

“Higher Oxidation State Organopalladium and Platinum Chemistry”

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An essay book review by Martyn V. Twigg*

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Both heterogeneous and homogeneous platinum group metal (pgm) catalysts have remarkable properties: invariably they have outstanding activities, longevity, and often particularly attractive selectivities so they are used in many demanding situations. Therefore perhaps it is not surprising that the discovery of heterogeneous catalysis involved platinum. In 1817 Humphry Davy discovered catalytic combustion by placing a heated coiled platinum wire into a town gas/air mixture that became and stayed white hot as it sustained combustion (1, 2). This illustrated the exceptional activity of platinum since the wire had a very low surface area, and soon there were a number of reports concerning catalysis by platinum, including selective oxidations such as the oxidation of ethanol to acetaldehyde or acetic acid (3). The interest in catalysis continued to grow but the introduction of a successful large scale industrial heterogeneous catalytic process did not take place until Oswald's work (4) culminated in the introduction of the high-temperature selective oxidation of ammonia to nitric oxide over platinum/rhodium *en route* to nitric acid at the beginning of the 20th century (5). Now heterogeneous pgm catalysts are at the heart of many industrial processes, and also in environmental areas where platinum, rhodium and palladium catalysts control exhaust emissions from vehicles to keep urban air clean (6). In these solid heterogeneous catalysts the reaction takes place on surface atoms, often *via* mechanisms that have yet to be completely elucidated.

In contrast, homogeneous soluble pgm catalysts have the advantage of being discrete molecular compounds that can be characterised in the solid state and in solution by techniques used in organic chemistry. The mechanisms of reactions catalysed by them can be probed in this way, and as a result of intense work over more than three decades much is

understood about the intimate mechanistic details of homogeneously catalysed reactions. These include hydrogenations, hydroformylations, carbonylations, and especially carbon–carbon bond forming processes that often provide elegant routes to desirable organic compounds that are not easily accessed by other means. The importance of this work has been recognised by several Nobel Prizes, most recently for C–C bond forming Heck-type coupling reactions (7). Initially rhodium homogeneous catalysts were the most significant of the pgms, and now palladium has this position, but platinum and rhodium as well as ruthenium and iridium catalysts are important in some areas.

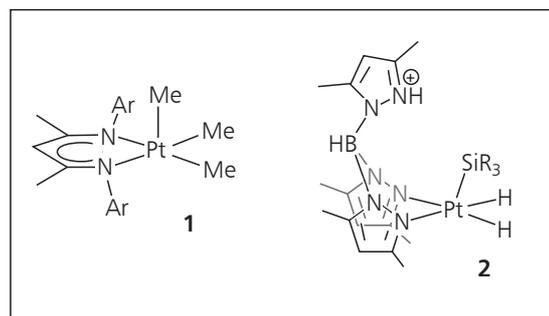
During the catalytic cycle the metal centre in these homogeneous reactions usually moves between two oxidation states differing by two units, with the lower oxidation state being stabilised by soft ligands like mono- and polydentate phosphines.

These catalysts can be remarkably selective. For example, in suitable situations when chiral ligands are present chiral products can be obtained. The facile oxidation state interchange is key for catalytic activity, and for rhodium it is rhodium(III) and rhodium(I) that are usually involved (and similarly for iridium), while for platinum and palladium it is the 0 and +II oxidation states. For instance, oxidative addition of a R–X compound to a palladium(0) centre affords a palladium(II) species, which after suitable transformations, undergoes a reductive elimination process to complete the catalytic cycle and reform palladium(0) and an organic product.

Less well investigated are two oxidation state interchanges at higher oxidation state levels in organopalladium and organoplatinum compounds. Almost two decades ago Allan Canty reviewed the evidence for the possible presence of the +IV oxidation state in homogeneous reactions catalysed by organopalladium species (8). A lot of work has been done in this area since then, and the role of palladium(IV) has been firmly established in some important processes. The present monograph, edited and partially written by Allan Canty, is concerned with the ability of platinum and palladium species to access these higher oxidation states, and their involvement in stoichiometric and catalytic reactions. It is becoming increasingly apparent that this chemistry may be important in a variety of situations including oxidative reactions. The book covers both basic chemistries and applications in seven chapters written by authors eminent in their fields of specialisation.

Higher Oxidation State Platinum Species

The first chapter, by Kyle Grice, Margaret Scheuermann and Karen Goldberg (University of Washington, Seattle, USA), is concerned with five-coordinate organometallic platinum(IV) complexes. Based on kinetic studies it has long been believed that the slow first order reactions of octahedral low-spin d^6 platinum(IV) ‘coordination complexes’ are dissociative in nature and involve reactive five-coordinate intermediates (9). Five-coordinate platinum(IV) intermediates are required as the preliminary step in some ‘organometallic’ insertion reactions like C–C, C–X and C–H reductive eliminations, and in β -hydride eliminations. Although isoelectronic rhodium(III) and iridium(III) five-coordinate complexes have long been known, it is only in recent years that five-coordinate platinum(IV) complexes have been isolated and characterised and their reactivity directly observed. The first was reported some ten years ago and is shown in **Structure 1**. This is an almost perfect square pyramidal compound, while the second one to be isolated, **Structure 2**, is a distorted square pyramid in which the metal is not in the plane of the base.

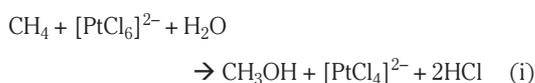


Clearly steric effects are important stabilising factors in moderating their reactivity which enable them to be characterised by nuclear magnetic resonance (NMR) spectroscopy in solution and by X-ray diffraction in the solid state. Notwithstanding this, processes involving the addition of small molecules such as dioxygen and carbon monoxide that can access the metal centre have been observed, and study of several of these compounds is shedding valuable light on the chemistries of five-coordinate platinum(IV) complexes.

The next chapter, by Jay Labinger and John Bercaw (California Institute of Technology, USA), is about higher oxidation platinum species in C–H alkane activation. For many years low-temperature ‘methane activation’ has been a major goal of catalysis. At high

temperatures deuterium exchange takes place over heterogeneous nickel catalysts (and others), and the industrially important methane steam reforming reaction takes place also over a nickel catalyst with a similar activation energy. Under much milder conditions unsaturated hydrocarbons and arenes undergo deuterium exchange in solution (10) while remarkably methane does so in the presence of $[\text{PtCl}_4]^{2-}$ in solution (11). Therefore alkane activation *per se* is not necessarily the major difficulty in producing useful chemical products directly from methane. The need is to intercept short lived, highly reactive intermediate species to give desired products more rapidly than, for instance, reaction with hydrogen (or deuterium) which gives no overall meaningful reaction.

The Shilov system remarkably directly produces methanol from methane at low temperature! Originally an aqueous mixture of platinum(II) and platinum(IV) chloroplatinates was used, and modified systems were subsequently developed. The original reports (12, 13) of this amazing chemistry were published in the Russian literature during the late 1960s and early 1970s, and the overall oxidation of methane by $[\text{PtCl}_6]^{2-}$ is shown in Equation (i).



The key step in this process is the initial reaction of alkane with $[\text{PtCl}_4]^{2-}$ which is rapidly followed by oxidation of the thus formed alkyl complex with $[\text{PtCl}_6]^{2-}$, presumably *via* a chloride bridge, which is a unique oxidant because it cannot destroy platinum(II), whereas to be effective alternative oxidants must oxidise the alkyl complex while not oxidising the platinum(II). Copper in conjunction with molecular oxygen appears to be the most effective alternative oxidant system (copper alone is ineffective so the presence of oxygen is not simply to re-oxidise the copper), and it is pertinent to compare this process with the Wacker reaction where palladium is also re-oxidised by oxygen in the presence of copper (14). The practical difficulties with the powerfully oxidising platinum(IV) Shilov system are reproducibility and shortened life caused by erratic precipitation of platinum metal. It is mainly because of this that the highly appealing and intriguing reaction has not been commercialised, although the mechanistic understanding that has

been gained shows the direction in which further development needs to go.

Reactions of Palladium(IV) Complexes and Their Mechanisms

The next chapter, by Joy Racowski and Melanie Sanford (University of Michigan, USA), deals with the formation of C–heteroatom bonds by reductive elimination reactions from palladium(IV) complexes. It is a comprehensive review covering published material from 1986 to 2010. Transient palladium(IV) intermediates have been proposed as the product release stage in a number of important transformations including arene and alkane functionalisations, allylic acetoxyations, alkene borylations etc. And indeed palladium(IV) compounds such as $\text{Pd}(\text{bipy})(\text{CH}_3)_3\text{I}$ (formed by oxidative addition of CH_3I to $\text{Pd}(\text{bipy})(\text{CH}_3)_2$) undergo facile reductive elimination to give ethane. Since this reaction was reported (15), the area has expanded considerably with examples of C–S, C–Se, C–O, C–I, C–Br and C–Cl bond forming reactions, and each of these are covered in some detail, including the considerable amount of work that is being done to confirm the mechanisms of these processes. Very importantly C–F bonds can be formed using XeF_2 as a fluorine source (16), and although this area is still in its infancy it may be expected to be developed as a route to important fluoro-compounds that are otherwise difficult to access.

'Palladium(IV) Complexes as Intermediates in Catalytic and Stoichiometric Cascade Sequences Providing Complex Carbocycles and Heterocycles' is the title of the next chapter, by Helena Malinakova (University of Kansas, USA). This deals with the capability of some palladium compounds to mediate sequential functionalisation of one substrate to create multiple C–C or C–heteroatom bonds in a single operation, for example in multicomponent annulation reactions in which palladium(IV) complexes are implicated as intermediates. Studies on isolatable palladium(IV) compounds have been used to obtain evidence for the participation of such intermediates, and stoichiometric reactions in palladium provide routes to 1,3-dienes, norbornene derivatives, benzoxepines, benzopyrans and benzofurans that are discussed in detail, as is the spectroscopic and crystallographic characterisation of the relatively rare palladium(IV) intermediates. Further work on moderately stable palladium(IV) compounds is likely

to clarify whether they can participate in fundamental processes other than reductive eliminations.

Organic Reactions Mediated by Palladium and Platinum Complexes

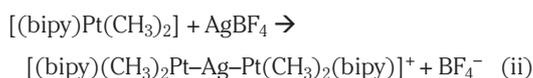
The fifth chapter is by Allan Canty and Manab Sharma (University of Tasmania, Australia) and is concerned with higher oxidation state palladium and platinum η^1 -alkynyls. That is, species in which the metal in an oxidation state greater than +II is bonded to alkynyl ligands, which can be prepared by oxidation of alkynylmetal(II) complexes and reactions of organometal(II) complexes with alkynyl(aryl) iodine(III) reagents. The metal(IV) compounds obtained are octahedral, and only platinum compounds have been characterised in the solid state by X-ray crystallography. Some of these compounds decompose *via* reductive elimination, generating C–C bonds (diacetylenes) (17). Stoichiometric reactions of the palladium(II) and platinum(II) complexes suggest that the higher oxidation state complexes are feasible (undetected) intermediates in some organic synthetic procedures. Interesting metal–metal bonded systems that can be seen as Pt(III)–Pt(III) or Pt(II)–Pt(IV) species have been characterised as intermediates in the oxidation of Pt(II) to Pt(IV) compounds, and the potential implications for mechanisms of organic reactions mediated by higher oxidation metal centres are discussed. Clearly this is a very fertile area for much future research.

There then follows a chapter on palladium(III) species in synthetic and catalytic reactions by David Powers and Tobias Ritter (Harvard University, USA). Unlike platinum(III) coordination complexes their palladium(III) counterparts are very rare, and for example, PdF₃ is better described as the Pd(II) salt of the Pd(IV) complex anion [PdF₆]²⁻. As previously noted, few organometallic palladium(III) compounds have been isolated and characterised – examples of these are given in the book. There is however growing evidence that such species might be important in a variety of known palladium-catalysed reactions. For instance, silver(I) is often used as a beneficial additive in practical palladium-catalysed oxidative C–H coupling reactions, and one-electron oxidation of [(bipy)Pd(Me)₂] with AgPF₆ affords a moderate yield of ethane *via* a suggested mechanism involving disproportionation of the first formed palladium(III) complex [(bipy)Pd(Me)₂]⁺ to [(bipy)Pd(Me)(solvent)]⁺ and [(bipy)Pd(Me)₃]⁺, followed by elimination of ethane from the Pd(IV) compound – this mechanism

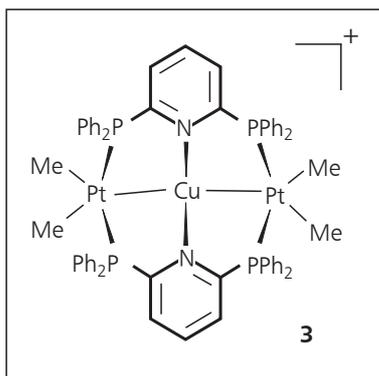
nicely explains the 50% yield of ethane. The possible involvement of methyl radicals was discounted because radical traps had no effect on the reaction. However, the addition of isopropyl iodide to Kumada and Negishi coupling reactions results in remarkable accelerations in reaction rates that were attributed to a radical pathway with transient palladium(I) intermediates and isopropyl radicals with palladium(I) and palladium(III) chain carriers. Palladium(III) has also been proposed in dioxygen insertion reactions into Pd(II)–methyl bonds, consistent with a radical process that is light sensitive, and addition of a radical inhibitor was needed to obtain consistent reaction rates. Photolysis of isolated palladium(III) complexes made by electrolysis gave products that were inhibited by radical scavengers, consistent with photoinduced homolytic Pd–C cleavage as the pathway to the observed organic products, although other routes are possible. It might be thought that palladium(III) forms dimers, and oxidation of dinuclear palladium(II) complexes can result in diamagnetic dinuclear palladium(III) complexes with a metal–metal σ -bond that is shorter than that in a comparable palladium(II) complex (18). There is also evidence that such species are present as intermediates in some catalytic reactions. Thus well defined palladium(III) complexes participate in productive organometallic reactions, and their presence in better studied processes seems likely, processes that previously were thought to proceed *via* traditional two-electron monometallic palladium redox cycles. This area is likely to yield many intriguing results in the near future that may substantially change the mechanistic view of some established reactions!

The final chapter is entitled ‘Organometallic Platinum(II) and Palladium(II) Complexes as Donor Ligands for Lewis-Acidic d¹⁰ and s² Centers’, by Marc-Etienne Moret (ETH Zurich, Switzerland, and California Institute of Technology, USA). The filled axial orbitals of square planar palladium and platinum complexes enable them to be ‘metalloligands’ for Lewis-acidic metal centres, and a wide range of such donor-acceptor metal–metal bonded species have been reported. This nucleophilic reactivity is key in the oxidative addition of alkyl halides to organopalladium(II) and organoplatinum(II) complexes *via* an S_N2 process, and electron-rich complexes can be protonated on the metal to give metal(IV) hydrides, which is the first step in the protonolysis of many Pt–C bonds. The early examples of isolated metal(II) square planar adducts with metal–metal bonds date from the early 1980s and have Pt–Hg or Pt–Ag bonds, and since then a wide

variety of related compounds have been prepared. There are several bonding patterns, some involving interactions with ligands bound to the central metal, but all have M–M interaction. Again methyl complexes undergo some particularly interesting reactions, as illustrated for instance in Equation (ii), which takes place in solution at low temperature.



This compound is not stable but the presence of metal–metal bonding in solution at low temperature was confirmed by NMR coupling constants. The palladium counterparts are less stable and have a reduced tendency to form donor-acceptor metal–metal bonds. More recently exotic complexes have been prepared in which a central metal, for example copper(I), is coordinated to two pyridine nitrogen atoms and two $\text{Pt}(\text{CH}_3)_2$ moieties forming part of a macrocycle, as shown in **Structure 3**.



Thallium forms stable palladium–thallium bonds, and a remarkable complex cation has a linear chain of four Pd(II)–Tl(I) bonds. This tendency of thallium(I) to be involved in extended structures is expanded upon later. The chapter then details a bewildering array of increasingly complex structures, mostly containing metal–metal bonds that include alkynyl complexes, diphosphine-bridged complexes and carbene complexes, before examining electron transfer, ligand migration and hydrocarbyl transmetalation reactions. The reactions of the polymetallic compounds of the type discussed in this chapter provide further chemical insight into why adding copper(I) and silver(I) salts to palladium and platinum-based catalytic systems can enhance reaction rates. This may happen *via* more facile alternative mechanisms involving

donor-acceptor metal–metal bonded species and understanding here may lead to more productive catalytic systems.

Concluding Remarks

Overall this is a nice up to date book that provides a very readable account of highlights in a topical and exciting area of developing chemistry. All the contributors and the editor, as well as the publishers, are to be congratulated for making available such a well produced and interesting monograph. The accepted mechanistic pathways of many established catalytic reactions are being questioned as increasing amounts of evidence suggest that alternative mechanisms involving higher oxidation state species are possible and may well take place. For example, where metal centres are in higher oxidation states they are likely to form reactive free radicals more readily than in lower oxidation state processes. This monograph will be of value to all those who are working in the area, and it should be in libraries wishing to keep up to date in these chemical areas that have so much potential.

Notes and References

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- 2 The same year, 1817, also saw the foundation of what was to become the present Johnson Matthey company. For further details see: "Percival Norton Johnson; The Biography of a Pioneer Metallurgist", D. McDonald, Johnson Matthey, London, UK, 1951; "A History of Platinum: From the Earliest Times to the Eighteen-Eighties", D. McDonald, Johnson Matthey, London, UK, 1960; L. B. Hunt, *Platinum Metals Rev.*, 1979, **23**, (2), 68
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