The First Organometallic Compounds

WILLIAM CHRISTOPHER ZEISE AND HIS PLATINUM COMPLEXES

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The great interest being taken in the organometallic compounds of the platinum metals is evident in the current literature, in the first International Conference on the Chemistry of the Platinum Group Metals held in Bristol in 1981, and now by the second conference to take place in Edinburgh in July. This article reviews the preparation of the first such compounds over a hundred and fifty years ago and the acrimonious debate that ensued over their true constitution, continuing with a brief account of the early development of a further range of platinum complexes that have come to play an important part in industrial chemistry.

During the last thirty years there has developed a concentration of interest upon the preparation, structure and properties of a wide range of organometallic compounds of the platinum group of metals, much of this directed towards their usefulness in the catalytic synthesis of a number of commercially valuable chemical products. The most familiar industrial examples of this type of reaction include, of course, the carbonylation of methanol to acetic acid, the conversion of ethylene to acetaldehyde and the hydroformylation of olefins to aldehydes, while other such large scale applications will undoubtedly be developed in the near future based upon the versatility of these complexes as homogeneous catalysts where they offer high activity per unit weight of metal, high selectivity and long life.

The original discovery of the first such compound—and in fact of the first organometallic compound of any metal—took place, however, as long ago as 1830, at a time when organic chemistry was in its infancy, when but a relatively few organic compounds were known, and when their constitution was barely if at all understood and the subject of great argument.

The credit for this discovery goes to William Christopher Zeise, born in Slagelse in Denmark the son of the local pharmacist. After leaving school Zeise was himself apprenticed for a time to Gottfried Becker, Royal Court pharmacist in Copenhagen who combined this activity with lecturing on chemistry at the university there, but poor health shortly caused him to return to the family business in Slagelse. Here he continued to study chemistry and to absorb the new concepts put forward by Lavoisier, while in 1806 he was able to return to Copenhagen where he was taken into the family of Hans Christian Oersted (1777–1851) who had recently been appointed extraordinary professor of physics and chemistry in the university. Both men were the sons of pharmacists who were well known to each other and Oersted invited Zeise to become his lecture assistant, a position from which he was able to continue studying chemistry and pharmacy, graduating in 1815 and going on to obtain his doctorate two years later with a thesis on the action of alkalies upon organic substances. The following two years he spent abroad, first under Professor Friedrich Stromeyer at the University of Göttingen and then in Paris where he was delighted to become acquainted with Berzelius, a friend of Oersted's who was then spending almost a year there. The great impression made upon the young man—Zeise was ten years junior to Berzelius—was to

William Christopher Zeise
1789–1847

Beginning his career as a pharmacist, Zeise became first an assistant to Hans Christian Oersted in the University of Copenhagen and then, after a period in Göttingen and Paris, returned as Professor of Chemistry there. He prepared the first organometallic compound of platinum—or of any metal—in 1830. This involved him in considerable controversy with Liebig but he was proved to be correct in his interpretation. He also discovered the xanthates and the mercaptans and in general helped to lay the foundations of organic chemistry in the first half of the nineteenth century

From a portrait painted by F. Helsted
by courtesy of the National Historic Museum of Denmark

influence him for the remainder of his career and the two remained on friendly terms for the rest of their lives. Zeise also met and talked with the older French chemists Berthollet and Laplace, attended several meetings of the Académie des Sciences as well as Vauquelin's lectures at the College de France. Among the younger men he enjoyed the friendship of Chevreul and Thenard.

Returning home at the end of 1819, Zeise was asked by Oersted to direct his laboratory experiments and in fact he established one of the first laboratories in Europe for analytical and organic chemistry. Two years later he was appointed extraordinary professor of chemistry at the University of Copenhagen and then, from 1829 until his early death in 1847, he served also as professor of organic chemistry at the Royal Polytechnic Institute of Copenhagen that had been established on the initiative of Oersted, who became its first director (1).

Oersted's high opinion of Zeise is clearly shown in the famous paper that he published first in Latin and then in English, French, German and Italian describing his classic experiment on 21 July 1820 on the discovery of electromagnetism. Repeating his earlier experiments now with a more powerful battery, Oersted wished to have present six trusted scientific colleagues as witnesses, and these included "that very skilful chemist Mr. Zeise, Doctor of Philosophy", so securing him a certain publicity throughout Europe (2).

Zeise's first incursion into the chemistry of platinum dates from 1827 when he reported to the Royal Danish Academy of Sciences the preparation by the action of alcohol upon platinous chloride of a compound of platinum, oxygen and carbon that had the properties of igniting not only oxygen and hydrogen but that also became red hot in alcohol vapour just as did the compound discovered by E. Davy, thereby liberating acetic acid. This he named "chloridum platinae inflammabile" (3).

Edmund Davy (1785–1857), the younger cousin of Sir Humphry, had published in 1820 an account of his preparation of very finely divided platinum by reducing a solution of platinum sulphate with alcohol and of its great activity at room temperature in the oxidation of a further quantity of alcohol (4). This swiftly encouraged Johann Wolfgang Döbereiner (1700–1849) to repeat the experiment, yielding what we should now refer to as platinum black, but unlike Davy he realised the great significance of the discovery, thus helping to initiate the study of heterogeneous catalysis (5).

Zeise's paper was published in German in 1827 (6) and also referred to by Berzelius in his Jahresbericht for 1828 (7) while a year later Liebig reviewed the work of all three, maintaining that

> "this black powder of Messrs. Davy, Zeise and Döbereiner is nothing else than extremely finely divided metallic platinum" (8).

The Classic Paper

It was in 1830 that Zeise presented a paper in Latin to the University of Copenhagen, published under the title

> "De chlorido platinae et alcohole vini sese invicem permutantibus nec non de novis substantiis inde oriundis."
>
> (The reaction between platinum chloride and wine alcohol and on the new substances arising therefrom.)

This paper, contained in the Anniversary Volume of the University for 1830, was quickly published in Poggendorff's *Annalen der Physik und Chemie* and in Schweigger's *Journal für Physik und Chemie* (9).

In his introduction Zeise referred to his earlier work as opening the way to his present research, adding that administrative work and other studies had delayed his pursuing the subject.

Using now platinic chloride instead of platinous chloride—although some platinous compound remained in the mixture—dissolving this in alcohol, evaporating excess solvent and reacting the residue with potassium chloride, Zeise obtained "very beautiful yellow crystals", while a similar salt was obtained when he used ammonium chloride instead of potassium chloride. This he described in a shorter paper immediately following his main publication (10). In the manner of the time, when many newly prepared compounds were given the name of their discoverer, the potassium compound became known, and is still known to this day, as Zeise's Salt, a compound we should now identify as $K[PtCl_3(C_2H_4)].H_2O$.

Zeise called the salt "sal kalico-platinicus inflammabilis" in his original Latin paper, and "entzündliches Kali-Platin-Salz" in the German version. At this time the adoption of Dalton's Atomic Theory together with the methods of organic analysis developed by Gay Lussac, Berzelius and Liebig made it possible, although rather lengthy and tedious, to determine empirical formulae although of course it was many years before either structural formulae or a reasonable system of nomenclature became possible. Zeise believed his salt to be a derivative of ethylene and he wrote:

> "In this compound a portion of the chlorine is present in the same manner as in metal chlorides, but another portion in the manner as in Chloräther (ethylene chloride) and Chlorwasserstoffäther (ethyl chloride).... Accordingly it is very probable that the flammable chloride is a compound of platinum chloride and chlorinated hydrocarbon."

He therefore set about a most painstaking series of analyses

> "which I have performed with great care; for the precise knowledge of the components of this substance seemed to me very desirable, not only because this compound offers a combination of elements that seldom occurs, but also because a correct determination of the proportions between carbon, hydrogen and chlorine might perhaps throw some light on the nature of chloräther and other compounds of this type".

The paper then continues with a long and detailed account of his analytical methods, using the atomic weights adopted by Berzelius in 1826 in which oxygen was taken as 100, and concluding with three alternative formulae:

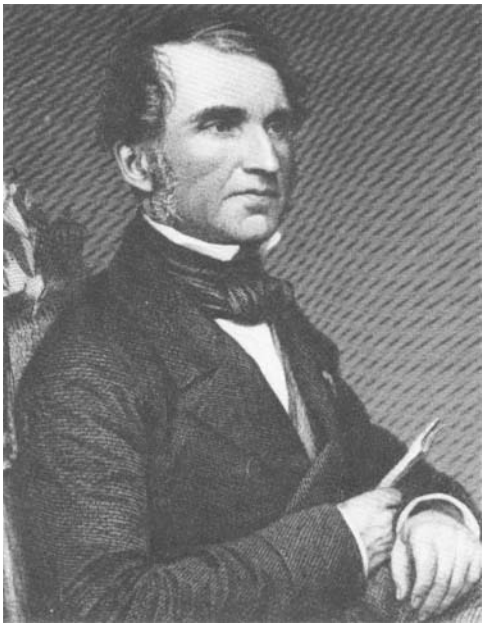
"$2\ PtCl^2 + 4H^2C + KCl^2$

or $2\ PtCl + 2(2H^2C + Cl) + KCl^2$

or, if desired

$2(PtCl + 2H^2C + Cl) + KCl^2$".

Zeise's paper attracted considerable attention, first from Berzelius and a little later from Liebig. Berzelius, who had himself prepared a



Justus von Liebig
1803–1873

The publication of Zeise's first paper in 1830 involved him in an acrimonious quarrel with Liebig who had successfully developed methods of organic analysis and thence the establishment of formulae for organic compounds. However his ideas on the constitution of Zeise's salt were proved to be incorrect

similar compound that he described in his Jahresbericht for 1830 (11) returned to the subject in 1833 (12), writing:

> "This salt was also observed by Zeise who, not satisfied with the simple observation of its existence, determined its highly curious composition. From his investigation it consists of the same hydrocarbon contained in the ethers and in alcohol combined with platinum."

Further approbation came from Poggendorff who wrote to Oersted:

> "May I congratulate your country which, through its latest work of Professor Zeise, has been assured of a place in the history of chemistry."

The Bitter Controversy with Liebig

But Zeise now became the victim of the long and sometimes bitter controversy that continued for more than twenty years among the leading chemists of the period. New organic compounds were being discovered, but their relationship was far from being understood and rival theories of their constitution were put forward. The term "olefiant gas" (ethylene), discovered in 1794 by four Dutch chemists and recognised by them as a compound of carbon and hydrogen, became adopted generally, and Berzelius referred to this as a radical that he named "Aetherin" writing $C^4H^8 = Ae$ and ascribing Ae + 2PtCl to Zeise's "Aethersalz" (13). Later he changed this to "Elayl" from the Greek word for oil and thus Zeise's compound became Elayl–Platinumchlorür, 2/4 El + PtCl, or one double atom of Elayl combined with one atom of $PtCl_2$ (14).

Dumas, with his assistant Polydore Boullay, had earlier considered alcohol and ether as hydrates of olefiant gas (15), and it was this that Berzelius referred to and which became the basis of the so-called Etherin theory.

Liebig on the other hand considered that alcohol and ether were derived from a hypothetical radical C_4H_{10} that he named Ethyl in a long paper in his *Annalen* in 1834 on "The Constitution of Ethers and their Combinations" (16). It was in the course of this paper that he attacked Zeise's findings and his concept of the proposed constitution of the platinum compound, arguing that this must contain oxygen and be a compound of ether, not of etherin (ethylene), and that its constitution supported his ethyl theory and not the views of Dumas and Boullay which Zeise favoured.

Zeise took strong exception to Liebig's criticism and repeated his careful analyses, completely substantiating his original concept of the composition of his platinum compound, publishing his results first in a paper to the

De chlorido platinæ et alcohole vini sese invicem permutantibus nec non de novis substantiis inde oriundis.

Introductio.

Si perpenderis, quanta sit chlorinæ facultas alcoholem vini permutandi, quam vero laxus ejusdem cum platina chemicus nexus, non certe miraberis, connubia quoque ex chlorina et platina conflata ipsam chlorinam quodammodo imitari. Rationem vero plenumque eventum hujus actionis non facile divinaveris. Docent enim, quæ jam traditurus sum, experimenta non ætherem tantum hic generari, sed novam oriri substantiam, platinam, chlorinam, carboneum et hydrogenium unita exhibentem.

Et quidem cum experimenta antea circa reciprocam chloridorum metallicorum et alcoholis actionem instituta id fere unice spectarent, num æther elici possit, fieri facile potest, ut postea in aliis quoque chloridis eundem deprehendamus agendi modum.

Jam quinque abhinc annis experimenta quædam institui, quæ viam hujus indagationis aperiebant, quæque in Recensione Actorum Societatis Regiæ Scientiarum Hafniensis anni 1825 & 1826 commemorata sunt. Agunt vero illa experimenta fere unice de pulvere nigro, virtutibus satis singularibus donato, qui existit, ubi protochloridum platinæ et alcohol invicem agunt. Postea, cum alios effectus hic concurrentes ulterius prosequerer, præcipue vero cum protochlorido deutochloridum substituerem, plura ani-

The opening page of the paper read by William Christopher Zeise in November 1830, reproduced from the Anniversary Volume of the University of Copenhagen for that year. Written in Latin, and running to forty six pages, it describes the preparation of the first organometallic compounds, the title reading in translation "The Reaction between Platinum Chloride and Wine Alcohol and on the New Substances Arising Therefrom"

Royal Academy of Science in Copenhagen in January 1836 and then in French and German translations (17). Not to be outdone, Liebig promptly reproduced this paper in his *Annalen* (18), following it immediately with one of his own on "The Aether Theory with Particular Reference to the foregoing Publication of Zeise" (19). Still maintaining that Zeise's salt contained oxygen and expressing doubts about his analyses, Liebig entered into a long polemical discussion of the shortcomings of the Etherin theory but curiously cited Zeise's recent discovery of the organic sulphur compounds that he named mercaptans, the earliest known organic compound containing sulphur combined, as Zeise realised, in the same manner as the alcohols and ethers (20) as supporting his own views. Shortly afterwards Liebig visited Paris in October 1837, discussed the matter fully with Dumas in a friendly way, and together they prepared a paper presented to the French Academy in which they settled their differences and concluded that:

> "In inorganic chemistry the radicals are simple; in organic chemistry they are compounds—that is all the difference" (21).

Writing to Wöhler on his return to Giessen Liebig commented

> "He (Dumas) now supported me in taking the disputed views on ether as correct and he has abandoned his Elaylgas Theory" (22).

Zeise's Formula Confirmed

Nearly a quarter of a century later Zeise's views were fully vidicated by two assistants of Hofmann in the Royal College of Chemistry in London. Johann Peter Griess (1829–1888) and Carl Alexander Martius (1838–1920) not only confirmed that "olefiant gas" (ethylene) was liberated when Zeise's salt was decomposed but

> "Confirmed perfectly the formulae given by Zeise in contradistinction to the opinion of Liebig who argued for the existence of oxygen in the group C_4H_5O in these compounds" (23).

In the third edition of his "Lehrbuch der Chemie" Berzelius included a full account of Zeise's platinum compounds but retaining his own term "Elayl" in each case. Thus the potassium salt was described as Elayl-Kalium-Platin-Chlorür which he maintained was investigated in his own laboratory by Gustav Magnus (1802–1870) during his stay in Stockholm in 1827, although Berzelius admitted that this was first studied and identified by Zeise (24).

In the last year of his life Zeise compiled a text-book in Danish on organic chemistry in which he naturally included details of his platinum compounds, although still following Berzelius in his terminology and describing his two new major compounds as Kalium-Elayl-Platinchlorür and Elayl Platinchlorür-Ammoniak (25).

The confirmation of Zeise's work by Griess and Martius has already been mentioned. These two workers went on to prepare further compounds of the same type. Identifying Zeise's salt as ethylene platinum chloride, they succeeded in producing compounds with some of the organic molecules recently discovered by Hofmann, diphenylamine, ethylene diamine and aniline (23). These compounds are now known to be bonded to platinum via nitrogen rather than via carbon as in Zeise's salt.

If further substantiation of Zeise's work was needed it came a little later from Karl Birnbaum (1839–1887) Professor of Chemistry in the Karlsruhe Polytechnic, who in 1867 undertook the synthesis of Zeise's original salt by passing ethylene gas (which he still referred to as Elaylgas) into a solution of chlorplatinic acid and adding potassium chloride. He obtained not only Zeise's salt but also its homologues with propylene and amylene (26).

The Work of Edward Frankland

No further work was carried out on these platinum complexes for many years, but in the meantime great strides forward were made in the general subject of the combination of metals with organic substances, chiefly by Edward (later Sir Edward) Frankland (1825–1899). His first discoveries, made in Bunsen's laboratory in Marburg in 1849, were of zinc methyl and zinc ethyl, and then of zinc amyl during a short stay with Liebig in Giessen, and it was Frankland who coined the term that describes this phase of chemistry:

> "I have applied the name organometallic to a family of compounds resulting from this investigation, the members of which contain a positive organic radical united directly with a metal. It serves to distinguish them from other organic compounds containing metals in which the metal and the organic radical are indirectly united or linked to each other" (27).

The zinc compounds discovered by Frankland have often been described in the literature, and even by Frankland himself, as

Sir William Jackson Pope
1870–1939
Professor of Chemistry at Manchester and later at Cambridge, Pope and his assistant S. J. Peachy prepared a further series of organometallic compounds of platinum in 1907 by the use of the new Grignard reagent

the first of the organometallic compounds, an obviously incorrect assessment, and it seems most probable that he was unaware of Zeise's original work. However, his own work yielded vital and valuable results in organic synthesis and he clearly foresaw the potential application that lay ahead. In his first major paper to the Royal Society in 1852—its publication delayed for over a year because the then secretary, Sir George Stokes, inadvertently left the manuscript in his desk for that length of time—includes this forecast:

> "The extraordinary affinity of zincmethylium for oxygen, its peculiar composition, and the facility with which it can be procured cannot fail to cause its employment for a great variety of transformations in organic compounds" (28).

Frankland's study of the analogues of his first compounds led him, as is also well known, to the first general statement on the definite combining powers of the elements and so to the theory of valency (29). He prepared many organometallic compounds of antimony, tin, lead and mercury, but later he had to admit that his zinc ethyl reagent failed when applied to the halide compounds of platinum as well as to copper and silver and that the organic group did not unite with these metals (30).

Another half century had to pass before the existence of a series of platinum alkyl compounds was established, and what made this possible was the discovery by Francois Auguste Victor Grignard (1871–1935), an assistant to Professor Philippe Barbier (1848–1922) in the University of Lyons. Between them they decided to replace zinc by magnesium in their organic halides, and then Grignard went on alone to develop their reactions, publishing his results as his doctoral thesis in 1901, and later, in 1912, being awarded the Nobel Prize.

Then came a preliminary announcement to the Chemical Society in 1907 by W. J. Pope (later Sir William Jackson Pope) and his assistant S. J. Peachy at the University of Manchester:

> "No alkyl compounds of metals belonging to Group VIII of the Periodic Table have hitherto been described. The authors find that the chlorides, or in some cases the oxides of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum react vigorously with magnesium methyl iodide: they desire to reserve the study of the action of Grignard's reagent on compounds of the metals named" (31).

They went on to describe the preparation of "trimethylplatinimethyl iodide", $(CH_3)_3PtI$ and "trimethylplatinimethyl nitrate" $(CH_3)_3Pt.NO_3$ and a number of other salts of this kind. The chairman of the meeting, Sir Henry Roscoe, congratulated the authors on having opened up an entirely new branch of investigation which might indeed be said to be a wonderful "find".

Two years later, Pope having now taken up the post of Professor of Chemistry at Cambridge, they presented a more detailed account to the Chemical Society on the organometallic compounds of platinum obtained by the action of magnesium methyl iodide on platinic chloride (32). These included those previously referred to above as well as diamminotrimethylplatinic iodide, trimethylplatinic cyanide, and potassium trimethylplatinic platinocyanide. The paper concluded with an expression of thanks to Mr. George Matthey, F.R.S., for generously allowing them the use of the platinum required for this work.

It is still later, in the third decade of this century, that the organometallic compounds of palladium and rhodium among the other platinum metals began to be investigated, and there is now of course an enormous compilation of literature on all these complexes. But in the many publications on the subject the names of William Christopher Zeise and of his salt still feature.

It has also been the tradition in Copenhagen for Zeise's successors in the teaching of chemistry to follow up his work. In 1900 Professor Sophus Mads Jørgensen, also a native of Slagelse, gave a long review of the constitution of platinum organometallic compounds and of Zeise's salt in particular (33) while at about the same time Professor Einar Biilmann described similar compounds with higher alcohols (34). More recently Professor Kai Arne Jensen, also of the University of Copenhagen, published several papers on the structure of platinum compounds with complex olefins (35). These and later investigations have not only confirmed the importance of Zeise's original work but have succeeded in showing exactly how the platinum atom is co-ordinated to the organic compounds.

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