

Organotransition Metal Chemistry

Fundamental Concepts and Applications

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Introduction

Few other fields in chemistry have developed as remarkably as organometallic chemistry in the past three decades. The number of papers published in international journals has grown rapidly, and we now have two journals dealing specifically with organometallic chemistry. One is the *Journal of Organometallic Chemistry*, issued now weekly, and the other is *Organometallics*, recently launched by the American Chemical Society, both bearing witness to the importance of organometallic chemistry and its relevance to other disciplines in chemistry.

Organometallic chemistry has attracted such tremendous attention because it is *interesting* and *useful*. Organometallic compounds are fun to study and useful in many respects. And many interesting discoveries and useful applications are still expected in the future. Organometallic compounds, particularly those of transition metals, are interesting to study because we encounter many examples of unexpected behavior and their chemistry is full of variety.

1.1. BACKGROUND OF ORGANOMETALLIC CHEMISTRY AND OVERVIEW

The history of organometallic chemistry may be described as one of unexpected discoveries (Table 1.1). The oldest compound in the history of organometallic chemistry was prepared by W. C. Zeise, a Danish chemist, in 1827 by the reaction of ethanol with a mixture of PtCl₂ and PtCl₄ in the presence of KCl.¹ This was about the same time as the first successful synthesis of urea in 1828 by Wohler and about 40 years prior to the proposal of the Periodic Table by A. D. Mendeleev in 1869.

The compound^{1b} prepared and formulated as PtCl₂(C₂H₄)·KCl·H₂O by Zeise must have been regarded as quite bizarre at the time. How can ethylene,

Table 1.1 Development of Organometallic Chemistry

1827	Discovery of Zeise's salt (W. C. Zeise)
1837	Synthesis of the first organoarsenic compound, cacodyl (tetramethyldiarsine) (R. Bunsen)
1849	Synthesis of diethylzinc (E. Frankland)
1859	Synthesis of the first organoaluminum compound (W. Hallwachs, A. Schafarik, A. Cahours)
1863	Synthesis of the first organosilicon compound (C. Friedel, J. M. Crafts)
1868	Synthesis of the first metal carbonyl (PtCl ₂ CO) (M. P. Schutzenberger)
1869	Proposal of the Periodic Table by A. D. Mendeleev
1890	Synthesis of Ni(CO) ₄ (I. Mond et al.)
1893	Proposal of octahedral and square planar coordination compounds (A. Werner)
1900	Discovery of Grignard reagents (V. Grignard; P. A. Barbier, 1899)
1907	Synthesis of the first organoplatinum compound (W. J. Pope, S. J. Peachey)
1917	The first isolation of alkyllithium compounds (W. Schlenk, J. Holtz)
1919	Synthesis of Hein's polyphenyl chromium complexes, which were subsequently shown to be η ⁶ -arene chromium complexes (M. Tsutsui, H. H. Zeiss, 1954)
1921	Synthesis of tetraethyllead for use as an antiknock agent in gasoline engines (T. Midgeley, T. A. Boyd)
1925	Discovery of the Fischer-Tropsch process; development of a direct preparative method for alkyllithiums (K. Ziegler, M. Colonius); the first synthesis of a butadiene complex. Fe(C ₄ H ₆)(CO) ₃ (H. Reihlen)
1931	The first synthesis of a metal carbonyl hydride, H ₂ Fe(CO) ₄ (W. Hieber)
1938	Discovery of the oxo process (O. Roelen); discovery of Kharasch reaction (M. S. Kharasch); synthesis of silver-olefin complexes (S. Winstein, H. J. Lucas)
1938-1945	Development of Reppe reactions
1939	Discovery of homogeneous catalytic hydrogenation by rhodium complexes (M. Iguchi)
1944	Discovery of a direct synthetic method for organosilicon compounds (E. G. Rochow)
1951	Discovery of ferrocene (T. J. Kealy, P. L. Pauson; S. A. Miller, J. A. Tebboth, J. F. Tremaine, 1952); proposal of a theory for the olefin-metal π bond (M. J. S. Dewar, 1951; J. Chatt, L. A. Duncanson, 1953)
1952	Preparation of the first phenyltitanium compound (D. F. Herrman, W. K. Nelson)
1953	Discovery of the Ziegler process (K. Ziegler et al.); proposal of molecular orbital (MO) theory to explain the bonding in electron-deficient compounds (G. N. Lewis, R. E. Rundle); discovery of the Wittig reaction (G. Wittig)

- 1955 Discovery of fluxional behavior of $C_5H_5Fe(CO)C_5H_5$ (G. Wilkinson, T. S. Piper)
- 1956 Discovery of hydroboration (H. C. Brown)
- 1957 Discovery of hydrosilylation (J. L. Speier et al.); discovery of Wacker process (J. Smidt)

2

accounting for the π bond was proposed by γ . . .

Chatt and Duncanson. d_h . . . , direct metal-to-alkyl σ bond

The first organometallic compound was synthesized also accidentally, by $E. F. C. C. K. L.$ and the discoverer of h_{1-1} .
In 1849. ry itself was . . . f . . . ran . . . F . . . $kland$ was trying to
chemist i . . . m its m a . . .

