On the Cover

$[(C_2H_4)PtCl_3]^-$, the Anion of Zeise's Salt, $K[(C_2H_4)PtCl_3]\cdot H_2O$

The first report by William Christopher Zeise of a reaction of a platinum chloride with ethyl alcohol appeared in a Danish journal in 1825.[1] This journal must not have been widely available, because news of this reaction reached the European chemical community by way of Berzelius' *Annual Report*[2] and republication of his report of Zeise's work in a German journal in 1827.[3] A translation of Berzelius' short account follows:

> Zeise, Professor of Chemistry in Copenhagen, has discovered a compound of platinum, oxygen and carbon which possesses the property that it not only ignites gaseous oxygen and hydrogen, but also that it heats up to glowing in alcohol vapor, like the compound discovered by Davy, and in this way generates acetic acid. This compound is obtained by mixing platinous chloride ($PtCl_2$) with 12 parts of alcohol of specific gravity 0.813 in a retort connected to a receiver and gently heating until the platinum chloride turns black and the liquid phase becomes clear and colorless. HCl is formed and the alcohol becomes acidic. After the alcohol has been decanted, the precipitate is washed with warm water until the washings no longer are acidic. During the washing, as well as during its storage under water, the precipitate evolves gas bubbles that have an ether-like odor. After drying, gentle heating of the precipitate results in weakly explosive ignition even in the absence of air. Carbon dioxide, oxygen and, generally, a small amount of acetic acid-containing water are given off. The same phenomenon of inflammation is observed when the solid starts to glow in alcohol vapors. Ether, petroleum (ether) and oil of turpentine do not cause inflammation.

After this not very illuminating preliminary communication, further work which shed more light on this rather strange chemistry was published by Zeise in 1830 (in a University Festschrift in Latin, with title "De chlorido platinae et alcohole vini sese invincem permutantibus nec non de novis substantiis inde oriundis commentatio, qua festo academico, mense novembri A. 1830 celebrato prolusit Dr. Willielmus Christophorus Zeise, etc.") which appeared in German translation in 1831.[4]

The black solid was investigated in more detail. Although it contained platinum and carbon, it was not an ethylene−platinum complex, consisting instead of finely divided metallic platinum (which is known to adsorb oxygen) and organic impurities.

Zeise found that the reaction of ethyl alcohol with platinum tetrachloride ($PtCl_4$) proceeded differently. When $PtCl_4$ was dissolved in 10 parts by weight of ethyl alcohol and the solution was concentrated by gentle heating to one-sixth of the original volume, a brown solution remained, usually containing some black powder. Evaporation of the concentrate left a brown residue that contained yellow and black particles. When heated more strongly, this residue swelled, giving off an inflammable gas and gaseous HCl and eventually inflamed, leaving behind platinum sponge. Zeise called the brown residue the "crude inflammable chloride".

The breakthrough, the isolation of a pure, crystalline compound, came when Zeise added potassium chloride to such a concentrated $PtCl_4$/ethyl alcohol reaction solution and evaporated the resulting solution. Beautiful lemon-yellow crystals, often one-half inch or more in length, were isolated. On longer exposure to air and light, they gradually became covered with a black crust. They contained water of hydration, which was lost when they were kept over concentrated sulfuric acid in vacuo or when heated to around 100° C. Chemists in those days often reported how the compounds that they had prepared tasted. Zeise described the taste of this potassium salt as metallic, astringent, and long lasting.

When heated in air to ∼200 °C Zeise's potassium salt became black; on stronger heating, gaseous hydrogen chloride and an inflammable gas were given off and a gray residue remained. Because it easily inflamed when heated in air over an open flame, Zeise called his potassium salt (that we now know as "Zeise's salt") "inflammatory potassium platinum salt" (*sal kalicoplatinicus inflammabilis*). When an aqueous solution of this potassium salt was heated to boiling in a "pneumatic apparatus", i.e., one with provision for catching the evolved gases, a large volume of inflammable, presumably hydrocarbon, gas was given off; the distillate was aqueous hydrochloric acid. The black residue on ignition in air gave metallic platinum.

Zeise devoted much effort to the elemental analysis of the inflammable potassium platinum salt and, after many experiments, came to the conclusion that the formula of the water-free salt was $[2\ PtCl_2 + 4\ H_2C + KCl_2]$, a composition that must be considered in terms of the atomic weight scale current in 1830, where water was HO, not H_2O. On the basis of this finding Zeise suggested a formula of $[PtCl + 2\ H_2C + Cl]$ for the originally formed "inflammable platinum chloride". In this paper Zeise also described the analogous ammonium salt, an "inflammable platinum ammonium

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[1] Zeise, W. C. *Overs. K. Dan. Vidensk. Selsk. Forh.* **1825−26**, 13.
[2] Berzelius, J. J. *Jahresber. Fortschr. Chem.* **1826**, *7*, 129.
[3] *Poggendorf's Ann. Phys. Chem.* **1827**, *9*, 632.
[4] Zeise, W. C. *Poggendorf's Ann. Phys. Chem.* **1831**, *21*, 497. Also published in German in: *Schweigger J. Chem. Phys.* **1831**, *62*, 393; **1831**, *63*, 121, 136.

10.1021/om000993+ CCC: $20.00

salt". It should be noted that all of this synthetic work and the very extensive analytical work were carried out by Zeise alone. These were the beginnings of chemical research in Denmark. In fact, Zeise had the first professorship devoted solely to chemistry in that country. He had no graduate students or assistants to help him in his research, which makes his contributions to chemistry all the more remarkable.

In a following short paper, which also appeared in German translation,[5] Zeise tried to develop an analogy between his "inflammable platinum chloride", i.e., [4 $H_2C + 2\ PtCl_2$], as he now wrote it, and an alkyl chloride [3 $H_2C + CCl_2$] (a "chloroether" in the nomenclature of the 1830s). He suggested, on the basis of such considerations, that his "inflammable platinum chloride" was a compound of platinous chloride ($PtCl_2$) and "olefiant gas" or, in German, "ölbildendes Gas", i.e., an unsaturated hydrocarbon. This led him to change the name of the derived potassium salt to "hydrocarbonated chloroplatinum-potassium". So now there is a first suggestion of an organoplatinum compound!

With this interpretation of his platinum complexes Zeise ran into the buzz saw of a major, spirited controversy between Justus Liebig and Jean Baptiste Dumas, both big names in European chemistry. The controversy concerned the "structure" (in terms of constitution and compound type) of known organic compounds.[6] Zeise's view of his platinum complexes followed the Dumas point of view. This did not sit well with Liebig, who championed an "ether theory" and saw in Zeise's platinum complex an example that would fit nicely into his theoretical framework *if* it contained oxygen. In a long paper[7] dealing with his ether theory, Liebig considered Zeise's platinum complexes. Praising Zeise for his unusually conscientious analytical work, he followed by saying that Zeise had it all wrong. Liebig said that his own repetition of the thermolysis of a sample of the (supposedly) dehydrated Zeise's salt gave a "visible" amount of water that had an ether odor, so it did indeed contain oxygen. Furthermore, he said, taking into consideration the averages of all of the many Pt, K, Cl, C, and H analyses that Zeise had reported, only a 97.5366% accounting of these elements resulted. So, said Liebig, the missing ~2.5% must reflect an oxygen content. Hence Zeise's organic part was an ether (i.e., an alkoxy group). So, to Liebig's satisfaction, this brought Zeise's platinum complex into the framework of his ether theory.

Zeise did not argue the matter; he repeated the elemental analyses of very carefully dried samples of the anhydrous potassium salt even more carefully.[8] The sum of the percentages by weight of Pt, K, Cl, C, and H was 99.64%, leaving no room for oxygen. Liebig's observation of the formation of water during the thermolysis of the anhydrous potassium salt Zeise ascribed either to incomplete drying or interaction of the HCl given off at higher temperature with moisture in the apparatus.

Liebig, obviously rather irked, replied with a pompous and condescending attack,[9] brushing aside Zeise's new analytical results as flawed and proceeding to give Zeise a lesson in modern analytical chemistry. (Among Liebig's recommendations was a universal empirical "correction" of −0.2% for *all* hydrogen analyses.)

Liebig believed that he had the last word, but, in the end, it was Zeise who prevailed. It took some time. Zeise died in 1847 and did not live to see his vindication. In 1861, Peter Griess and C. A. Martius, working in the laboratories of the Royal College of Chemistry in London, prepared Zeise's potassium salt and confirmed his analytical results, i.e., no oxygen. They heated it to 200 °C and absorbed the evolved gas in bromine water.[10] The product was 1,2-dibromoethane, which led these workers to regard Zeise's salt as the KCl adduct of ethyleneplatinum chloride, writing this equation:

$$C_4H_4Pt_2Cl_2,\ KaCl \rightarrow Pt_2Cl_2 + KaCl + C_4H_4$$

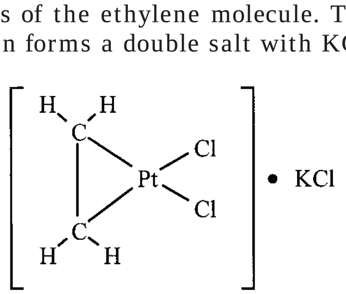
(still the old atomic weight scale)

Griess and Martius in the last paragraph of their paper stated their intention of trying to prepare Zeise's ethyleneplatinum chloride directly by the reaction of ethylene with $PtCl_2$ (which would be a better proof of its constitition) but apparently never reported doing so. It was Karl Birnbaum of the University of Karlsruhe who in 1868 reported the successful preparation of this compound by reaction of ethylene with $PtCl_2$ in concentrated HCl under a pressure of 6 in. of mercury.[11] Addition of KCl to the solution gave Zeise's potassium salt, which Birnbaum wrote as [$C_2H_4 \cdot PtCl_2 \cdot KCl$] + H_2O. (Today's atomic weight scale was now in place.) Birnbaum's complete elemental analysis of his product was in excellent agreement with that reported by Zeise. Analogous salts could be prepared starting with propene and 1-pentene.

Having demonstrated that Zeise's experiments and interpretations were indeed correct, Birnbaum suggested that Zeise's synthesis proceeded as follows:

$$PtCl_4 + 2\ C_2H_5OH \rightarrow C_2H_4PtCl_2 + CH_3CHO + 2\ HCl$$

noting he had found that in the reaction of amyl alcohol with $PtCl_4$ to give the 1-pentene−$PtCl_2$ complex the corresponding aldehyde, C_4H_9CHO, had been formed. He also made the first suggestion for the "structure" of Zeise's salt, namely that platinum, being tetravalent, was bonded to two Cl atoms and (equally) to the two carbon atoms of the ethylene molecule. The resulting molecule then forms a double salt with KCl, **1**.



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The constitution of Zeise's ethyleneplatinum chloride and of the derived potassium salt thus had been demonstrated. The structure of these complexes and the

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(5) Zeise, W. C. *Poggendorf's Ann. Phys. Chem.* **1831**, *21*, 542.

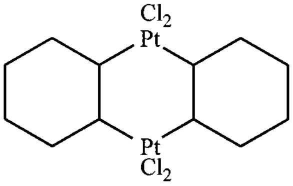
(6) A brief account of the Liebig-Dumas controversy may be found in a biography of Liebig: Holmes, F. L. *Dictionary of Scientific Biography*; Gillispie, C. C., Ed.; Charles Scribner's Sons: New York,- 1976; Vol. VIII, pp 329−350.

(7) Liebig, J. *Ann. Pharm.* **1834**, *9*, 1 (see pp 9−11).

(8) Zeise, W. C. *Poggendorf's Ann. Phys. Chem.* **1837**, *40*, 234.

nature of the bonding remained unknown for another 85 years. During this time main group chemistry, stimulated by Frankland's discovery of ethylzinc iodide and diethylzinc in 1849 and spurred on by the discovery of organomagnesium halides by Grignard in 1900, blossomed. During these years there also were notable, but for the most part isolated, discoveries in the area of transition metal organic chemistry: the trimethylplatinum compounds, e.g., $(CH_3)_3PtI$ (Pope and Peachey, 1909), the mysterious "polyphenylchromium" compounds (F. Hein, 1919), phenylcopper (R. Reich, 1923), alkylgold halides (Pope and Gibson, 1907; Kharasch and Isbell, 1931), and butadieneiron tricarbonyl (Reihlen, 1930).[12] The discovery of the platinum carbonyl halides by Schützenberger in 1869 and of homoleptic metal carbonyls ($Ni(CO)_4$ by Mond in 1888; $Fe(CO)_5$ independently by Berthelot and Mond in 1891) opened up a vast new subfield of organometallic chemistry.[13] Metal carbonyl chemistry was vigorously pursued in the 1920s to 1940s, in particular by Manchot and Hieber and their respective co-workers.

While these developments were providing the foundation of the new discipline of organometallic chemistry, Zeise's salt and the few other known platinum olefin complexes were languishing on the sidelines: chemical curiosities of unknown structure and unrevealed bonding. Krause and von Grosse[12] suggested the possibility of a heterocyclic, σ-bonded structure, as shown for the cyclohexene complex, **2**, but said that it was up to future investigations to determine the actual structure.



2

The discovery of ferrocene in 1951 (Kealy and Pauson; Miller, Tebboth, and Tremaine) and the recognition of its unprecedented sandwich structure (E. O. Fischer and W. Pfab; G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, 1952) initiated the explosive growth of transition metal organic chemistry that continues on with great vigor today, some 50 years later. The worldwide interest in ferrocene, an unusual (at that time), very stable, reactive organoiron compound, rekindled interest in the previously known but poorly understood transition metal organic compounds. Among these was Zeise's salt. It was M. J. S. Dewar who in 1951 proposed the correct bonding picture for metal–olefin complexes:[14] a normal molecular dative bond involving overlap of the filled π bonding molecular orbital of the C=C bond and a vacant metal orbital of appropriate symmetry, reinforced by back-bonding involving the π^* antibonding orbital of the C=C bond and a filled metal d orbital of appropriate symmetry. This concept was illustrated using as an example an Ag^+–olefin complex, but Dewar mentioned also the olefin complexes of nickel and platinum. Chatt (who earlier had proposed an ethylidene structure for Zeise's salt, **3**) and Duncanson[15] applied this concept to platinum–olefin complexes, and the figures published in their paper have become textbook examples (Figure 1, 2).[16]

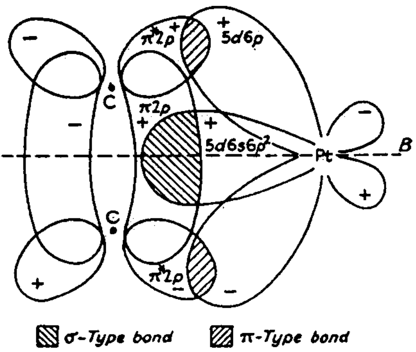
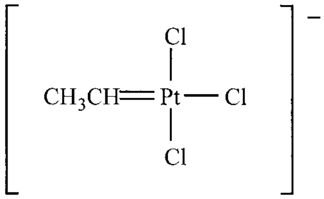


Figure 1. Orbitals used in the combination of ethylene and platinum (from ref 15; reproduced by permission of the Royal Society of Chemistry).



$$\left[\begin{array}{ccc} & \mathrm{Cl} & \\ & | & \\ \mathrm{CH_3CH}{=} & \mathrm{Pt} & -\mathrm{Cl} \\ & | & \\ & \mathrm{Cl} & \end{array}\right]^-$$

3

In Zeise's time X-ray crystallography had not even been imagined, but in one of his papers[4] he described the crystal morphology of his potassium salt, as chemists of that time liked to do when they had crystalline products, often with nice illustrations. The first determination of the structure of Zeise's potassium salt by X-ray diffraction was reported in 1954.[17] In succeeding years, several other such studies were published, and the final, most definitive study was one carried out by neutron diffraction.[18] Figure 3 shows the $[(C_2H_4)PtCl_3]^-$ anion (the cover picture), and Figure 4 the molecular structure of the complete molecule, $K[(C_2H_4)PtCl_3]\cdot H_2O$, as determined in this study. The carbon atoms of the ethylene ligand, whose C–C axis is perpendicular to the $PtCl_3$ plane, are equidistant from the Pt atom. Some d_π–p_{π^*} back-bonding from Pt to C_2H_4 is indicated by the fact that the C–C distance is 0.038 Å longer than that in free C_2H_4. The four C–H bonds are bent away from the Pt atom, another indication of such back-bonding. So 150 years after the discovery of the platinum–ethylene complexes, our understanding of their nature was finally complete!

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(9) Liebig, J. *Ann. Pharm.* **1837**, *23*, 12.

(10) Griess, P.; Martius, C. A. *Ann. Chem.* **1861**, *120*, 324.

(11) Birnbaum, K. *Ann. Chem.* **1868**, *145*, 68.

(12) See *Die Chemie der metall-organischen Verbindungen* (Krause, E.; von Grosse, A.; Gebrüder Borntraeger: Berlin, 1937) for a detailed account of the development of organometallic chemistry from 1850 to the 1930s.

(13) See Chapter XIV of *Modern Aspects of Inorganic Chemistry* (Emeléus, H. J.; Anderson, J. S.; 2nd ed., 1952; Routledge and Kegan Paul: London) for an account of the development of metal carbonyl chemistry from its beginnings through the 1940s.

(14) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.

(15) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(16) For a brief discussion of the development of ideas concerning the structure and bonding of platinum–olefin complexes see: Olsson, L.-F. In ref 19b, pp 57–72.

(17) Wunderlich, J. A.; Mellor, D. P. *Acta Crystallogr.* **1954**, *7*, 130.

(18) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653.

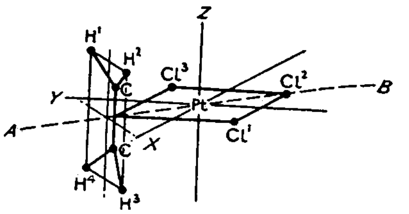

Figure 2. Spatial arrangement of atoms in $[(C_2H_4)PtCl_3]^-$ (from ref 15; reproduced by permission of the Royal Society of Chemistry).

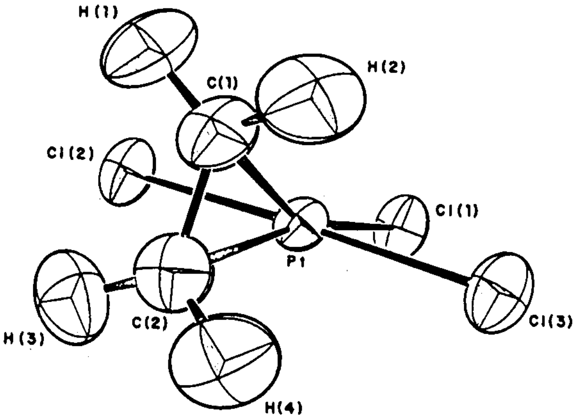

Figure 3. Molecular geometry of the Zeise anion, $[(C_2H_4)PtCl_3]^-$ (from ref 18).

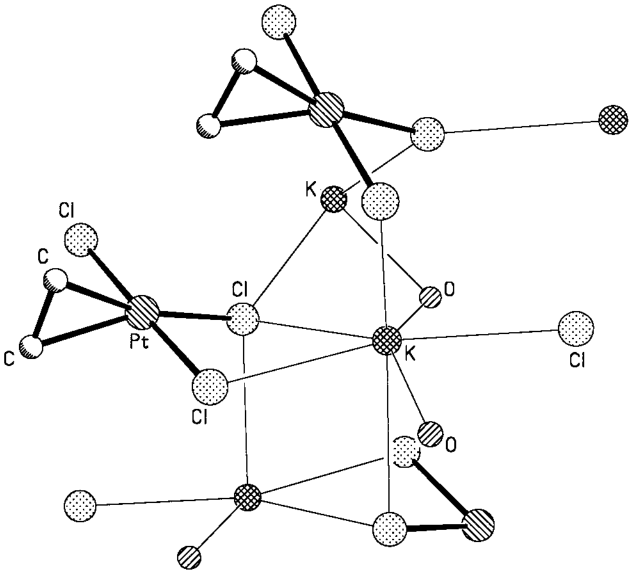

Figure 4. Structure of Zeise's salt, $K[(C_2H_4)PtCl_3]\cdot H_2O$.

So much for the molecule. Its discoverer also merits a few paragraphs since he was an important synthetic chemist of the first half of the 19th century.[19,] William Christopher Zeise (Figure 5) was born in 1789 in Slagelse, Denmark, the son of Friedrich Zeise, a pharmacist, and Johanna Helena Hammond. He was trained as a pharmacist in his father's pharmacy and then went to Copenhagen for further studies. There he lived with H. C. Oersted and his family. Oersted was professor of physics and chemistry at the University of Copenhagen (who later in his career discovered electromagnetism), and, for a time, Zeise was his lecture assistant. Zeise studied medicine, chemistry, and physics at the University of Copenhagen and obtained his degree in pharmacy in 1815 and his doctoral degree in 1817 (the latter on the basis of independent research on the action of alkalies on organic substances). As was usual in those days, Zeise's studies were followed by travels abroad, in particular, studies in analytical chemistry in Göttingen and a visit in Paris, where he spent some time in the laboratories of Chevreul. On his return to Copenhagen, Zeise again spent some time with Oersted, assisting him and carrying out independent research on organosulfur compounds (he discovered the xanthates in 1823). In 1822, Zeise was appointed Extraordinary Professor of Chemistry at the University of Copenhagen, and in 1829, Professor of Organic Chemistry at the newly founded Polytechnic Institute of Copenhagen, a position he held until his death in 1847.

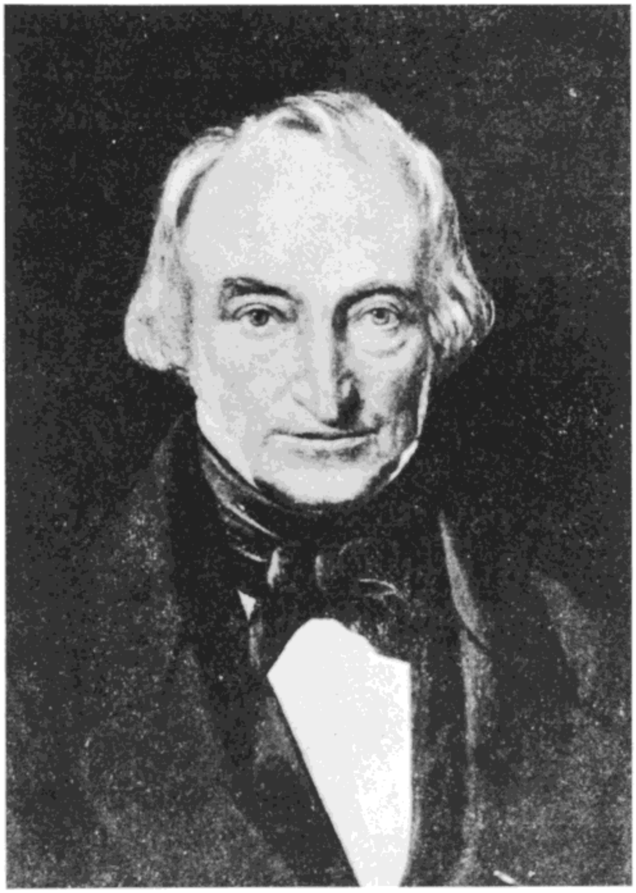

Figure 5. William Christopher Zeise (by permission, Edgar Fahs Smith Collection, University of Pennsylvania).

Zeise's research was devoted in large part to the organic chemistry of sulfur.[20] In addition to discovering the xanthates, he discovered the thiols in 1832, naming them mercaptans (a trivial name which has stuck) because they form insoluble mercury salts (derived from *corpus mercurium captans*).

Zeise apparently carried out some of his research in a home laboratory in the house where he lived. Here a

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[19] Biographical accounts of W. C. Zeise: (a) Veibel, S. In *Dictionary of Scientific Biography*; Gillispie, C. C., Ed., Charles Scribner's Sons: New York, 1976; Vol. XIV, pp 599–600. (b) *William Christopher Zeise—en dansk kemiker*; Morsing, T., Ed.; *Dansk Selskab for historisk Kemi, Historisk-kemiske skrifter nr. 2,* 1990. (c) Jensen, K. A. *Centaurus* **1989**, *32*, 324.

[20] An excellent account of Zeise's research in organosulfur chemistry is given in ref 19c.

study of the reactions of phosphorus and P_2S_5 with acetone and ether resulted in formation of some products that he could not identify. Nevertheless, he reported on this work at the Third Meeting of Scandinavian Natural Scientists in Stockholm in 1842. Berzelius, who was present at Zeise's talk, gave an account (in German) of what Zeise said in a letter to his friend, the noted German chemist Friedrich Wöhler.[21,22] A translation follows.

> Zeise gave a lecture about his experiments on the action of phosphorus and phosphorus pentasulfide on acetone and ether. He showed off several of the products obtained in this way, of which three were crystalline solids and one a liquid. The latter, he recounted, was so malodorous (a smell reminiscent of cat piss) that during the course of his experiments he had stunk up the entire house in which he rented an apartment. First the landlord drowned all the cats in the house in the belief that one of them was the culprit. However, when the stench did not go away, further investigations aimed at removing this very annoying odor showed Zeise to be the real cat. Of course, they could not drown Zeise, but they got so nasty that Zeise did not dare to continue his experiments in the house.

Certainly one of the more notable conference reports! The odiferous product with a catty odor was thought by later workers to be thioacetone, but in 1967, a compound that had just such an odor was identified as 4-mercapto-4-methyl-2-pentanone.

Among Zeise's other research areas was a study of tobacco—of the products of the dry distillation of tobacco and of the components of tobacco smoke (in 1843)—and he was one of the earliest investigators of carotene (1846). But in the organometallic community, he is remembered as the man who prepared the first organometallic compounds, and his $[(C_2H_4)PtCl_3]^-$ anion, our cover molecule, is, and will remain, a textbook example in structure and bonding.[23]

Zeiss suffered ill health most of his adult life. This is, perhaps not too surprising in view of his continuing activities in the laboratory involving toxic materials including all sorts of volatile sulfur compounds, platinum complexes, and mercury compounds (and tasting them)—work carried out not in an efficient fume hood but in a poorly ventilated room.

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(21) Wallach, O. *Briefwechsel zwischen J. Berzelius und F. Wöhler*; Engelmann: Leipzig, 1901; Vol. 2, p 309.

(22) This story is contained in a Letter to the Editor by Stig Veibel (*Chem. Ind.* (*London*) **1964**, 1621), which gives the German text. My apologies to those who might be offended, but Berzelius did say "Katzenpisse". Veibel's letter notes that "Zeise was once ordered out of the Royal Theatre because the smell adhering to his clothes was unbearable for his fellow-listeners in the theatre."

(23) For earlier accounts concerning Zeise's salt see: (a) Thayer, J. S. *J. Chem. Educ.* **1969**, *46*, 442. (b) Thayer, J. S. *Adv. Organomet. Chem.* **1975**, *13*, 1.