



Seventeen-electron compounds in an eighteen-electron world – An historical perspective

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ABSTRACT

Beginning in about the 1920s, it was realized that the structures and stoichiometries of all known, structurally characterized metal carbonyls obeyed what came to be known as the effective atomic number (EAN) rule, whereby the sum of the electrons donated by the carbonyl ligands plus the number of electrons contained in the metal valence shell equals the number of valence electrons in the next inert (noble) gas element. While extraordinarily useful for predicting the constitutions of new metal carbonyls and their derivatives, universal acceptance of the validity of the EAN (or inert gas, noble gas, and, eventually 18-electron) rule resulted in a number of rule-breaking compounds being misrepresented. This historical perspective will show how several such organometallic compounds, initially formulated as obeying the 18-electron rule, were eventually recognized as 17-electron species with radical-like properties, the first to be known in what became an important branch of organotransition metal chemistry.

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1. Background: metal carbonyls from the beginning to about 1960

The basic outlines of chemical structures, i.e. common stoichiometries and dispositions of atoms around the central atoms of complex molecules (coordination numbers and stereochemistries in modern parlance) of many of the main group and transition elements had been well established by the 1920s. As is clear in a Science article by Langmuir in 1921 [1], sufficient information was by that time available that the importance of electron pairs for binding atomic nuclei together in molecules had been universally accepted. Langmuir also promoted, implicitly at least, and possibly introduced – at this distance in time it is difficult to know – the idea that the number of electrons in the valence shell of a central atom in many types of molecules is equal to the number in the next inert gas. Thus the central carbon atoms of many organic compounds contain eight electrons shared by the central carbon atom and the four atoms bonded to it (neon electron configuration) and the iron atom in the then recently reported $\text{Fe}(\text{CO})_5$ enjoys the same electron configuration as krypton.

Although a quantum mechanical rationale for this postulate would not, of course, be available for several decades, the concept had obvious appeal and Sidgwick [2–4] quickly expanded

Langmuir's ideas in terms of the effective atomic number (EAN) rule, whereby the sum of the electrons donated by the atoms bonded to the central atom (ligands bonded to a metal atom or ion in the case of transition metal complexes) plus the number of electrons contained in the central atom valence shell equals the number of valence electrons in the next inert (noble) gas element.

Of interest here, Blanchard [5,6] and Sidgwick and Bailey [7] extended the EAN rule to a variety of metal carbonyls. In addition to the simple carbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$, their discussions included the known dinuclear compounds $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$ and the known clusters $\text{Fe}_3(\text{CO})_{12}$ and $\text{Co}_4(\text{CO})_{12}$ [7]. While the suggested structures of tetrahedral $\text{Ni}(\text{CO})_4$ (Fig. 1a) trigonal bipyramidal $\text{Fe}(\text{CO})_5$ (Fig. 1b) and octahedral $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (Fig. 1c) [6,7] stand the test of time, the total absence of useful spectroscopic and crystallographic information for all resulted in erroneous conclusions for the dinuclear and cluster compounds. Metal–metal bonds had not yet been conceptualized, and instead MCOM linkages were presumed for e.g. $\text{Fe}_2(\text{CO})_9$ (Fig. 1d) and $\text{Fe}_3(\text{CO})_{12}$ (Fig. 1e).

The crystal structure of $\text{Fe}_2(\text{CO})_9$ was published by Powell and Ewens in 1939 (Fig. 2) [8], and was the first example where the atomic positions could be determined sufficiently accurately that it could be established that the CO ligands bind through carbon rather than oxygen. This structure also provided the first evidence that carbonyl ligands could bridge metal atoms through carbon atoms alone rather than linearly as in Fig. 1d,e, and that pairs of metal

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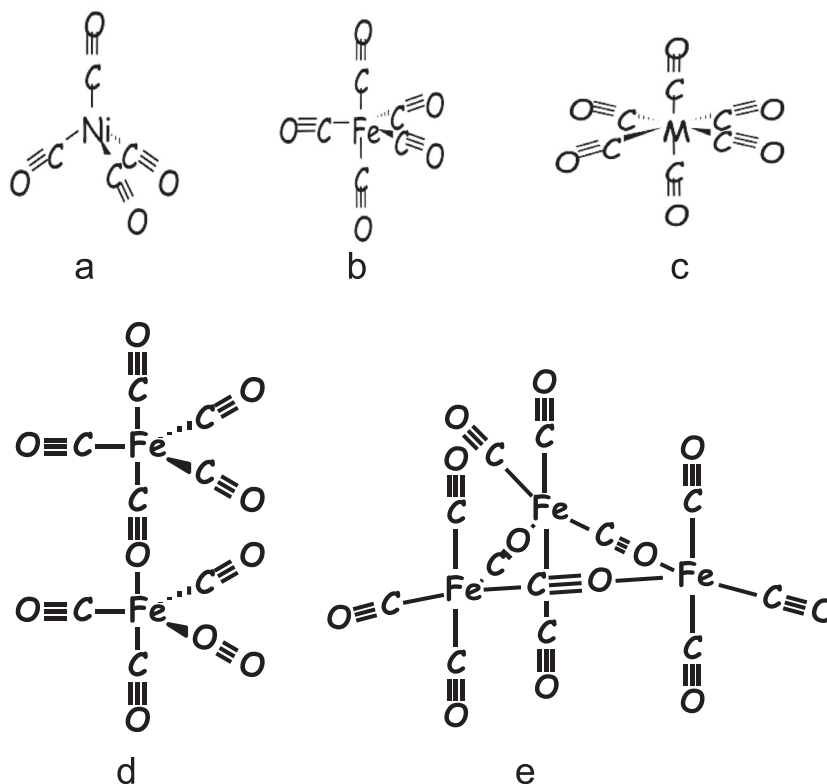


Fig. 1. Structures proposed for Ni(CO)₄ (a), Fe(CO)₅ (b), M(CO)₆ (M = Cr, Mo, W) (c), Fe₂(CO)₉ (d) and Fe₃(CO)₁₂ (e) [7].

atoms could form metal–metal bonds. Both concepts appear to have been quite novel at the time.

In 1957, Dahl, Ishishi and Rundle published the crystal structures of Mn₂(CO)₁₀ and Re₂(CO)₁₀ (Fig. 3) [9], demonstrating the unequivocal presence of unsupported (by bridging carbonyl ligands) metal–metal bonds. They noted also that the metal–metal bonded dimeric structures are consistent with the known diamagnetism of these compounds and, more importantly, with the “closed electronic shell rule”, i.e. the EAN rule. In this way, the importance of the EAN rule, also known as the inert/noble gas rule, became at least tentatively established as a factor in metal carbonyl chemistry.

2. From the effective atomic number rule, to the noble/inert gas rule, to the 18-electron rule

Before extending this discussion, we shall briefly follow a complementary theme. We have used above the generally interchangeable terms “effective atomic number rule”, “noble gas rule” and “inert gas rule”. The first is still used in a variety of contexts, usually non-organometallic, but the latter two slowly fell out of

favor as it became recognized that the several of the noble/inert gases can take part in chemical reactions and thus are neither noble nor inert. As is well known, the chemical reactivity of xenon was reported by Bartlett in 1962 [10], and the now very extensive literature of the chemistry of xenon and some of its congeners has been frequently reviewed [11,12].

As it became ever clearer that the group 18 elements are not “noble”, in the sense of being chemically inert, there developed an awareness that the terms “noble gas rule” and “inert gas rule” were obsolescent although neither has been totally abandoned in the literature. The alternative, satisfyingly descriptive and obviously appropriate term “18-electron rule”, apparently first mentioned in the literature by Craig and Doggett in 1963 [13] and subsequently more widely promoted by Mitchell and Parish in 1969 [14], is being used increasingly by organometallic chemists working in metal carbonyl chemistry.

One can see this development in important textbooks during the second half of the twentieth century. One of the classic mid-century texts was that of Emeléus and Anderson [15], which served the inorganic community for over 20 years through three

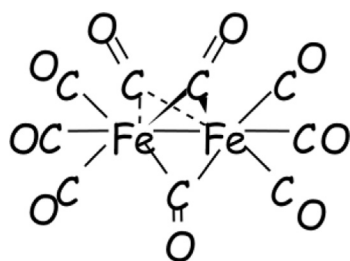


Fig. 2. Structure of Fe₂(CO)₉.

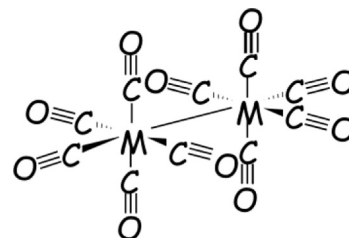


Fig. 3. Metal–metal bonded structures of Mn₂(CO)₁₀ and Re₂(CO)₁₀; the two square pyramids are in fact staggered in the crystal structures.

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