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REVIEW

Nickel, palladium and platinum

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This report summarizes the literature from 2010 relevant to the chemistry of the group 10 transition elements. Novel coordination and organometallic compounds of these elements are presented and selected applications in the areas of catalysis, bioinorganic/medicinal chemistry are discussed.

Highlights

Notable highlights from 2010 include a promising alternative to the I^-/I_3^- redox couple used in DSSCs based on a Ni(III)/(IV) redox shuttle,¹ a report on the direct Pd(II)-catalyzed C–H olefination between phenylacetic acid derivatives and 3-phenylpropionic acid substrates using oxygen at atmospheric pressure as the oxidant⁴² and the isolation of the first stable monomeric platinum oxoboranes ($B \equiv O$).⁷⁷

1 Introduction

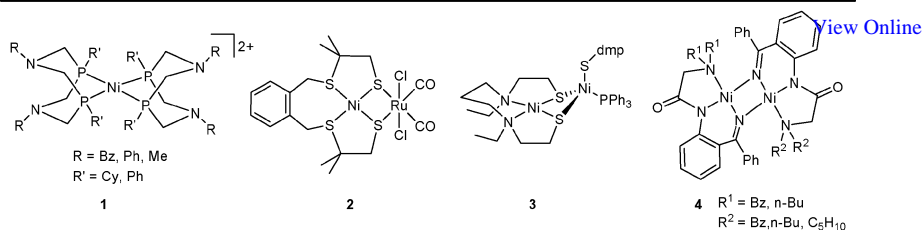
As in previous years it is not possible to provide a comprehensive review of all the nickel, palladium and platinum chemistry in this report. Therefore, to complement material covered in this review the reader is referred in each section to specialised reviews that have appeared in the last year.

2 Nickel

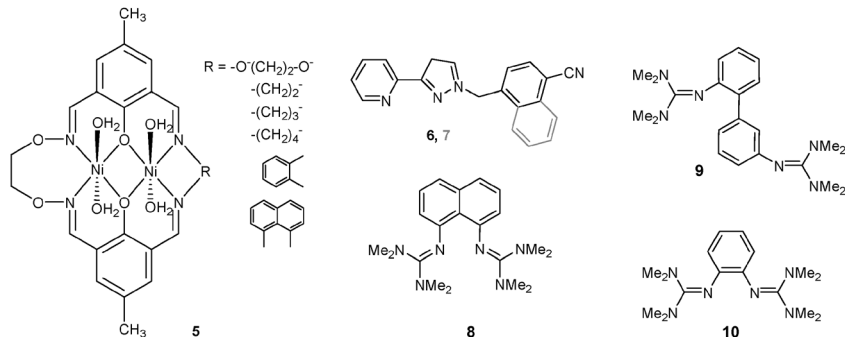
Coordination chemistry

A promising alternative to the I^-/I_3^- redox couple used in DSSCs has been reported based on the Ni(III)/(IV) noncorrosive redox shuttle of a Ni-based metallacarborane complex.¹ The supramolecular chemistry of metal-based anion receptors has been discussed in a tutorial review, containing case studies from group 10 metals.² Nickel(II) bis(diphosphine) complexes (**1**) catalyze the reduction of O_2 with H_2 to selectively form water. The pendant amine arms function as proton relays, in a manner similar to that of enzymes.³

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The natural enzyme, [NiFe]hydrogenase, and its [NiRu] hydrogenase mimic were used simultaneously in such a manner that isotope exchange between D₂ and H₂O could be conducted over an extended pH range (2–10) in one pot under mild conditions at ambient temperature and pressure.⁴ DFT modeling was used to investigate a previously proposed mechanism of proton reduction to H₂ catalyzed by the [NiFe]hydrogenase model (2).⁵ The dinuclear complex (3) was synthesized as a Ni(II)–Ni(I) model of the A-cluster in acetyl CoA synthase. In a few successive steps, (3) reacted with CO to afford the acetylthioester CH₃C(O)Sdmp *via* reductive elimination.⁶ The oxidation of methane to HCO₃[−] with sulphate in anaerobic microorganisms has been the subject of several reports. In methanotrophic archaea bacteria methane activation involves a key nickel(I)-hydroporphin enzyme, namely methyl-coenzyme M reductase (MCR) as the activating enzyme.^{7–9} To shed light on the influence of the configuration (*cis* or *trans*) of a single peptide bond on the activity of the Ni-superoxide dismutase (NiSOD) model peptides, a new *cis*-prolyl bond surrogate was developed. The results indicated that the influence of the conformation of the prolyl peptide bond on the catalytic activity (the conversion of O₂^{•−} into H₂O₂ and O₂) of the metallopeptides is of minor importance.¹⁰

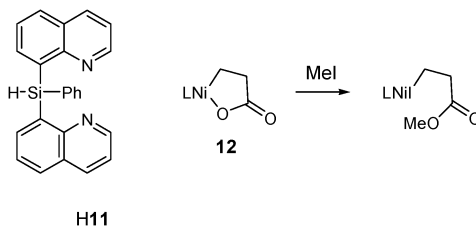


The binuclear square planar Ni(II) complexes (4) present new types of *ridge-tile*-like chiral compounds that are reasonably stable in the appropriate “bent” conformation (defined by the angle between the two coordination planes).¹¹ The influence of the coordination geometry and the ring size of the salicylaldiminato dinuclear Ni(II) complexes (5) on the electronic, redox, phosphate hydrolysis, DNA binding and cleavage properties have been reported.¹² The bifunctional ligands (6) and (7), with a chelating pyrazolylpyridine unit and pendant nitrile, show interesting coordination behaviour which allows heterometallic networks, *e.g.* {[AgNi(6/7)₃](BF₄)₃}_∞, to be built up in a stepwise manner.¹³ The synthesis of pyrazole Ni(II) complexes and pyrazolate MOFs by simple grinding of the components has been reported.¹⁴ A neutron diffraction study on the adsorption of hydrogen molecules in the

$\text{Ni}_2(\text{dhtp})(\text{H}_2\text{O})_2 \cdot 8\text{H}_2\text{O}$ MOF has been reported.¹⁵ In a contribution, investigations on the thermal and magnetic properties of several coordination polymers based on metal thiocyanates and 4,4-bipyridine as an organic spacer ligand were reported. Starting with the 1 : 2 hydrate $[\{\text{Ni}(\text{NCS})_2(\text{bipy})(\text{H}_2\text{O})_2\}(\text{bipy})]_n$, the corresponding ligand-rich 1 : 2 anhydrous compounds $[\text{Ni}(\text{NCS})_2(\text{bipy})_2]_n$ were prepared by thermal decomposition.¹⁶ The syntheses and magnetic properties of several new Ni(II) complexes featuring the chelating bisguanidines **8–10** were reported.¹⁷

Organometallic chemistry

The unusual $\text{Ni}_3(\mathbf{11})_2\text{Cl}_2$ cluster containing six-coordinate silicon atoms was prepared and its bonding investigated by computational methods to obtain descriptions of the molecular orbitals.¹⁸ The alkynylselenolato complex $[\text{Ni}(\text{SeC}\equiv\text{CR})(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, SiMe_3) was formed from $[\text{NiCl}(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$.¹⁹ The nickel-induced coupling of ethylene and CO_2 represents a promising pathway toward acrylates. Although this process is not yet catalytic, the stepwise *in situ* methylation of nickelactone (**12**) and subsequent liberation of methyl acrylate has been achieved.²⁰ The historical development and current state-of-the-art in the Ni-catalyzed homocoupling, cross-coupling, and functionalization of C–O bonds has been reviewed.²¹



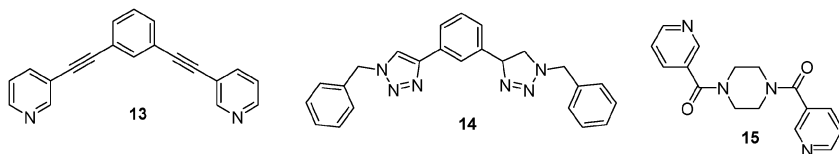
3 Palladium

As in previous years, palladium has attracted considerable attention due to its catalytic activity in carbon–carbon coupling reactions.^{22–26} The palladium-catalyzed trifluoromethylation of aryl chlorides under mild conditions, allowing the transformation of a wide range of substrates, including heterocycles, in excellent yields has been reported.²⁷ The transition-metal-catalyzed hydroxylation of aryl derivatives has been reviewed. Two reaction protocols were considered, the C–H activation/hydroxylation and cross-coupling hydroxylation of aryl halides.²⁸

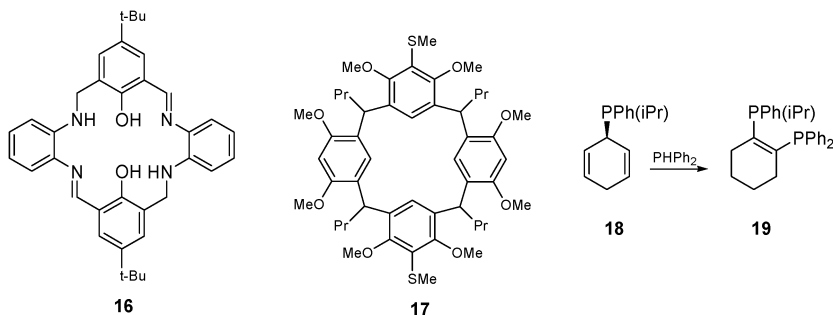
Coordination chemistry

Ligand (**13**) formed a new self-assembled $[\text{M}_2\text{L}_4]^{+4}$ palladium-pyridyl cluster with a “paddle-wheel” structure with a binding affinity for neutral organic guests (e.g. 1,4-terephthalonitrile) of the correct size and electrostatic complementarity.²⁹ The triazole ligand (**14**) self-assembles into a $[\text{M}_2\text{L}_4]^{+4}$, quadruply stranded helicate cage with Pd(II) ions.³⁰ Another example of a quadruply stranded helicate is the palladium(II) $[\text{M}_2\text{L}_4]^{+4}$ cage formed from reaction of ligand (**15**) (anti conformation) with $\text{Pd}(\text{NO}_3)_2$, encapsulating one nitrate ion at the middle of the Pd–Pd axis.³¹ The salen-type ligand (**16**) forms the bridging dimeric complex, *trans*- $\text{Pd}_2(\mathbf{16})_2\text{Cl}_4$, the ligand is bonded to the metal centre through the amine nitrogens only.³² The synthesis of S,S resorcinarene ligand (**17**) and its sulfur-bonded Pd(II) complex,

[Pd₂(**17**)(μ-Cl)₂Cl₂], have been reported.³³ In a tutorial review metal-based amino receptors in the context of first- and second-sphere coordination are presented.³⁴

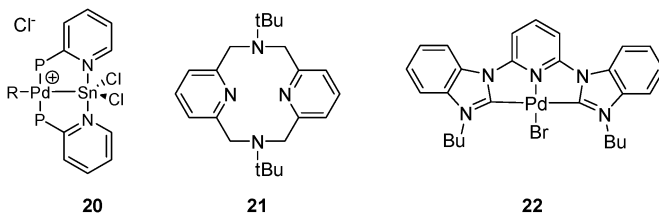


The first examples of an optically active Birch reduced tertiary phosphine (**18**) and successful hydrophosphination to (**19**) have been reported.³⁵ Methyl-, phenyl-, and *n*-butyltin trichloride RSnCl₃ reacted selectively with Pd(0)–phosphine precursors through the unprecedented oxidative addition of the Sn–C bond to afford complexes **20**.³⁶



Organometallic chemistry

Mechanistic pathways involving either Pd(II)/(IV) or Pd(II)/(III) couples in palladium-catalyzed C–C coupling and C–H activation reactions continue to be vigorously debated. The emergence of palladium(IV) chemistry in synthesis and catalysis has been reviewed.³⁷ A bimetallic Pd(II)₂/Pd(III)₂ catalytic cycle for the Pd(OAc)₂-catalyzed aromatic C–H chlorination has been proposed on the basis of kinetic measurements.³⁸ In this study relevant dinuclear Pd(III) complexes were prepared and observed to undergo selective C–Cl reductive elimination. The stable mononuclear six-coordinate Pd(III) complexes [Pd(**21**)(R)Cl] (R = Me, Ph) have been isolated. Ethane formation was observed from the corresponding palladium-methyl complex.³⁹



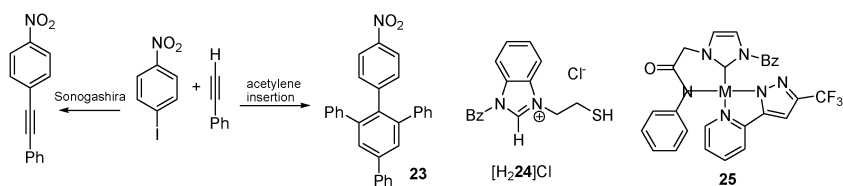
Transition-metal-catalyzed C–H activation has recently emerged as a powerful tool for the functionalization of organic molecules. A review has appeared on palladium-catalyzed, ligand-directed C–H functionalization reactions.⁴⁰ A minireview highlights recent work in the C–H bond activation of alkyl groups.⁴¹

The carboxylate-directed Pd(II)-catalyzed C–H olefination reaction between phenyl acetic acid and 3-phenylpropionic acid substrates, using oxygen at atmospheric pressure as the oxidant, has been reported.⁴² In a review the potential of several C-based leaving groups including alkyl, carbinol, CN, COOH, and carbonyl groups in arylation reactions is illustrated accordingly for the preparation of biphenyl-, vinyl-, alkynyl-, and alkyl-substituted aromatics.⁴³ The reaction of [Pd(PCP)R] complexes {R = Me, crotyl; PCP = 2,6-bis[(di-*tert*-butylphosphino)methyl]phenyl} with CO₂ has been studied and an S_E2 mechanism proposed.⁴⁴ In a related report, a family of palladium allyl complexes of the type [Pd(η³-2-methylallyl)(η¹-2-methylallyl)(L)] (L = PMe₃, PEt₃, PPh₃, NHC) inserted selectively CO₂ into the M-(η¹-2-methylallyl) bond to form the corresponding carboxylate complexes.⁴⁵

The mechanism of the reaction of *trans*-[ArPdX(PPh₃)₂] (Ar = *p*-Z-C₆H₄; Z = CN, F, H; X = I, Br, Cl) with Ar'B(OH)₂ (Ar' = *p*-Z'-C₆H₄; Z' = CN, H, OMe) was established in DMF in the presence of the base OH⁻ in the context of real palladium-catalyzed Suzuki–Miyaura reactions. The role of the OH⁻ base was also studied.⁴⁶ The hydrophilic palladium pincer complex (**22**) acted as a highly efficient robust recyclable molecular catalyst towards Suzuki–Miyaura coupling reactions in aqueous media and tolerated various functional groups (even heterocycles) with extremely low catalyst loading.⁴⁷ A palladium-catalyzed reductive cross-coupling of 1,3-dienes with boronic esters in which a π-allyl Pd species is generated directly from a 1,3-diene *via* a Pd-catalyzed aerobic alcohol oxidation was reported.⁴⁸

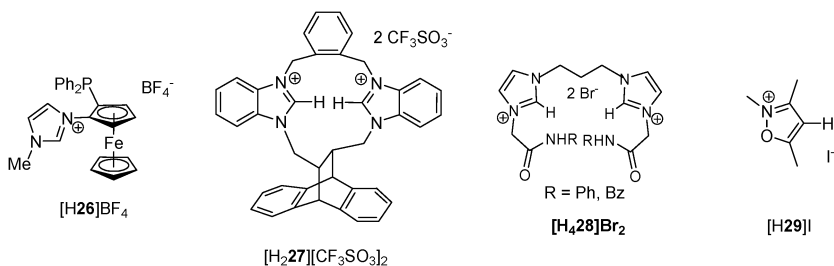
(**23**) is the unreported product outcome from an intended Sonogashira coupling. The generality of the reaction has been demonstrated by screening a range of pre-catalysts. Mechanistic studies are consistent with the tetra-aryl benzene product forming by interception of the aryl halide oxidative addition intermediate by repeated acetylene insertion.⁴⁹ A superparamagnetic nanoparticle MNP (γ-Fe₂O₃/polymer) supported dendritic catalyst based on a chelating alkyl phosphine Pd(II) complex has been prepared and its high reactivity on the Sonogashira cross-coupling reaction in water reported.⁵⁰ Deposited Pd onto carbon nanotubes-metal oxide hybrid nanoparticles creates a catalyst that works at the water–oil interface. The coupling of water soluble 5-methyl furfural and acetone and subsequent hydrogenation of the oil soluble product, demonstrated the efficiency of the catalyst.⁵¹

trans-PdCl₂{PPh_n[CH₂C₆H₄O(CH₂)₄CH=CH₂]_{3-n}}₂, with ortho or meta C₆H₄ linkages and *n* = 0, 1 (tribenzyl- or dibenzylphenylphosphine cores), were treated with Grubbs' catalyst and then H₂/PtO₂, to isolate the corresponding P₂-macrocycles in high yields.⁵² An efficient and practical method to a wide range of perfluorinated unsymmetrical diarylmethanes with good to excellent yields and high regioselectivities was developed by Pd-catalyzed direct benzylation of highly electron-deficient perfluoroarenes; excellent compatibility of functional groups was also established.⁵³



Thiolato-bridged dimeric Pd(II) benzimidazolin-2-ylidene complexes, with a [Pd₂S₂] core, were formed with NHC precursor [H₂24]Cl.⁵⁴ The Pd(II) and Pt(II)

NHC amido-functionalised complexes (**25**) have been prepared and tested in the Heck reaction of deactivated ArCl substrates.⁵⁵ The chiral NHC precursor $[\text{H26}]\text{BF}_4$ formed Pd(II) complexes that catalyze the asymmetric coupling of aryl bromides with arylboronic acids in good yields and moderate enantioselectivities (up to 42% ee).⁵⁶ The chiral bis-NHC cyclophane ligand $[\text{H}_2\text{27}][\text{CF}_3\text{SO}_3]_2$ and its palladium allyl complex were prepared. The complex was tested for 1,4-conjugate addition of phenylboronic acid to 2-cyclohexen-1-one and provides *R*-3-phenylcyclohexanone in 50% enantiomeric excess.⁵⁷ The tetradentate NHC-amido ligands $[\text{H}_4\text{28}]\text{Br}_2$ form the air- and water-stable $[\text{M}(\text{28})]$ complexes ($\text{M} = \text{Pd}, \text{Ni}$).⁵⁸ Abnormal isoxazolyliene complexes, a new subclass of mesoionic complexes containing an isoxazolium-derived carbene type ligand (**29**), were synthesised *via* oxidative addition and compared to structurally related mesoionic complexes by using ^{31}P NMR spectroscopy as a convenient probe for their donor ability and in catalytic cross-coupling reactions.⁵⁹ A series of isomeric complexes with the general formula *trans*-(pyridylidene) $\text{M}(\text{PPh}_3)_2\text{Cl}$ ($\text{M} = \text{Pd}, \text{Ni}$) were investigated and a systematic comparison of *normal*, *abnormal*, and *remote* bonding modes was presented. X-ray structural and ^{13}C NMR data indicate the importance of carbenoid mesomeric contributions in their compound class.⁶⁰



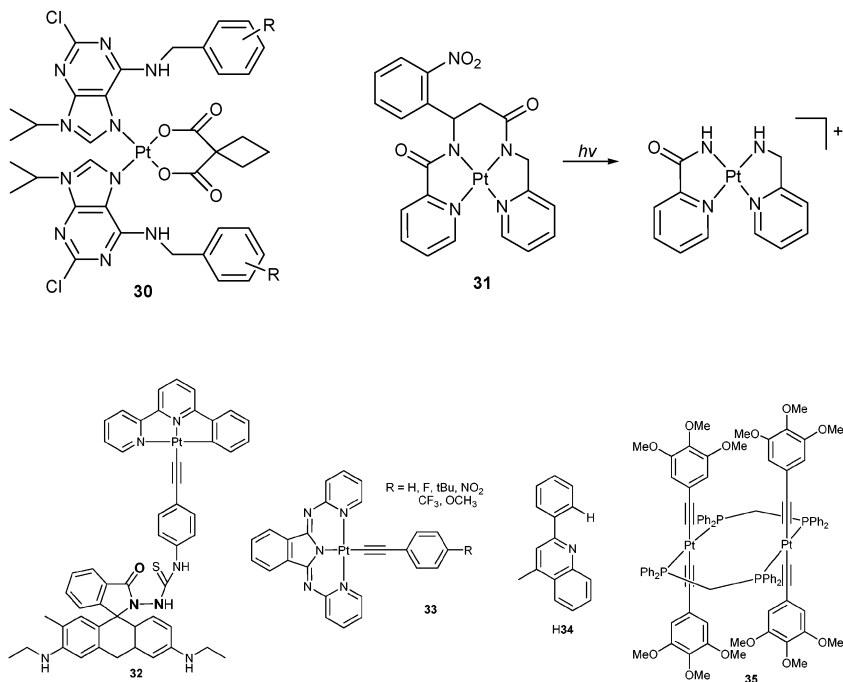
4 Platinum

As in previous years platinum has attracted great attention for its antitumour properties, with several reviews and papers appearing in the literature.^{61–63} Another area of continuing interest in platinum chemistry revolves around their luminescence properties and consequent applications.^{63–70}

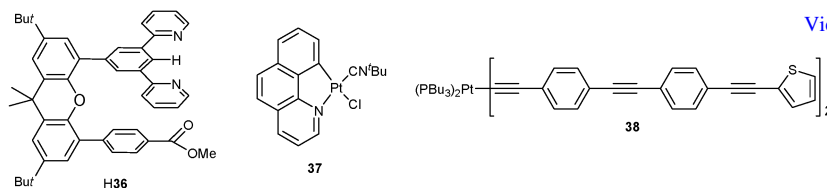
Coordination chemistry

The approved platinum(II)-based anticancer agents cisplatin, carboplatin and oxaloplatin are widely utilised as therapeutics, although with numerous disadvantages. With the aim of circumventing unwanted side-effects, a great deal of research is being conducted in the areas of cancer-specific targeting, drug administration and drug delivery. Recent advances in the field of platinum chemotherapeutics, with a focus on the technologies that attempt to utilise the cytotoxic nature of cisplatin, whilst improving drug targeting to reduce side-effects have been reviewed.⁶¹ Six platinum(II)-purine derivatives have been synthesized by the reaction of $[\text{Pt}(\text{cbdc})(\text{dmsO})_2]$ with the corresponding purine compound. Type-(**30**) complexes were tested for their *in vitro* cytotoxicity against chronic myelogenous leukaemia and breast adenocarcinoma. Their *in vitro* cytotoxicities were in several cases comparable or even higher than those of therapeutically used platinum-based anticancer drugs, cisplatin, carboplatin and oxaliplatin.⁶² The Pt(II) complex (**31**) contains a

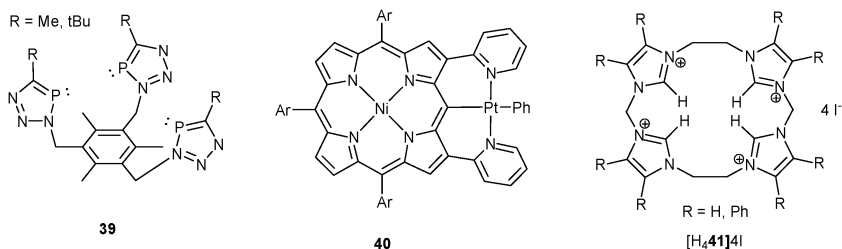
photolabile nitrophenyl group incorporated into the backbone of the tetradentate ligand. **(31)** is unreactive toward ligand-exchange reactions until activation with UV light cleaves the ligand backbone. *In vitro* tests with human breast cancer cells showed that upon brief UV exposure cell death was induced at a level approaching that of cisplatin.⁶³



Luminescent platinum(II) complexes is a topic of current interest, many of such complexes prove to be luminescent even in solution under ambient conditions, and this is a feature that has led to the recent interest in them as triplet emitters in OLEDs or as interesting biosignalling species. The cyclometallated Pt(II)-containing rhodamine probe **(32)** with two-photon induced luminescent properties was synthesized and investigated for mercury detection. A highly selective colour change of **(32)**, from light yellow to pink, was observed only in the presence of Hg(II) due to the formation of a 1,3,4-oxadiazole ring in the complex (heteroatoms forming this ring shown in bold in structure **32**). The water-soluble probe was successfully applied in the visualizing of the site of Hg(II) accumulation as well as estimating of trace amounts of mercury ions in live cells by two-photon microscopy.⁶⁴ A series of Pt(II) complexes **(33)** with monoanionic tridentate isoindoline derivatives display bright-orange to red, room-temperature luminescence in fluid dichloromethane solutions with microsecond to sub-microsecond ranges of emissive lifetimes.⁶⁵ A series of lepidine containing cyclometallated Pt(II) complexes [Pt(**34**)acac] have been synthesized. These complexes are highly phosphorescent in fluid as well as in the solid state, covering a rather broad spectral range from yellow to saturated red.⁶⁶ Several luminescent face-to-face dinuclear Pt(II) alkynyl phosphine complexes **(35)** with trimethoxyphenyl and carbazole moieties were synthesized. Correlations of their emissive properties with the Pt...Pt distance, the nature of the alkynyl and bridging phosphine ligands, and the nature of the encapsulated metal ions on the alkynyl ligands were made.⁶⁷

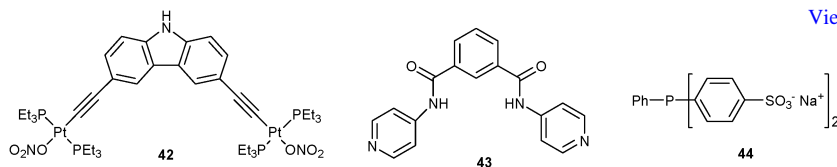


The phosphorescent Pt(II)-N,C,N pincers [Pt(**36**)Cl] featuring a conformationally rigid organic linker, and a binding group were reported. The luminescent responses of these Pt(II) hosts to amino acids were investigated: emission quenching and UV-vis absorption changes in polar/aqueous media were detected for terminal thiols only, and unusual preferential binding was apparent for cysteine over homocysteine.⁶⁸ The photophysical properties of the isocyanide-cyclometallated platinum complex (**37**) and of other isocyanide derivatives have been studied.⁶⁹ A series of four new *trans*-diphosphine Pt(II) diacetylide complexes (*e.g.* **38**), with a thiophene and two benzenoid rings in each acetylide ligand, were synthesized and characterized with respect to optical absorption, spectrally and time-resolved luminescence, and optically nonlinear properties such as two-photon absorption cross section and optical power limiting.⁷⁰



High yielding ‘click’ reactions between phosphalkynes and organo-triazides afforded examples of tris(triazaphospholes) (**39**), the utility of which as a new class of tripodal P₃-ligands was demonstrated with the preparation of mono- and di-nuclear Pt(0) complexes.⁷¹ In the presence of secondary phosphine oxide, PtCl₂(COD) was converted to a series of *cis/trans* platinum complexes PtCl₂[R¹R²POH]₂ featuring phosphinous acids as ligands.⁷² Ni(II)-porphyrins bearing Pt(II) (**40**) and Pt(IV) pincer complexes were synthesized and characterized. Their structures and electronic properties were influenced by the valence state of platinum at the outer coordination site. The considerable distortion in the porphyrin core of the Pt(II) complex was relieved in the Pt(IV) complex, due to the change of the coordination geometry of platinum. Oxidation of complex (**40**) with iodine induced a facile carbon–carbon bond formation reaction at the meso position *via* reductive elimination.⁷³ The 18-atom-ringed macrocyclic tetra-imidazolium ligands [H₄**41**]**4I** were prepared by a two-step procedure. *In situ* deprotonation formed monomeric tetra-carbene Pt(II) complexes.⁷⁴

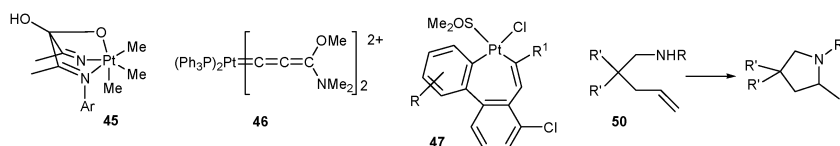
A shape selective Pt(II)₂ organometallic 90° building block (**42**) self-assembles with flexible ditopic pyridyl donors (**43**) resulting in the formation of [2 + 2] macrocycles. These macrocycles were found to be fluorescent in nature and showed dramatic fluorescence enhancement in a DMF/H₂O solvent mixture upon titration with P₂O₇⁴⁻, which plays important roles in various biological functions such as energy transduction in organisms and controls metabolic processes by participating in



various enzymatic reactions.⁷⁵ The water soluble mono-*N,N*-dialkylamino- β -CD-**44** inclusion complexes with Pt(II) were reported.⁷⁶

Organometallic chemistry

Monomeric oxoboranes (B \equiv O) are known only as short-lived species in gas-phase or low-temperature matrix experiments. The formation of the oxoboryl complex *trans*-[(C_Y3P)₂BrPt(B \equiv O)] by means of reversible liberation of trimethylsilylbromide from the boron–bromine oxidative addition product of dibromo(trimethylsiloxy) borane and [Pt(PC_Y3)₂] was reported.⁷⁷ The Pt(IV) complex (^tBuMe₂nacnac)PtMe₃ (^tBuMe₂nacnac = [[(4-^tBu-2,6-Me₂C₆H₂)NC(CH₃)₂CH]) was reacted with molecular oxygen to form a peroxo complex, in which one oxygen atom is bound to the platinum centre and the other to the central carbon of the nacnac ligand backbone. Over time, the peroxo complex converts to a new Pt(IV) species (**45**) wherein the O–O bond has been cleaved.⁷⁸ Depending upon the reaction conditions *cis*- and *trans*-bis(allyl)idene Pt(II) complexes (**46**) were obtained.⁷⁹ The reaction of *cis*-[PtCl₂(SOME₂)₂] and aromatic imines [for example, 2,6-Cl₂C₆H₃CH=NCH₂(4-C₆H₅)] carried out in toluene at 90 °C in the presence of sodium acetate dissolved in methanol produced compounds containing seven-membered platina-cycles (**47**) via ‘formal insertion’ of a toluene molecule in the metallacycle.⁸⁰ The reductive elimination of biphenyl from *cis*-[Pt(Ph)₂(diphosphine)] was studied to clarify the electronic effects of diphosphine ligands on the reaction. Reaction kinetic data were evaluated in *d*₈-toluene within 80–110 °C using 1,2-bis(diphenylphosphino)ethane (dppe) and seven of its fluoroaromatic analogues as ancillary diphosphine ligands. The fastest reaction rate corresponded to the electron-poor 1,2-bis[bis(pentafluorophenyl)phosphino]ethane (dfppe) ligand, and was 1240 times faster than that for the dppe-bearing complex, which was the slowest.⁸¹ The protonolysis of Pt(II) and Pd(II) methyl complexes were investigated by both experiment and computation. DFT calculations indicate that protonation at the metal centre followed by reductive coupling to the methane σ adduct (stepwise pathway) is favoured for Pt complexes with good electron donor ligands, whereas direct protonation of the M–CH₃ bond to generate the methane σ adduct (concerted pathway) is favoured for Pt with electron-withdrawing ligands.⁸² Two cationic olefin complexes of Pt(II) with electron-withdrawing substituents on the allylic carbon, [PtCl(η^2 -CH₂=CHCH₂X)(tmeda)]⁺ (X = –C(O)OCH₃ (**48**), –OC(O)CH₃ (**49**)) were synthesized and their reactivity toward nucleophiles investigated. The reaction of (**48**) with various nucleophiles, including water, causes allylic deprotonation and formation of the η^3 -allyl complex [Pt{ η^3 -CH₂CHCHC(O)OCH₃}(tmeda)]⁺,



whereas the reaction of (49) with nucleophiles does not lead to deprotonation but to substitution of the acetate group followed by addition to the olefinic double bond.⁸³ The efficacy of phosphine-free Pt precatalysts including PtCl₂ and Pt(COD)Cl₂ in promoting the cyclohydroamination of primary as well as secondary alkyl/arylamines tethered to α -olefins (50) is demonstrated for the first time. Further catalytic studies examining the use of phenylene-P,N co-ligands, as well as neutral, cationic, and formally zwitterionic complexes derived from the new ligand precursor 1-PPh₂-2-P(^tBu)₂-indene, revealed comparable reactivity in Pt-catalyzed cyclohydroamination catalysis relative to these phosphine-free catalysts.⁸⁴

Abbreviations

acac	acetylacetonato
cbdc	cyclobutane-1,1-dicarboxylate
CD	cyclodextrin
COD	1,5-cyclooctadiene
Cy	cyclohexyl
DFT	density functional theory
Dmp	2,6-dimesitylphenyl
DSSC	dye-sensitised solar cell
H4dhtp	2,5-dihydroxyterephthalic acid
MOF	Metal–Organic Framework
NHC	<i>N</i> -heterocyclic carbene
OLED	organic light emitting device
SOD	superoxide dismutase

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