

A Half Century of Platinum Metal Chemistry

REMINISCENCES OF PROGRESS FROM ACADEMIC BACKWATER TO INDUSTRIAL IMPORTANCE

By Professor Joseph Chatt

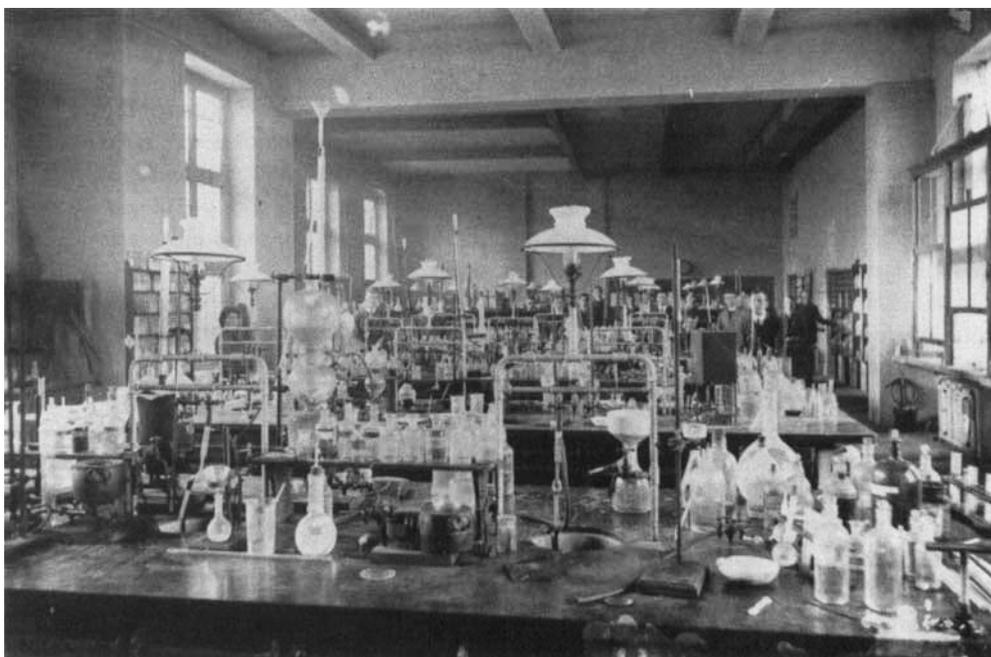
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It was about fifty years ago that I first developed a serious interest in platinum metal chemistry from my research supervisor Dr. F. G. Mann (1) in the University Chemistry Laboratory in Pembroke Street, Cambridge. It was then quite a different world: each student bench had its own individual gas light and you can imagine the fire hazard. (We students joked about our Professor, Sir William Pope, having shares in the gas company!) Even to get £10 for a piece of equipment was a feat which I

achieved only once. Students bought their own research chemicals and paid for their breakages. I was lucky as Dr. Mann allowed me to draw on his personal account for chemicals, but even then we made n-propyl bromide and such from the cheaper alcohols rather than buy the alkyl halide. Thus I found myself engaged in a very productive investigation of halogen bridged palladium complexes. We must remember that in the early 1930s many chemists did not believe that monovalent halogens such as



Professor Chatt has been an active participant throughout the remarkable growth of interest in the unique chemistry of the platinum metals which has taken place over the past fifty years, leading to the development of the industrially important field of homogeneous catalysis, to a greater understanding of cluster chemistry and more recently to the successful use of platinum compounds in medicine. Here he gives his impressions of the enormous progress made since he first became involved in research in this area, and of the prospects for further important discoveries



This view of the University Chemistry Laboratory in Pembroke Street, Cambridge, shows the facilities that were available to research students some sixty years ago. In addition to the usual glassware and reagent bottles, each student bench had its own individual gas light which provided an adequate degree of illumination, but also constituted a potential fire hazard. By the mid 1930s the gas lights were of a more modern design and one or two bare domestic light bulbs per laboratory had been suspended on long flexes to provide sufficient illumination to allow passage after dark without need of a portable lamp. This photograph is from the private collection of Mrs. Barbara Mann, widow of Dr. F. G. Mann and is reproduced here with her permission. Photographs of the laboratory taken just a few years earlier show the academic staff dressed in gowns and wearing mortar board caps

chlorine could bind covalently two metal atoms although the idea was at least ten years old (2). Halogen bridging was only finally established in 1937 by an X-ray structure of the dimeric "diethylmonobromogold" (3).

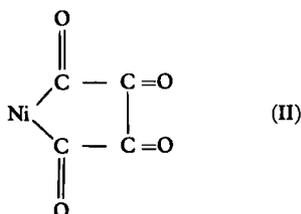
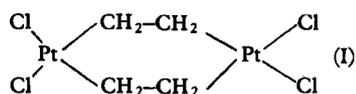
Complex Chemistry in the Doldrums

The general character of platinum metal chemistry was well established before 1935. The main point at issue had been the nature of the isomerism of its various compounds, especially of the α - and β -isomers of the platinum(II) complexes. With the advent of Werner's famous theory (4) the planar configuration had slowly, but eventually, been accepted by most chemists. The isomeric amines had been oriented by him using

methods closely akin to the classical methods used to orient the products of aromatic substitution. The deeper coloured α -[PtCl₂(NH₃)₂] was correctly assigned a *cis*- and the paler β -isomer a *trans*-configuration, but the remaining such isomers, for example of the tertiary organic phosphines and sulphides, had been assigned incorrect configurations by analogy of colour. So they remained until 1936 when K. A. Jensen in Copenhagen, by measuring the dipole moments of platinum(II) complexes soluble in organic solvents, showed that the paler coloured isomers, except the amines, were the *cis*-isomers (5). It was also at about this time that X-ray structure determination came to the aid of co-ordination chemists, although not entirely reliably.

This advance in structural technique is

important because acceptance of Werner's ideas had been so slow that still they had not entered the main stream of chemistry. Even in the early 1930s Professor H. D. K. Drew (6) whom I remember well, was trying to show that the isomeric platinum(II) complexes were structural rather than geometrical isomers, according to the ideas of Blomstrand (7) and Jörgensen (8) from the last century. They had eventually been discredited by Werner after long controversy with Jörgensen, but not completely laid to rest. Drew produced evidence which he claimed to show that α -[PtCl₂(SEt₂)₂], now known as the *trans*-isomer, had a tetrahedral structure and that the β -isomer was a disulphonium salt of structure $\text{Cl} \cdots \text{Et}_2\text{S}-\text{Pt}-\text{SEt}_2 \cdots \text{Cl}$ where \cdots represents an electrovalency. Even such nonsensical structures as (I) for "ethylene platinous chloride" (9) and (II) for "nickel carbonyl" (10) were appearing in the 1930s and even the 1940s.



That such structures could appear at the time without furore in chemical circles shows how little co-ordination chemistry and Werner's theory were appreciated by the general body of chemists. "British Abstracts" had condensed Werner's famous 68 page paper (4) expounding his Nobel Prize winning theory to eight lines of trivial abstract (11); clearly the abstractor did not understand it at all. The olefin complexes were still regarded as chemical curiosities of little significance. Around 1950 when I was making my study of platinum(II) olefin complexes which led to the proposal, with supporting evidence, of what is now the generally accepted structure, I was visited by a senior

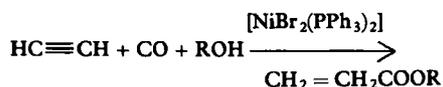
academic who later became a Nobel Laureate. After I had discussed my work with him he finally commented "Nice little field you have carved out for yourself, Chatt, but . . ." and then in the nicest possible way indicated that I had entered a backwater of chemistry of little interest to anyone. The paper (12) is now a citation classic, counting only citations since 1965 (13).

Even after the Second World War there had been no conference on any aspect of transition metal chemistry so long as I could remember. My complaint about this to the Acting Manager Mr. M. T. Sampson, of the Butterwick Research Laboratories of Imperial Chemical Industries Limited where I was employed led to the first of the now well known series of International Conferences on Co-ordination Chemistry (I.C.C.C.). It was held on 21st-22nd September 1950 in the Butterwick Laboratories, financed by our company, and organised privately by myself and Dr. R. G. Wilkins. We invited everyone in the U.K. who had published anything on co-ordination chemistry since 1930: only one, who was ill, did not come. We collected 31 participants from outside I.C.I. and two from abroad, K. A. Jensen and G. Schwarzenbach. The size of the meeting reflects the abysmal interest in complex chemistry in the U.K. at that time, rather than the poor life expectancy of co-ordination chemists. K. A. Jensen carried the torch to Copenhagen where the next I.C.C.C. was held three years later.

Spectacular New Development

From about 1950 interest in transition metal chemistry grew apace. When the fifth I.C.C.C. was held under the auspices of the Chemical Society in London in 1959 there were about 750 registrants and it has recently been agreed that the fiftieth anniversary conference will be held in London under the auspices of the Royal Society of Chemistry in the year 2000. What caused this sudden upsurge of interest during the 1950s? It was the development of the petrochemicals industry, especially after the war, with its supply of olefins together with the

appearance of Reppe's reports of some remarkable catalytic cyclisations and carbonylations of acetylenes and olefines carried out on certain nickel complexes (14). The following reaction particularly attracted attention:



This suddenly made influential organic chemists in industry aware of the potential of transition metal chemistry and loosened the purse strings of both Industry and Government. Thus although my work in the I.C.I. Laboratory and that of R. S. Nyholm at University College London, and of others overseas stood on the base of what had been initiated in academic laboratories before the war, it was now accepted more favourably by those controlling finance; at last transition metal chemistry started to flourish. We must not forget that Ronald Nyholm was a great propagandist who preached loud and long to the great benefit of our science as did John C. Bailar, Jr. and W. C. Fernelius in the U.S.A. Then came the discovery of the cyclopentadienyls (15), not particularly useful in themselves, but they brought transition metals even more into the realm of organic chemistry and so to the attention of a greater section of the chemical community. The greatest single event which finally revitalised transition metal chemistry was Ziegler's discovery of the low pressure polymerisation of ethylene to a high polymer on various early transition metal compounds activated by aluminium alkyls (16) followed quickly by the discovery of isotactic polymerisation by Natta (17) in the 1950s. The remarkable production of stereo-regular polymers of propene and such olefins on titanium-aluminium alkyl catalysts fired the imagination of industry. So there was a great blossoming of research into the chemistry of transition metals in the late 1950s and early 1960s, especially into the area of the platinum metal complexes and their use in homogeneous catalysis (18). Despite increased financial stringency, it is still flourishing today as testified by the recently established series of

international conferences devoted entirely to platinum metal chemistry.

What of the Future?

Catalysts continue to be developed, but there are more wonderful substances to be discovered in the realm of platinum metal chemistry: new and more highly specific catalysts, complexes to effect useful photosplitting of water perhaps, or a cure for cancer. We cannot tell. The most spectacularly important discoveries are often made by accident and so we must continue to probe the unknown. Speculative research is slow with its rewards, and becomes slower as less remains to be discovered, but if your instinct is good I believe that you will eventually break into a new area.

When I started research all chemists who thought about it at all knew that the transition metals had virtually no hydride or organic chemistry because the bonds between transition metal atoms and hydrogen or alkyl or aryl groups were considered to be too weak to survive at ordinary room temperatures. Organoplatinum metal compounds had been sought by the well established methods of Main Group metal chemistry and found scarcely to exist. The relative position of organoplatinum metal chemistry in the 1930s and now is well illustrated by consideration of the space allotted to them relative to organomercury compounds in the two comprehensive textbooks of those periods. In the Goddards' four volumes published 1928 to 1937 there are 190 pages devoted to mercury, but only one and a half to the platinum metals (19). It appeared self evident that there was nothing worth looking for in organoplatinum metal chemistry, hence the remarks of my Nobel Prize winning mentor, but look where it is now. In Wilkinson's *Comprehensive Organometallic Chemistry* there are only 115 pages devoted to mercury, but 1,432 to the platinum metals (20). Scientific discovery is not yet predictable. If you have an exciting road to follow do not be put off by those who say that there is nothing at the end of it; they do not know. Persevere, and enjoy the excitement of exploring the unknown.

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A Massive Work of Reference

Dictionary of Organometallic Compounds, Vols. 1, 2 and 3

EDITED BY DR. JOHN BUCKINGHAM, Chapman and Hall/Methuen, London, 1984, 3000 pages, £495

That organometallic chemistry has now come of age as a scientific discipline is obvious from the enormous number of publications that have appeared on the subject in the last twenty or more years. This quite astonishing growth is also brought out by the reminiscences of Professor Chatt in the preceding pages, where, after describing the growth of activity from his early years to the present time, he refers to the nine-volume "Comprehensive Organometallic Chemistry" edited by Sir Geoffrey Wilkinson and published by Pergamon in 1982.

The objective of the present work is to review the whole field of organometallic chemistry, to select those compounds which, in the opinion of the numerous specialist contributors, are most typical and either useful or potentially useful and then to present their properties and bibliography in a systematically indexed manner.

The elements are treated in alphabetical order, each entry giving details of stoichiometry, molecular weight and basic properties together with structural diagrams. Each entry is numbered to assist location from

the indexes in Volume 3 which themselves detail compound name, molecular formula and CAS registry number, respectively. In terms of numbers of platinum metal compounds listed ruthenium leads the field with 870, followed by platinum, osmium and rhodium with over 400 each, palladium some 346 and iridium 242. The literature has been covered to mid-1983, but annual supplements are to be published, beginning in late 1985.

Since the publication of the dictionary a number of separate parts have been issued dealing only with small groups of metals. These include a volume on the organometallic compounds of nickel, palladium, platinum, copper, silver and gold edited by Dr. R. J. Cross, one on cobalt, rhodium and iridium by Dr. C. White and another on ruthenium and osmium by Dr. G. R. Knox, each available at £22.50.

These volumes will undoubtedly make an important contribution to the yet further development of organometallic chemistry and possibly encourage the greater use of organometallic compounds in industry.

L.B.H.