

Geoffrey Wilkinson and Platinum Metals Chemistry

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At this time, the second anniversary of Geoffrey Wilkinson's death on 26th September 1996, his work and influence on the development of inorganic chemistry and the chemistry of the platinum group metals are recalled by two of his former students and colleagues. Geoffrey Wilkinson's early life and career, important areas of his platinum metals research and work leading to the award in 1973 of the Nobel Prize are surveyed. He is remembered by his relationship with Johnson Matthey, his work at Imperial College and by affectionate anecdotes from the laboratory.

Professor Sir Geoffrey Wilkinson, F.R.S. (or Geoff as he was always called by his students and colleagues) was one of the greatest international post-war inorganic chemists; he made remarkably original contributions to many areas of transition metal chemistry, especially homogeneous catalysis, organometallic and co-ordination chemistry. His research career, spanning some 54 years, involved well over half of the elements of the Periodic Table – he worked with almost every *d*-block transition metal, most of the lanthanides and some of the actinides and main group elements. Much of his work concerned the six platinum group metals, and indeed many of his most important discoveries involved them. Of his 557 publications (1), well over one third are concerned with the platinum metals.

The Johnson Matthey Connection

The platinum metals Geoff used were invariably supplied by Johnson Matthey through the loan scheme (inaugurated in 1955 by his great friend, the late Frank Lever). This scheme has done much to foster university research in platinum metals chemistry in the U.K. and overseas. Over the years Geoff developed a close connection with Johnson Matthey: not only were there the patents (involving for the most part his rhodium catalysts) and consultancy, but also he had many friends in the company – and some

of his ex-students came to work for it. On his twice-yearly visits to the Technology Centre in Sonning Common he would always take a plastic shopping bag filled with platinum metals residues, garnered from his research group and from his colleagues – the used materials from the loan scheme.

On his retirement in 1988 to become Professor Emeritus, Johnson Matthey expressed their appreciation of this mutually productive relationship by providing Geoff with the spacious Johnson Matthey laboratory at Imperial College. Here he continued very productive work with a small, creative team to the day before his death.

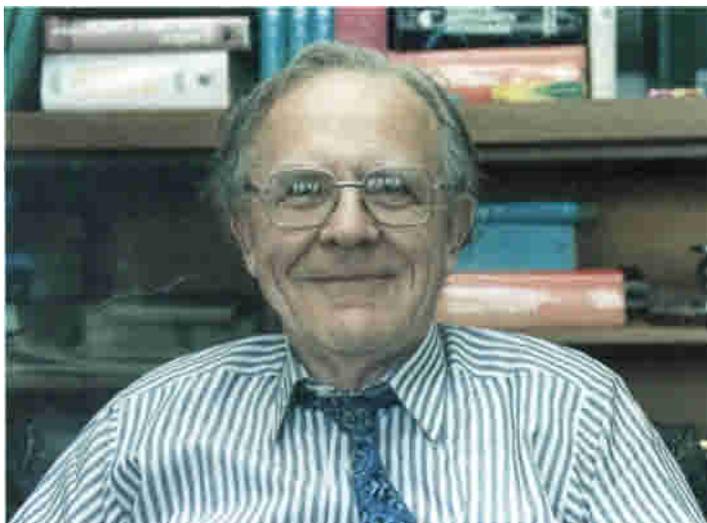
In 1964 Geoffrey Wilkinson wrote an article for *Platinum Metals Review* on platinum group organometallic π -aromatic complexes (2). This article, however, preceded his important discoveries in the catalytic chemistry of these elements. As a fuller account of Geoff's chemistry has already been published (1), this report will focus on his life and work with the platinum metals in the order of their interest to him, listing items published in *Platinum Metals Review*.

Early Life and Education

Geoffrey's grandfather (also Geoffrey Wilkinson) came to Todmorden, a small 'cotton town' in the West Riding of Yorkshire, close to Lancashire, from the Yorkshire town of

**Professor Sir
Geoffrey Wilkinson
1921–1996**

A Yorkshireman by birth, Geoffrey Wilkinson started his working life, during World War II, on the atomic bomb project in Canada and then the United States. He returned to England in 1956 to the Sir Edward Frankland Chair of Inorganic Chemistry, at Imperial College in London. He was awarded the Nobel Prize for Chemistry in 1973



Boroughbridge. Geoffrey's father, Harry, married Ruth Crowther, a weaver, and Geoffrey was born on 14th July, 1921, the first of three children, in the village of Springside on the outskirts of Todmorden.

In 1926 the family moved into Todmorden, which lies at the junction of three deep valleys in the heart of the Pennines, where the surrounding moors rise 1000 feet above the town. The present population of 13,000 is about half that before the decline of the cotton industry, but there is still a strong local pride and sense of community which Geoff shared all his life. His eyes would light up when he spoke of "Tod" or of the superb countryside close by. He often returned to the town to see friends and family, and enjoyed walking and climbing in the area, in the Lake District and the Yorkshire Dales.

Geoff's interest in chemistry began early. At the age of six he was fascinated to see his father – a house painter and decorator – mixing his materials. His uncle managed a factory making Epsom and Glauber's salts in Todmorden, and Geoff would recall how he loved to go on Saturday mornings to tinker in the small laboratory at the factory. Indeed, the family hoped that he would eventually become its manager. His parents, like most people at that time, had left full-time education by the age of 12 and they were determined that their children should be

better taught. Geoff won a County Scholarship in 1931 to Todmorden Secondary School (later Todmorden High School). A remarkable number of its pupils later became famous, including Sir John Cockcroft, who worked with Rutherford at Cambridge and was to become, in 1951, the first of the school's two Nobel Laureates. Geoff made exceptional progress and in 1939 won a Royal Scholarship to the Imperial College of Science and Technology, London University.

At Imperial his main subject was chemistry but he also studied geology as an ancillary subject, indeed in those early days he almost gave up chemistry in favour of geology. He graduated in 1941 with a first class honours B.Sc. degree, the top student of his year, and went on to do a Ph.D. under H. V. A. Briscoe (at that time the only Professor of Inorganic Chemistry in the country) on "Some Physico-chemical Observations on Hydrolysis in the Homogeneous Vapour Phase". This rather Delphic title conceals the fact that the main substrate studied was phosgene (Geoff later remarked that Briscoe "directed his Ph.D. research from a safe distance").

In 1942 he was selected by the Joint Recruiting Board as a scientific officer at the Atomic Energy project in Canada, and sailed to Halifax, Nova Scotia in January 1943. In Canada he worked at the University of Montreal and then at Chalk

River, Ontario, on nuclear fission with many celebrated scientists – John Cockcroft (from his old school), Bertrand Goldschmidt, Charles Coryell, Alfred Maddocks (later to go to Cambridge), Jules Guéron and Pierre Auger being amongst them, and two scientists later convicted of being spies for the Soviet Union, Alan Nunn May and Bruno Pontecorvo.

After the war Geoff returned briefly to Britain and then went to the Lawrence Livermore Laboratory at the University of California, Berkeley, to work with Glenn T. Seaborg on the production of neutron-deficient isotopes of the transition elements and the lanthanides. It was said by Seaborg (and Geoff) that he made more artificial isotopes – eighty nine – than anyone has ever made. From this time he started to amass his vast knowledge of descriptive inorganic chemistry, since in those days it was essential for nuclear chemists to have a profound knowledge of the chemistry of the transition metals, the lanthanides and the actinides in order to devise appropriate means of separating and identifying the products of nuclear fission reactions. One of his nuclear transmutations was that of platinum into gold, which caught the public imagination after a report in 1948 in the ‘San Francisco Chronicle’ (“Scientist discovers gold mine in the cyclotron”).

In 1950 he went to M.I.T. and turned to coordination chemistry research. His first paper on this concerned the isolation of the unusual zerovalent complex, $[\text{Ni}(\text{PCl}_2)_4]$ (3). In 1951 he was appointed Assistant Professor of Chemistry at Harvard, and it was here that he did the research on ferrocene and other cyclopentadienyl compounds which was to lay the cornerstone of his Nobel Prize. In 1976, after this award in 1973, he received his knighthood.

The Structure of Ferrocene and Early Platinum Metals Work

In 1951, the joint recognition by Wilkinson and R. B. Woodward of the unique “sandwich” structure of ferrocene (*bis*(cyclopentadienyl)iron, Cp_2Fe) was perhaps the most crucial point in his career; it launched the new wave of ‘organo-transition metal chemistry’ which remains to

this day. Twenty years later Geoff wrote a vivid personal account of the discovery (4). From 1952 to 1953 he made a number of other *bis*(cyclopentadienyl) complexes, including those of ruthenium, rhodium and iridium. During this period he used the fledgling technique of nuclear magnetic resonance (NMR) to show that covalent metal hydrides (in this case Cp_2ReH) gave high-field ^1H NMR shifts. This was crucial to his later work on rhodium hydrido complexes and their catalytic properties.

Return to Imperial College

In 1955 Geoff was appointed to Briscoe’s old chair at Imperial College – still the only established chair of inorganic chemistry in Britain – and arrived there in January 1956. At 34 he was one of the youngest professors that the College has ever had, and here he did most of his platinum metals work. It is tempting to trace this profound interest in platinum metals chemistry to his wartime and early peacetime radiochemical work, when he had made new radioisotopes of rhodium and ruthenium. However, it is much more likely that his fascination with these metals derived from his early experience and knowledge of their general chemistry, and in particular with the remarkable versatility of oxidation state changes exhibited by the metals, later harnessed for his catalytic work.

Rhodium Chemistry

Geoff once said that much of his chemistry concerned the ‘three Rs’ – rhodium, ruthenium and rhenium. At Berkeley, as part of his radiochemical work, he isolated the short-lived ^{106}Rh , one of the many fission products of ^{235}U , and in 1953 he made salts of the $[\text{Cp}_2\text{Rh}]^+$ cation. Then in 1961, in work that he himself carried out, he reacted *cis*- and *trans*- $[\text{RhCl}_2(\text{en})_2]^+$ with sodium borohydride in aqueous solution to give $[\text{RhHCl}(\text{en})_2]^+$ (detected by the high-field shift of the hydridic proton by ^1H NMR) (5). It was on this occasion that he rushed into the laboratory, demanded a Bunsen burner and a test tube, and returned later with the tube full of a foaming brown liquid which he brandished about, calling “Who wants a Ph.D?” This early

work led to a paper on the isolation of $[\text{RhH}_2(\text{en})_2](\text{BPh}_4)$, and the establishment of the reduction of quinone to quinol by hydride transfer from $[\text{RhH}(\text{trien})\text{Cl}]^+$. In collaboration with that wizard of platinum metals chemistry, A. R. Powell of Johnson Matthey, salts of $[\text{RhH}(\text{NH}_3)_5]^{2+}$ and $[\text{RhH}(\text{H}_2\text{O})(\text{NH}_3)_4]^{2+}$ were isolated; these materials were used to prepare hydrido complexes of ethylenediamine and propylenediamine (6).

Hydrogenation and Hydroformylation with Rhodium Complexes

Geoff's work on this topic has revolutionised our view of homogeneous catalysis effected by transition metal complexes and constitutes some of his most celebrated work. It is well reviewed in articles by his graduate student, Fred Jardine, who was the first to isolate the compound $\text{RhCl}(\text{PPh}_3)_3$, universally known as Wilkinson's catalyst (7).

In 1965 Geoff reported that catalytically small amounts of reducing agents (such as hypophosphorous acid, zinc amalgam and dihydrogen itself) would catalyse the otherwise slow substitution reactions of rhodium(III) complexes. He had earlier shown that $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ would absorb dihydrogen and convert hex-1-ene to hexane, and in 1965 he found that *fac*- $\text{RhCl}_3(\text{PPh}_3)_3$ would convert hex-1-ene to *n*-heptaldehyde, with dihydrogen and carbon monoxide under pressure at 55°C. However $\text{RhCl}_3(\text{PPh}_3)_3$ is difficult to make, and it was during an attempt to make some that $\text{RhCl}(\text{PPh}_3)_3$ was produced. This compound was a much more effective catalyst for the hydrogenation of alkenes and alkynes and also hydroformylated hex-1-yne to *n*-heptaldehyde and 2-methylhexaldehyde. $\text{RhCl}(\text{PPh}_3)_3$ was made from the surprisingly simple reaction between $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ in ethanol with excess triphenylphosphine. It is described in a classic paper of 1966 (8).

Although $\text{RhCl}(\text{PPh}_3)_3$ is a hydrogenation catalyst (and subsequently chiral analogues were developed by others for asymmetric synthesis, for example for L-Dopa) Geoff later showed that it was not a hydroformylation catalyst, and that the compound responsible for the latter process

was $\text{RhH}(\text{CO})(\text{PPh}_3)_3$. Nowadays most of the butyraldehyde used for synthesis of *bis*(2-ethylhexyl)phthalate, a plasticiser for PVC, uses $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ as the catalyst.

The early hydrogenation and hydroformylation work was documented in a short article in this journal exactly thirty years ago, with fuller papers in 1975 and 1988 (9). There is no doubt that this catalysis work, together with his work in so many other areas, contributed to his Nobel prize of 1973, though the citation was for "sandwich" compounds.

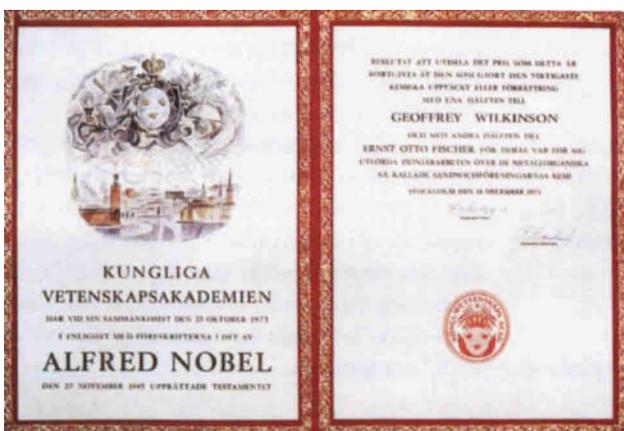
Other Work with Rhodium

One of Geoff's major fascinations (foreshadowed in his only paper in this journal (2)) was with homoleptic alkyl and aryl complexes, mainly of the early transition metals. In 1968 he made $[\text{Rh}(\text{C}_2\text{H}_5)_3(\text{NH}_3)_3]^{2+}$ and, much later, in 1988 and 1990, isolated salts of the remarkable methyl complex $[\text{Rh}(\text{CH}_3)_6]^3$ and of the dimeric oxo-bridged neopentyl complex $\text{Rh}_2(\mu\text{-O})_2[\text{CH}_2\text{C}(\text{CH}_3)_3]_6$, respectively. Another achievement was the synthesis in 1991 of $\text{Rh}(\text{mesityl})_3$, which has a pyramidal structure in the solid state.

Ruthenium Chemistry

Ruthenium he called "an element for the connoisseur". Again his first approach to this metal was via its radiochemistry in his early work in Canada and the United States, followed by the preparation of ruthenocene Cp_2Ru and the rutheninium $[\text{Cp}_2\text{Ru}]^+$ cation as a logical follow-up to his classic ferrocene paper.

In the 1960s he isolated a number of ruthenium(II) and (III) complexes of phosphines, arsines and stibines, including $\text{RuX}_2(\text{LPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{P}, \text{Sb}$) and $\text{RuX}_3(\text{LR}_3)_2(\text{CH}_2\text{OH})$ ($\text{L} = \text{P}, \text{As}$). These were precursors for many other complexes with a wide variety of ligands, such as dithiocarbamates, amines, nitriles and carboxylates, and a number of them had useful catalytic activities. Another highlight was the isolation of the first paramagnetic second-row transition metal complexes, $\text{Ru}_2(\text{OCOR})_4\text{Cl}$ ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}$). A variety of carboxylato complexes of the form $\text{RuH}(\text{OCOCH}_3)_3(\text{PPh}_3)_3$ were found to be efficient hydrogenation catalysts for



The Nobel Prize for chemistry awarded to Sir Geoffrey Wilkinson in 1973 for his work on “sandwich” compounds

alk-1-enes. A review of this and other work on ruthenium carboxylates has been described by Steve Robinson, one of his former students (10).

His later work with ruthenium was also very productive. In 1986 the novel aluminohydride complexes $L_2HRuAlH(\mu-H)_2AlH(\mu-H)_2RuHL_2$ ($L = PMe_3, PEtPh_2, PPh_3$) were obtained from $RuCl_2L_2$ and lithium aluminium hydride. In the mid-1980s he isolated the alkyl complexes $Ru_2(IV)(\mu-O)_2R_6$ ($R = neopentyl, CH_2SiMe_3$), the tetrahedral homoleptic RuR_4 ($R = o-CH_3C_6H_4$, mesityl), salts of $[Ru(CH_3)_6]^{2+}$, and some unusual ruthenium(IV) and (V) imido complexes. Alkyl complexes had become of increasing interest to him; in fact, his Nobel Prize award speech in 1973 was entitled “The long search for transition metal alkyls” (11) and in 1993 he wrote a review paper on the homoleptic alkyls and aryls of the platinum group metals (12).

Osmium Chemistry

Although he made ruthenocene and the ruthenicinium cation in 1952, soon after his ferrocene work, it was E. O. Fischer (with whom he shared the Nobel Prize) who first made osmocene, Cp_2Os , in 1958. Geoff’s first paper at Imperial College concerned $K[OsO_3N]$, but apart from this he came to osmium chemistry relatively late in his research career.

In the 1980s he made the acetato complexes: $[Os(OCOCH_3)_3(PMe_3)_3]Cl$, $Os_2(OCOCH_3)_4Cl(py)$, and sky-blue $K[OsO_2(OCOCH_3)_3] \cdot 2CH_3COOH$, the X-ray crystal structure of which was obtained

in 1982. His most celebrated work with osmium however lay with the aryl and imido complexes – he liked to refer to such highly unusual species as “text-book cases”. He made the alkyl complexes $Os(VI)O(CH_2SiMe_3)_4$ and also the dimeric neo-pentyl $Os_2(VI)(O_2CCH_3)_2(CH_2SiMe_3)_4$.

In 1984 the tetrakis phenyl complex $Os(IV)Ph_4$ was isolated and in 1988, the tetrahedral complexes $Os(IV)(2-CH_3C_6H_4)_4$ and $[Os(V)(2-CH_3C_6H_4)_4]^+$ were prepared. At that time, tetrahedral co-ordination was unprecedented for the tetra- or pentavalent oxidation states of second or third-row transition elements.

For imido chemists, the ‘Holy Grail’ was the isolation of a homoleptic complex containing the =NR ligands, and in 1991 Geoff achieved this with the isolation and structural characterisation, by electron diffraction, of the tetrahedral tertbutylimido complex $Os(IV)(N^tBu)_4$.

Iridium Chemistry

Geoff did some work in the late 1960s on “iridium iodate” (13), but he then seems to have neglected the metal until 1989 when he isolated salts of $[Ir(CH_3)_6]^{3+}$.

In 1991 he made the tetrahedral complexes $Ir(IV)R_4$, where R is a sterically hindered aryl, such as 2-tolyl, 2,5-xylyl; and in 1992 he made $Ir(mesityl)_4$. In the same year he made $Ir(mesityl)_4$, which, like its rhodium analogue, has a pyramidal structure in the solid state. Also in 1992 he isolated $Ir(mesityl)_2(SET_2)_2$, a very rare example of a planar iridium(II) complex, by reaction of *mer*- $IrCl_3(SET_2)_3$ with the Grignard reagent $Mg(mesityl)_2(SET_2)_2$.

Palladium and Platinum Chemistry

Of the six platinum group metals, palladium and platinum received far less attention from Geoff than did the other four, perhaps because

these elements are less versatile in their oxidation states and also, perhaps, because other well-known chemists in the country were doing much palladium and platinum work. But, between 1966 and 1970, he did show that the zerovalent complex $\text{Pt}(\text{PPh}_3)_3$, reacts with CS_2 to give $\text{Pt}(\text{PPh}_3)_2(\text{CS}_2)$, while the reaction of $\text{Pt}(\text{PPh}_3)_2(\text{O}_2)$ with CO , CO_2 and CS_2 yielded $\text{Pt}(\text{PPh}_3)_2(\text{CO})$, $\text{Pt}(\text{PPh}_3)_2(\text{CO}_2)$ (a peroxocarbonate) and $\text{Pt}(\text{PPh}_3)_2(\text{O}_2\text{CS}_2)$, respectively.

Wilkinson the Man

For both of the authors of this article, Geoff was an academic supervisor in the late 1950s. We wrote, in our joint obituary of him for 'The Independent': "The spirit in his research group was more like that of an urgent gold rush in the West than the scholarly and disciplined calm expected in academia." (14). If anything this understates the truth: he expected his students to work as hard as he did – seven days a week or at least six, from early morning to late evening. He was, however, not a slave driver and was generally tolerant of eccentric behaviour. When thwarted or stirred he made creative and ingenious use of expletives – quite unsuitable for quotation here – and he always had a ready sense of fun. His enthusiasm was always infectious, and he was an excellent raconteur and anecdotalist, with a remarkable memory. In those days (the late 1950s) Geoff would often emerge from his office in the late afternoon and wander up to each student in turn and say "Well, what's new?": his whole ethos being the search for some new aspect of chemistry.

He was a severe critic of derivative chemistry

which he would dismiss as 'stamp collecting'. Sometimes when a reaction seemed not to be working he would offer the suggestion "Why don't you goose it up" meaning, raise the temperature. Geoff was not sympathetic to theoretical chemistry and would often cite the story of how the brilliant young Harvard theoretician Bill Moffitt had advised him that *bis*-benzene chromium would be unlikely to be stable. E. O. Fischer shortly afterwards reported this famous compound.

Geoff was always in a great hurry to publish new results and, from time to time, this led to errors; one example was the reaction product between thiophene and iron pentacarbonyl which was published as thiopheneirontricarboxyl. Gordon Stone later showed that there was no sulfur present and the product was the unexpected butadieneiron tricarboxyl. Geoff was not given to sulking over such matters but looked forward to the next new compound.

Geoff was a doughty fighter for chemistry in the U.K., writing in blunt style to Prime Ministers, ministers of education, vice chancellors and others charged with the care of fundamental scientific research. He would refer to such powerful people in administration dismissively as "the apparatchiks".

Geoffrey Wilkinson was a remarkable scientist and an unforgettable person. His belief that innovative and creative synthesis is a powerful tool for new chemistry is borne out by his vast range of scientific achievements. His legacy to his former students and his enthusiastic influence on chemistry have given us all many long-term, far reaching benefits.

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