# Frankland — the First Organometallic Chemist

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Let me begin with an assertion of almost brutal simplicity: *our subject, organometallic chemistry, was founded by Sir Edward Frankland*. In two respects this can be challenged: Frankland was not the first to isolate an organometallic compound. This honour belongs to Zeise, who in 1827 isolated potassium trichloro(ethylene)platinate though he had not the faintest idea of its nature or significance. And Frankland was also preceded by Bunsen, with his organo-arsenic compounds derived from cacodyl (though some would argue that arsenic was not a true metal). Also, Frankland was not then a "Sir", having been knighted nearly half a century later, and then for reasons that had nothing to do with organometallic chemistry. Otherwise, our opening statement is unambiguously true.

Edward Frankland was a young Lancashire lad, devoid of any normal university training, but intrigued by the possibilities of applied chemistry, and bewildered by the fog of ignorance concerning finer points of chemical constitution. Despite momentous efforts by Davy, Berzelius, Liebig and many others no one was any the wiser about the nature of chemical compounds. True Berzelius had dominated the subject with his notion that every substance was electrically polarised, in which he greatly improved and expanded the simpler concept of the English chemist Sir Humphry Davy. Inorganic salts in solution could be decomposed by electrolysis, but this was not usually true of organic compounds. Nevertheless there was some evidence for the existence in organic molecules of parts that remained intact through many reactions, and these were called "radicals". The benzoyl radical had been shown to persist unchanged by the very early work of Liebig and Wöhler (1832), so perhaps benzoyl which formed a chloride, hydroxide and even peroxide could be deemed analogous to sodium or potassium, which did the same thing and were unquestionably "positive". The great Berzelius had further supposed that ether was an oxide of the radical ethyl, and shortly afterwards that acetic acid was composed of methyl, oxalic acid and water. These were nightmare scenarios for many chemists, but some were impelled to search for the simple radicals methyl and ethyl. Amongst these was Edward Frankland.

Though largely a self-taught chemist, he went to London in a search for jobs and soon landed a place as assistant to Lyon Playfair, chiefly teaching chemistry at the College of Civil Engineering and general studies at Putney. At this ephemeral institution he taught civil engineers in a makeshift laboratory, and also made the momentous acquaintance of the slightly older Hermann Kolbe. Some joint research by them was able to establish the identity of nitriles as aliphatic cyanides (1847).

Soon after this Frankland was persuaded by Kolbe to make a 3-month break with Putney and accompany him to the laboratory of Bunsen at Marburg in Germany. It was made much more attractive by Bunsen's known interest in organic derivatives of arsenic, and summarised below:
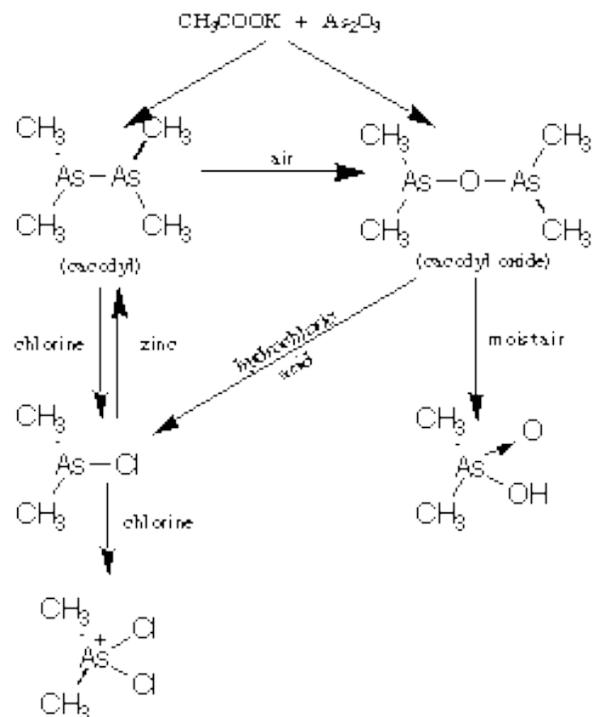

Bunsen was also becoming known as a master of gas analysis. This was likely to become useful as in his experiments on aliphatic acids Kolbe had already formed a gas at the anode. He had taken pentanoic acid and obtained a product which he thought was "butyl" but was in fact octane. The production of what seemed a radical much excited Frankland, and Bunsen's new facilities would serve him well. The two English friends accordingly attempted to isolate by chemical means ethyl from propionyl nitrile, now understood to be ethyl cyanide. Potassium was the reactive metal that would hopefully expel ethyl In the event ethyl was not recognised and the reaction was complicated by impurities in the reagents. A solid ("kyanethine') was isolated, presumably through a base-catalysed trimerization:
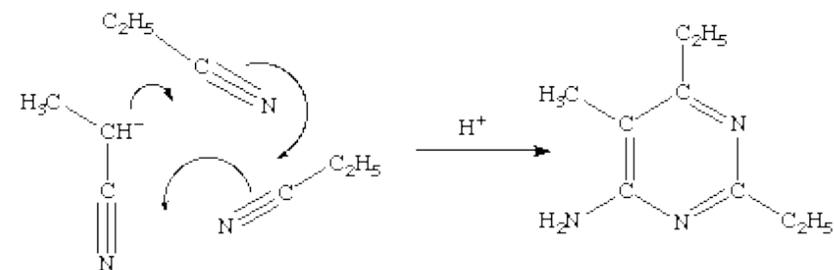
Other activities intervened, including the first meetings with his future wife, Sophie. After three months Frankland returned to England, leaving Kolbe behind to complete his own researches. He was now to receive another call, to teach at Queenwood College in Hampshire, a short-lived institution founded by the Lancastrian Quaker, George Edmondson, schoolmaster and visionary Socialist.
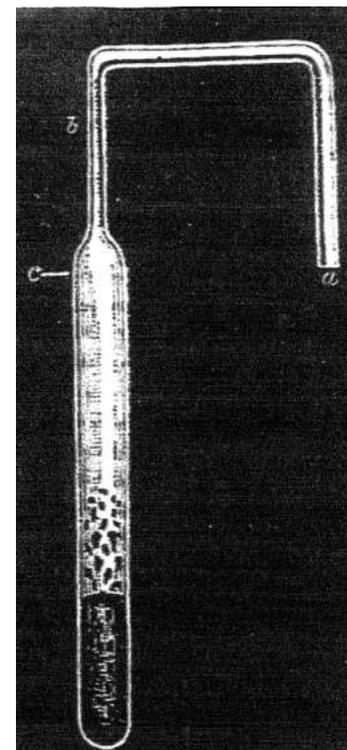
Here Frankland settled in, soon meeting his physicist colleague John Tyndall, and here he taught chemistry with a syllabus that still survives. As time permitted (not very often), he was able to continue his search for the elusive radicals. He decided on the momentous reaction between potassium and ethyl iodide. He used a very simple apparatus, a sealed tube, immersed in hot oil, obtaining and examining the gaseous product. It was not, as he had hoped, ethyl but a mixture of ethylene and ethane in approximately equal proportions, together with some hydrogen. Alas the experiments were terminated by a disastrous explosion from which he escaped injury. Seeking a less active metal than potassium he determined to try the gentler reagent zinc. This was placed in a tube into which the ethyl iodide was introduced; the tube was then sealed, and that was the end of his chemical work at Queenwood, for the simple reason that a eudiometer to examine the gaseous product was no longer available and the tube remained sealed.
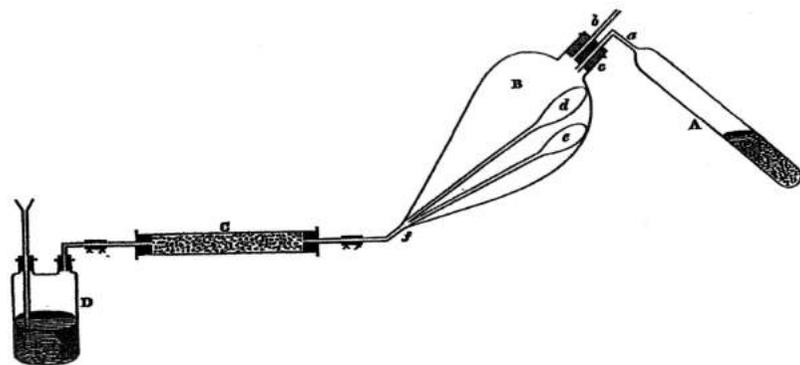
In this apparatus
    A is the dialkylzinc
    B is the receiver, containing several bulbs.
    C is a calcium chloride tube
    D is a hydrogen generator
When the apparatus has been flooded by hydrogen, the tubes at b and f are sealed.

The 14 months at Queenwood came to an abrupt end when Frankland, this time urged by Tyndall as well as Kolbe, returned to Marburg to work with Bunsen. For the first three months he worked, largely unsupervised, on a range of odd experiments involving metals and organic compounds, but with no clear result. After the festivities of Christmas, 1848, he returned to the attack, examining first the action of sodium on fatty acids. A hydrogen-containing gaseous product was unsatisfactory, and then his thought reverted

to those sealed tubes from Queenwood, in February he opened one under water. A violent reaction took place, and an "enormous" quantity of gas evolved. Analysis implied that ethyl [butane] had indeed been formed, and other experiments were begun. In one of them needle-like crystals and a limpid liquid were noticed in the tube before it was opened. Frankland also thought of replacing ethyl iodide by its methyl cogener, and reported in 1849 what we should call dimethylzinc. He also refers to the availability of diethylzinc. In a much later publication he depicts the apparatus in which the volatile, reactive zinc alkyls could be distilled, an early example of distillation in an inert atmosphere.

Thereafter he was known in Germany as "the discoverer of ethyl". A short sojourn in Giessen enabled him to report the preparation of "zinc amyl" in 1850.

He returned to England in January, 1850, to take up another, more senior, job at Putney. Here he taught chemistry, to a syllabus that has also survived. It had a strong emphasis on applied chemistry and also (curiously enough) on arsenic. He had little time for research, but did manage to launch one long-term project. He writes:

> I was particularly anxious to try the effect of tight in producing or favouring the decomposition of the iodides of the alcohol radicals by various metals. The chemical laboratory at Putney was particularly well situated for carrying out such experiments. It was an isolated building, situated in the middle of an extensive lawn, sloping down to the Thames ... and had a flat place upon the roof, on which experiments in the open air could be conveniently carried on. Having provided myself with a concave platinised reflector to concentrate the sun's rays, I proceeded, as the spring advanced, to expose iodide of ethyl in contact with various metals to intense solar light. When it was desired to exclude the simultaneous action of heat, the sealed tubes containing the iodide and metals were placed under water, coloured blue, by a solution of ammonio-sulphate of copper.

In our terms there is a suggestion of a radical-ion mechanism, photochemically triggered by a homolytic fission of a carbon-halogen bond.

Frankland also tried replacing zinc by other metals, though at first only tin appeared to undergo appreciable reaction. But he found that tin and ethyl iodide *did* react, at elevated temperatures or on exposure to strong sunlight. A complex pattern of subsequent reactions led to a yellow oil, "stanethylium". Other reactions that he reported to the Royal Society in 1852 were these:

iodide of ethyl + tin

sulphide of stanethylium

sunlight ↓

↑ acid + H_2S

iodide of stanethylium —alkali→ oxide of stanethylium —HCl→ chloride of stanethylium

heat; water ↓   HI ↘   air ↑   zinc ↗ HCl

STANETHYLIUM

hydride of ethyl + olefiant gas

heat above b.t.   HBr ↘

tin + liquid, possibly bimethide of tin

bromide of stanethylium
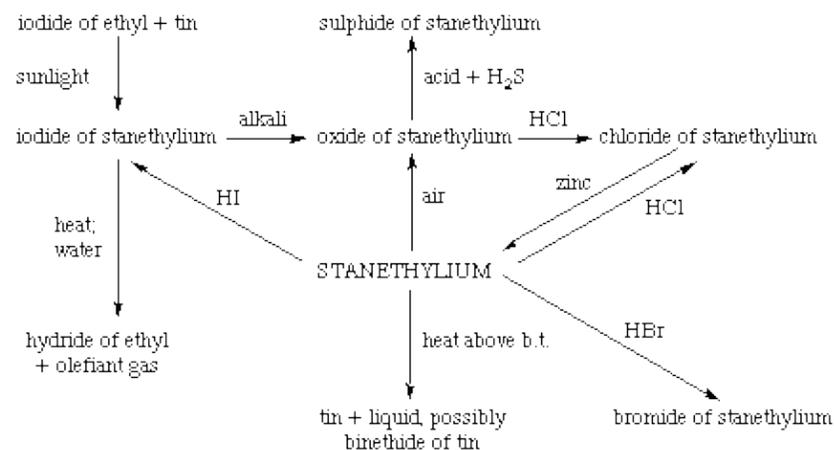
The nature of "stanethylium" is certainly not diethyltin, as Frankland may have supposed, but is more likely to be a polymer $(Et_2Sn)_n$, where n is probably about 5. His "bimethide of tin" was almost certainly tetraethyltin.

But this was not all. Further work at Putney led to arsenic, antimony and mercury analogues of some of the organic compounds of zinc and tin. He arranged them thus:

Inorganic types   *Organo-metallic derivatives*

As { S, S }   As { C_2H_3, C_2H_3 } cacodyl

As { O, O, O }   As { C_2H_3, C_2H_3, O } oxide of cacodyl

As { O, O, O, O, O }   As { C_2H_3, C_2H_3, O, O, O } cacodylic acid

Zn O   Zn C_2H_3

Zn { O, O_H }   Zn { C_2H_3, O_H }

Sb { O, O, O }   Sb { C_4H_5, C_4H_5, C_4H_5 }

Sb { O, O, O, O, O }   Sb { C_4H_5, C_4H_5, C_4H_5, O, O } and Sb { C_4H_5, C_4H_5, C_4H_5, C_4H_5, O }

binoxide of stibethine   oxide of stibethylium

Sn O   Sn C_4H_5

Sn { O, O }   Sn { C_4H_5, O }

Hg { I, I }   Hg { C_2H_3, I }
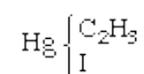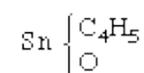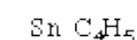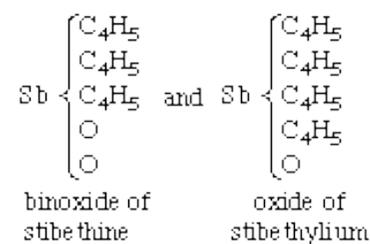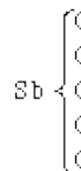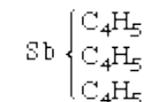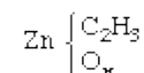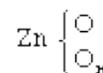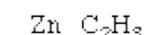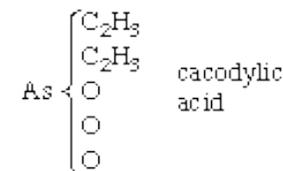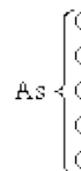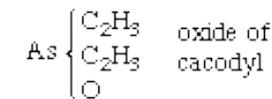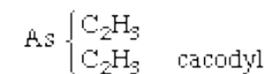
The curly "brackets" do not indicate bonds and may perhaps be thought of as "parcels" of atoms, the symbolism being that of the contemporary Type Theory.

But in arranging these organometallic bodies that way Frankland had stumbled on a crucial fact of chemistry, that of valency or regular combining powers of an elementary atom.

He wrote:

> When the formulae of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of the elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied, thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may he allowed the term, is always satisfied by the same number of these atoms.

And where did, this doubly momentous discovery take place? As Frankland writes of his 1852 paper:

> The reception of that law [of valency] was first forced upon my attention by my study of Organometallic bodies when holding the Chair of Chemistry at the Putney College of Civil Engineers three years previously.

So one happy event led to another! The birth of organometallic chemistry led directly to his formulation of the law of valency. Two questions remain:

1. In what sense can Frankland claim to be the founder of organometallic chemistry?

2. Why is his recognition so late?

Regarding the first Frankland may justifiably be recognised as the discoverer of a whole range of compounds of this type. He did not explore all their properties in detail, but was aware of the great reactivity of some, of their sensitivity to air, water and many other substances. Then, he recognised their essential nature: a metal linked directly to a carbon atom. And finally he gave them their name, which entered common parlance from at least 1853.

It is not so simple to explain why so few have heard of him, especially remarkable as in is lifetime he was widely held to be the leading chemist. Part of the blame must go to him, for he was excessively shy, would rarely give interviews, and in the end failed even to get a Chemical Society obituary until 6 years after his death. Much can be written about this characteristic, which probably stems ultimately from his being illegitimate. He desperately sought popularity and for that reason entered into academic alliances which made him *persona non grata* to some people. And it is well to recall that the very reactivity of these new compounds rendered them unfit for most organic uses, and not until Grignard was organometallic chemistry a useful synthetic tool. Partly for that very reason Frankland himself soon moved into other fields and is more likely to be remembered for these. But nothing can ever dislodge him from being the founder of organometallic chemistry. For that reason alone each one of us is in his debt.

So, in conclusion, what can be said about the proposition that Edward Frankland was the true founder of organometallic chemistry? In the following ways, I think:

1. Although not the first man to isolate what we might call an organometallic compound, he was certainly the first to prepare a number of such compounds.

2. He was the first to explore their nature and to relate them to each other by virtue of their composition.

3. He was the first to differentiate these compounds from ordinary organic chemicals.

4. He coined the name organometallic.

5. He defined them as having a metal atom directly linked to carbon.

6. He used them systematically in synthesis.

Such were the achievements of this notable 19th century chemist.

References and bibliography

For broad surveys of this work, see C. A. Russell, 'Edward Frankland, founder of organometallic chemistry', *Chem. Brit.*, 1982, 18, 737; and D. Seyferth. 'Zinc alkyls, Edward Frankland, and the beginnings of main-group organometallic chemistry', *Organometallics*, 2001, 20, 2940.

For predecessors of Frankland see W. C. Zeise, *Ann. Phys.*, 1827, 9, 632; and also J. S. Thayer, 'Historical origins of organometallic chemistry, Part I, Zeise's salt', *J. Chem. Educ.*, 1949, 46, 442, and D. Seyferth on 'the anion of Zeise's salt', *Organometallics*, 2001, 20, 2. Earlier research on organoarsenic

compounds is described in D. Seyferth, 'Cadet's fuming arsenical liquid and the cacodyl compounds of Bunsen', *Organometallics*, 2002, 20, 1488.

Many details of Frankland's life may be found in his autobiographical *Sketches* (privately printed, 1901); and his hitherto unpublished papers; see also C. A. Russell, *Lancastrian Chemist: The Early Years of Sir Edward Frankland*, Open University Press, Milton Keynes, 1987; *Edward Frankland: chemistry, controversy and conspiracy in Victorian England*, Cambridge University Press, 1996 and 2003.

Frankland's chemical work may be found in his *Experimental researches*, London, 1877, and in many unpublished documents; the following publications, amongst others, contain further details of his early organometallic work:

1. E. Frankland and H. Kolbe, *Ann*., 1848, **65**, 269, 288.

2. E. Frankland, *J. Chem. Soc*., 1849, **2**, 263, 297.

3. E. Frankland, *J.Chem. Soc*., 1851, **3**, 30, 301, 322.

4. E. Frankland, *Phil. Trans*., 1852, **142**, 417.

5. E. Frankland, *J. Chem. Soc*., 1854, **6**, 52.

6. P. Frankland, *Phil. Trans*., 1855, **145**, 259.

Finally some details of his superb experimental technique may be found in C A. Russell, 'Chemical techniques in a preelectronic age: the remarkable apparatus of Edward E. Frankland', in F L. Holmes and T. H. Levere (eds.), *Instrumentation and experimentation in the history of chemistry*, MIT Press, 1999, pp. 311-334.

Archives of Sir Edward Frankland

Edward Frankland (1825 - 1899) was arguably the most distinguished of British chemists of the 19th century, leaving legacies of organometallic chemistry, the theory of valency, the notion of a chemical bond, methods of water analysis and a whole new tradition of chemical education. For some strange reason his work has not been appreciated until our own time, and only now is his importance being understood. Much of our recent knowledge has been derived, at least in part, from the vast collection of letters, private notes and diaries that have fortunately survived. While this material has been widely scattered, by far the largest collection came to light a few years ago and was held as the family collection (in the custodianship of Mr. Raven Frankland), safely preserved in a house in Cumbria.

It gives me much pleasure to announce that this collection has now been generously donated on behalf of the Frankland family by Drs. Juliet and Helga Frankland to the archives of the John Rylands Library in the University of Manchester. This is singularly appropriate as Frankland was Manchester's first Professor of Chemistry, and as his collection will now join those of other distinguished chemists, most notably John Dalton.

The Frankland archive at the John Rylands Library will hopefully be supplemented by further material from other sources. All enquiries about access should be addressed to: Mr. John Hodgson, Keeper of Manuscripts and Archives, The John Rylands University Library, The University of Manchester, 150 Deansgate, Manchester M3 3E11; email john.hodgson@manchester.ac.uk