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
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
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
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 [PtCl₂], NH₃, CO, CH and KCl in H₂O under reflux.

Pd(II) and Pt(II) Complexes with Chalcogenide Derivatized Phosphinat Ligands
The mixed phosphine sulfide/thioether and phosphine selenide/thioether ligands L⁻⁻L' react with PdCl₂ or PtCl₂ in the presence of TIPF₅, in MeNO₃ solution to give the distorted square planar complexes [Pd(L)]₂(PF₆)₄ or [Pt(L)]₂(PF₆)₄. The complexes are characterised by IR spectroscopy and ¹⁹⁵Pt NMR studies and the X-ray crystal structure of L' is reported.

Face-Coordinated C₆₆ Complexes with Carbido Pentaruthenium Cluster Cores Including a Bimetallic Platinum-Pentaruthenium Complex
The interaction of C₆₆ with Ru₂(CO)₁₀ or PtRu₂(CO)₁₀(COD) in hot chlorobenzene, followed by treatment with solubilising phosphines, gave compounds with a hexahapto co-ordination of C₆₆ to a Ru₆ face of the square pyramidal Ru₆C or octahedral PtRu₆C cluster framework. The C₆₆-cluster bond is robust.

Convergent and Divergent Noncovalent Synthesis of Metalloendrimers
A new building block, with one pyridine and two kinetically inert complexed Pd(II) ions, is reported for controlling the assembly of metalloendrimers by a convergent or a divergent route. A double pincer ligand was cyclopalladated with Pd(CH₃CN)₂(BF₄) 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)₅(PPh₃)(η-C₆Me₅)] [Fe₃(μ₃-C₄Bu')(CO)₉]
The reaction between RuCl(C≡CHBu')(PPh₃)(η-C₆Me₅) and Fe₃(CO)₉ produced the Ru salt [Ru(CO)₅(PPh₃)(η-C₆Me₅)][Fe₃(μ₃-C₄Bu')(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 Fe₁ cluster.

A Simple and Convenient Synthesis of cisitrans-RuH₂(Ph₃PCH₂PPh₂) and of trans-RuHCl(Ph₃PCH₂PPh₂)
Treatment of a suspension of cis-RuCl₂(Ph₃PCH₂PPh₂), (cis-1) in EtOH or 2-propanol with a large excess of KOH, gave cis/trans-RuH₂(Ph₃PCH₂PPh₂) (2) in ≤ 90% yields, with the reaction taking < 2 min in EtOH. A similar reaction with a small excess of KOH gives trans-RuHCl(Ph₃PCH₂PPh₂) 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
The synthesis of a series of Ru nitrosyl complexes of formula trans-[Ru(NH3)2L(NO)]BF4, where L = imidazole, L-histidine, pyridine or nicotinamide, is described. The compounds have relatively high v(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(NH3)2nicNO](SiF6)2 confirms the presence of a Ru=NO' moiety.

Reaction of [Ru(PPh3)2Cp]2(μ-C≡C) with Tetracyanoethene: Macrocyclic Formation by Intermolecular CN Coordination
Reactions between [Ru(PPh3)2Cp]2(μ-C≡C) and C6(CN)4 add the cyanocarbon to one of the C=C bonds forming the allylic complex Ru[η-\(\eta'\)-C(CN)2C≡CC≡C(Ru(PPh3)2Cp)]C≡C(CN)2(PPh3)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
Dipolar Ru(II) tetra- or pentaammine complexes of N-substituted 4,4'-bipyridinium ligands show static first hyperpolarisabilities, \(\beta_s\), among the largest reported for transition metal complexes. The d18-electron Ru(II) centres function as powerful n-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 \(\beta_s\) in MLCT-based chromophores.

ELECTROCHEMISTRY
Electrocatalytic Dehalogenation of Chloroaromatics on Palladium-Loaded Carbon Felt Cathode in Aqueous Medium
The selective dechlorination of highly toxic chloroaromatic herbicides based on phenoxyacetic acid is reported. This was achieved under mild conditions in H2O 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
Os(VIII)O4 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 H2 wave.

PHOTOCONVERSION
Photocatalytic Degradation of Trichlorobenzene using Immobilized TiO2 Films Containing Poly(tetrafluoroethylene) and Platinum Metal Catalyst
A new photocatalyst film is described which has Pt-loaded TiO2 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-TiO2 or TiO2/Ni-PTFE films. The decomposition rate was enhanced by the efficient consumption of photogenerated electrons and holes in the reduction of O2 and oxidative degradation of trichlorobenzene, respectively.

When subjected to low-power UV illumination for 10–30 min, the wide band-gap, dye-sensitised heterojunctions, n-TiO2/Ru-dye/p-CuSCN (Ru-dye = Ru polypyridyld 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 RuS2/SiO2 for Water Decomposition
H2 and O2 were produced from the photocatalytic decomposition of H2O using a RuS2 powder catalyst (1) in the presence of sacrificial agents. The activity towards H2 production was greatly improved by supporting (1) on SiO2, with a 1 wt.% Ru/SiO2 catalyst giving 213 μmol of H2 after 46 hours. No O2 was formed over a non-supported (1), but O2 was produced over 1 wt.% RuS/SiO2 (121 μmol O2 after 25 hours) and 0.2 wt.% Pt/1 wt.% RuS/SiO2, with the yields increasing with increasing irradiation time.
Fine-Tuning the Electronic Properties of Binuclear Bis(terpyridyl) ruthenium(II) Complexes


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**, Cd** or Ba**, 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 \( \eta^1 \text{SO}_2 \text{Pt} \) Bond Formation as a Novel Application for Periphery Functionalised Metallo-Dendrimers


Multimetalloc dendrimers, functionalised at their periphery with square planar Pt(II) metal centres, reversibly absorb SO\(_2\) to yield macromolecules with significantly enhanced solubility. Drastic colour changes from colourless to bright orange occur in the presence of traces of SO\(_2\) as low as 10 mg dm\(^{-3}\), giving highly active sensors for toxic SO\(_2\) gas detection.

Pd-Doped SnO\(_2\) Thin Films Deposited by Assisted Ultrasonic Spraying CVD for Gas Sensing: Selectivity and Effect of Annealing


Polycrystalline Pd-doped SnO\(_2\) thin films (1) (0.25–1.75 \( \mu \)m) 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 CH\(_4\) (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 CH\(_4\) 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 \([\text{Ru(bpy)}_2^{2+}\text{(Ph,B)}_2]\)-Based Optical Oxygen Sensor


The quenching of the electronically-excited, lumophoric state of \([\text{Ru(bpy)}_2^{2+}\text{(Ph,B)}_2]\) by O\(_2\) was studied in various neat plasticisers. The compatibility of the polymer-plasticiser combination is the dominant factor in determining the O\(_2\) sensitivity. For highly compatible combinations, such as TPP-PMMMA, the plasticiser with the lowest viscosity, TPP, produces films of the highest O\(_2\) sensitivity.

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


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 \(3 \times 10^{-3} \text{M}\).

HETEROGENEOUS CATALYSIS

Mechanistic Considerations for the Reduction of NO\(_x\) over Pt/Al\(_2\)O\(_3\) and Al\(_2\)O\(_3\) Catalysts under Lean-Burn Conditions


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 C,H\(_n\)-NO\(_x\) over Pt/Al\(_2\)O\(_3\) ), and is active at the lowest temperatures and resistant to S poisoning. In (2), DeNO\(_x\) reactions occur on Al\(_2\)O\(_3\) with a weakly adsorbed reductant (such as C,H\(_n\)-NO\(_x\)-O\(_2\) over Pt/Al\(_2\)O\(_3\) ), and C,H\(_n\)-NO\(_x\)-O\(_2\) over Al\(_2\)O\(_3\) ). They are strongly poisoned by S and occur via formation of a surface nitrate species on the Al\(_2\)O\(_3\), which activates the reductant.

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


0.5–5 wt. % Pt/MCM-41 (1) catalysts were used for the selective catalytic reduction of NO with C,H\(_4\), C,H\(_2\), C,H\(_n\) and C,H\(_n\)-NO\(_x\)-O\(_2\) were used. High activity was seen with C,H\(_4\), or C,H\(_n\), as the reductant, with a maximum NO reduction rate of 4.3 mmol g\(^{-1}\) h\(^{-1}\). The activity was observed with C,H\(_4\) or C,H\(_n\), (1) showed good stability and H\(_2\)O and SO\(_2\) did not cause deactivation.

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


Rh catalysts supported on a diphenylphosphinomethyl 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


The SiO₂-tethered Rh thiolate complex catalysts (CO)₃Rh[S(CH₂)₂Si(OCH₃)₂] were prepared by condensation of SiO₂ with Rh[(S(CH₂)₂Si(OCH₃)₂]–(CO)₃ or Rh[(S(CH₂)₂Si(OCH₃)₂]–[Ph₃P(CH=CH₂)]–Si[OC(H₂)₃)]–(CO)₃. 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 stabilization of Rh(SR)(CO)(PR₃) species on the catalyst surfaces.

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


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, which was highly dependent on the support in the order: TiO₂ > ZrO₂ > Y₂O₃ > La₂O₃ > MgO > Al₂O₃ > SiO₂.

Palladium-Catalyzed Cross-Coupling Reactions in Supercritical Carbon Dioxide


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[5-bis(trifluoromethyl)phenyl]phosphate (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


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.


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.

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


Biphase systems comprise toluene solutions of various alkenes and CF₃C(FC)₃ solutions (1) of the pre-catalyst, [P(C₆H₅CH(FC)₃)₂]₃P. 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
Chiral diRh(II) carboxamidate catalysts, with bridging chiral pyrrolidone, oxazolidinone, azetidinone 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. Reactions occur with high turnover numbers and give products in high yield with enantiomeric excesses ≥ 90%.

Rhodium Complex-Catalysed Allylic Alkylation of Allylic Acetates
[Rh(COD)Cl],P(OPh)3 (P:Rh = 2–3) is an efficient catalyst for the allylic alkylation of allylic acetates giving products in ≤ 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
Studies of the kinetics and mechanism of the Ir(III) (10–15 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
The cationic 18-electron allenylidene Ru complexes [Ru=C≡C=CR,(L)(Cl)(arene)]PF6 (L = P(Up)3, 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 (η5-C5H5)RuCl3
The catalyst precursor (η5-C5H5)RuCl3 was used for the hydrogenation of benzene and various alkyl-benzen derivatives. Under biphasic conditions, cyclohexane derivatives were obtained with turnover rates of 20–2000 cycles per hour. The less active species, [(η5-C5H5)RuH2]4 and [(η5-C5H5)RuH]4, were found in the reaction mixture after the catalytic runs. A more active intermediate, [Ru(η5-C5H5)(μ-Cl)(μ-O)(μ-H)]+ was also detected.

Selective Aerobic Oxidation of Primary Alcohols Catalyzed by a Rh(PPh3)3Cl2/Hydroquinone System
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
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
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)3N][Pd(dmit)],
β-[((CH3)3N][Pd(dmit)], (1) is isomorphic to [(CH3)3N][Ni(dmit)], 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 Tc was 6.5 K.