensors for Testing Nuclear Waste Repositories

Three H2 sensors (1, 2, 3) were developed and used to monitor H2 concentrations (0–4%) near high radioactive wastes. (1) a semitransparent Pd film, uses the collimators in optical fibre, but the β-phase formation caused irreversible damage. (2) a long-length single-mode optical fibre is free of corrosion, but has a slow response time. (3) a fibre Bragg grating coated with Pd, has fast response, sensitivity, repeatability and multiplying possibilities, but faults are its fragility and the Pd–nuclear radiation interaction.

HETEROGENEOUS CATALYSIS
Adsorption Calorimetry in Supported Catalyst Characterization: Adsorption Structure Sensitivity on Pt/γ-Al2O3

The structure sensitivity of H2, O2 and CO on adsorption on 2% Pt/Al2O3 was investigated by changing the metal particle size. Pt/Al2O3 was prepared by an incipient wetness method with the particle size being modified by calcination at different temperature. Differential heats of adsorption of H2, O2 and CO were obtained. The adsorbate:total metal stoichiometries at saturation systematically decreased with increasing particle size. The site energy distribution changed for H2 with increasing particle size, but not appreciably for the O2 and CO.

Phase Properties of Carbon-Supported Gold–Platinum Nanoparticles with Different Bimetallic Compositions

The title catalysts were prepared by two-phase synthesis involving organic monolayer encapsulation on bimetallic AuPt cores (~ 2 nm), followed by assembly on C black support and calcination. The bimetallic AuPt(0.01–0.18) nanoparticles possess the properties of alloys, which contrasts with the bimetallic miscibility gap shown by the bulk Au-Pt metals.

Redox Behaviour of Pd-Based TWCs under Dynamic Conditions: Analysis Using Dispersive XAS and Mass Spectrometry

The redox behaviour of 1 wt.% Pd supported on three carriers: (a) alumina; (b) 10 wt.% CeO2 on alumina; and (c) 10 wt.% Ce/ZrO2 on alumina, was studied under dynamic, cycling conditions, such as λ oscillations on a 50 ms scale. An O transfer effect occurs at the metal-promoter interface of the three-way catalyst systems. The Zr of (c) is efficient in enlarging the O transfer under dynamic conditions.

A Palladium-Catalyzed Route for α-Alkylation of Ketones by Primary Alcohols

Ketones were shown to undergo α-alkylation with primary alcohols in the presence of a Pd/C catalyst and KOH along with 1-decene as a sacrificial H acceptor. The reactions were carried out in dioxane at 100°C. The catalytic pathway to coupled ketones proceeds via a sequence involving initial oxidation of primary alcohols to aldehydes, cross aldol condensation, and regioselective reduction.

Interaction between Pd and Ag on the Surface of Silica

Pd, Ag and Pd-Ag catalysts supported on SiO2 were prepared by coinimpregnation of SiO2 with AgNO3 and Pd(NO3)2. XRD and TPR confirmed that an interaction between Pd and Ag on the SiO2 surface after oxidation (500°C) and reduction (260°C) leads to the formation of solid solutions. ToF-SIMS images of the surface of 5% Ag/SiO2 after oxidation (500°C) and reduction (260°C) established that Ag atoms on the SiO2 form regions of enhanced Ag concentration. Positive ion images of the surface of 5% Pd/SiO2 show regions of enhanced concentration, of Pd atoms, but with a more homogeneous distribution. The Pd-Ag/SiO2 surface is enriched with Ag atoms.

Polymer-Supported α-Heterocyclic Carbene–Palladium Complex for Heterogeneous Suzuki Cross-Coupling Reaction

Poly(1-methylimidazoliummethyl styrene-surface grafted-poly(styrene) resin (1) was made by first synthesising 1-methyl 3-(4-vinylbenzyl)imidazolium hexafluorophosphate as a monomer followed by copolymerising with styrene and DVB in H2O. (1) containing imidazolium ligand, present only on the surface of the resin, readily formed a stable complex with Pd(OAc)2; the latter exhibited excellent catalytic activity for Suzuki coupling in an aqueous medium. The catalyst could be reused with consistent activity.
**HOMOGENEOUS CATALYSIS**

**Synthesis of Isocoumarins via Pd/C-Mediated Reactions of α-Iodobenzoic Acid with Terminal Alkynes**


2-Iodobenzoic acid was coupled with terminal alkynes using a 10% Pd/C–Et3N–PPh3–CuI catalyst system (1). In EtOH (1) is effective for a one-pot synthesis of 3-substituted isocoumarins in good yields and with good regioselectivity. This process shows more selectivity than the PdCl2(PPh3)2–Et3N–CuI system in DMF, and does not use air-sensitive Pd(0) catalyst, as in the Pd(PPh3)4–Et3N–ZnCl2 system.

**Chiral Sulfoxideoxathiane Ligands for Palladium-Catalyzed Asymmetric Allylic Alkylation**


Chiral S–S type sulfoxideoxathiane ligands (1) were easily prepared in two steps. (1) exhibited excellent activity and enantioselectivity (96–99% ee) in the [PdCl2(η3-C3H5)]-catalysed allylic alkylation of 1,3-diphenyl-2-propenyl acetate with alkyl malonate groups at the 2-position on the phenylthio group in nucleophiles. N0-Bis(trimethylsilyl)acetamide was also required. The reactivity and enantioselectivity depends greatly on the existence of a substituent group at the 2-position on the phenylthio group in (1). (1) are very stable in air and may be superior to ligands containing P atom(s), and could be used for other allylations and asymmetric processes.

**Carbinol Derivatives via Rhodium-Catalyzed Addition of Potassium Trifluoro(organo)borates to Aldehydes**


Reaction of K arytrimfluoroborates with aldehydes, in the presence of [Rh(CH2CH2)2Cl]2/PBu3 catalyst, gave carbinol derivatives in high yields under mild aqueous conditions. This efficient reaction proved to be general, allowing the production of a range of highly hindered diarylmethanols and aliphatic aldehydes. The reaction with hexanal afforded the expected 1-phenylhexan-1-ol (98% yield) in a 3/2 mixture of toluene/H2O at 80°C.

**Synthesis and Catalytic Activity of a Novel Ruthenium(III) Complex Containing a Sugar-Based Ligand**


The complex [RuIII(TDL)(bipy)(H2O)]+ (1) (TDL = N,3,5-diteriarybutylsalicylidine-D-glucosamine) was synthesised. (1) can be used as a catalyst for the enantioselective epoxidation of styrene (37% ee) and the oxidation of 1-indanol to 1-indanone in CH2Cl2 using t-BuOOH as a terminal oxidant. The catalytic oxidative species is a high valent Ru(V)-oxo species.

**FUEL CELLS**

**Combinatorial Electrochemical Synthesis and Screening of Pt-WO3 Catalysts for Electro-Oxidation of Methanol**


An automated system (1) was used for high-throughput electrochemical synthesis and screening of electrocatalysts. (1) has an electrode probe possessing counter and reference electrodes that can be positioned inside an array of electrochemical cells within a polypropylene block. A Pt-WO3 library was synthesised and investigated using CV for reactivity towards MeOH electrooxidation.

**Preparation and Characterization of Multi-Walled Carbon Nanotubes Supported PtRu Catalysts for Proton Exchange Membrane Fuel Cells**


PtRu nanocomposites (1) supported on H2O2-oxidised MWCNTs were prepared via two reduction methods, either using aqueous HCHO or ethylene glycol, as reducing agent. (1) were evaluated as PEMFC anode catalysts for oxidation of 50 ppm CO contaminated H2 and compared with a commercial PtRu/C catalyst. Superior performance was obtained for (1) prepared using ethylene glycol.

**Performance Characterization of Pd/C Nanocatalyst for Direct Formic Acid Fuel Cells**


Finely dispersed Pd particles were deposited on supports of Vulcan XC-72® C. The performance of 20 wt.% Pd/C (1) and 40 wt.% Pd/C (2) as an anode catalyst for DFAFC, with different formic acid feed concentrations at a moderate temperature, was investigated. The (1) and (2) DFAFCs with dry air and zero backpressure were able to generate a maximum power density of 145 and 172 mW cm–2, respectively, at 30°C. Their open cell potentials are 0.90 V. (1) exhibits a lower total current, but a higher current per gram of Pd than an unsupported Pd black catalyst.

**Pd–Ti and Pd–Co–Au Electrocatalysts as a Replacement for Platinum for Oxygen Reduction in Proton Exchange Membrane Fuel Cells**


A high throughput screening method identified good electrocatalyst compositions: Pd-Co-Au and Pd-Ti. Catalysts were then prepared by loading 20 wt.% on C by reverse microemulsion (Pd-Co-Au/C) and by impregnation (Pd-Ti/C); and optimised by heat treatments in flowing 90% Ar/10% H2. The catalysts had equal or slightly better performance than the Pt currently used for the O reduction reaction.