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 inter- national journals has grown rapidly, and we now have two journals dealing specifically with organometallic chemistry. One is the *Journal of Organome- tallic Chemistry*, issued now weekly, and the other is *Organometallics*, recently launched by the American Chemical Society, both bearing witness to the importa nce 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 applica- tions 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 unex-pected discoveries (Table 1.I). The oldest compound in the history of or-ganometallic chemistry was prepared by W. C. Zeise, a Danish chemist, in 1827 by the reaction of ethanol with a mixture of PtCii and PtCk in the presence of KCJ.¹ This was about the same time as the first successful synthe- sis of urea in I828 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 $PtCh(C_2H_4) \cdot KCI \cdot H_2O$ by Zeise must have been regarded as quite bizarre at the time. How can ethylene,

Table 1.1 Development of Organometallic Chemistry

- I 27 Discovery of Zeise's salt (W. C. Zeise) 1"37 Syntlesis of the first organoarsenic comp
- 1^{"'37} SyntJlesis of the first organoarsenic compound, cacodyl (tetramethyldiarsine) (R. Bunsen)
- 189 Synthesis of diethylzinc (E. Frankland)
- 1859 Synthesis of the first organoaluminum compound (W. Hallwachs, A. Schaferik, A. Cahours)
- 63 Synthesis of the first organosilicon compound (C. Friedel, J. M. Crafts)
- 68 Synthesis of the first metal carbonyl (PtC'2COh (M. P. Schutzenberger)
- I 69 Proposal of the Periodic Table by A. D. Mendeleev
- 1890 Synthesis of Ni(C0}4 (1. 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)
- 1 907 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 rr-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 butadienc complex. $Fe(C4H_6)(C0)3$ (H. Reihlen)
- 1931 The first synthesis of a metal carbonyl hydride, H $Fe(CO)_4$ (W. Hieber)
- 1938 Discovery of the oxo process (0. 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. lguchi)
- 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 olefinmetal rr 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)

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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 C₅H₅Fe(CO)iC₅H₅ (G. Wilkinson. T. S. Piper)
 1956 Discovery of hydroboration (H. C. Brown}
 1957 Discovery of hydrosilylation (J. L. Speier et al.}; discovery of Wacker
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process (J. Smidt)

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<u>Table 1.1</u> <u>D</u> evelopm	o ^f Organom t 11.	3
11)58	e a IC Chemistrya ($C_{on}t_{mue}d$)	
1961	I>rncovery of hutadienc oli o Discovery of V $k \cdot k \cdot g$ mcn1.at1on process (G. Wilke)	
196)	structural analysis of vitamin B' r CO)(PPh1)i (L. Vaska); X-ra llolding of the first I t .12 coenzymc (D. Crowfoot-Hodgkin) 1stry (Cincinnati 01 n crnatlonal Co C: .n crence on Organometallic Chen line mi./try .110 · publication 0 ^f Journal of Organometallic	ıy 1- ic
1964	Discovery of nitrogen fixation	s).
1965	 very of olefin metathesis reaction (R Ranks) 1scover of W'Ik: y thson s catalyst (G. Wilkinson, R.S. Coffey); discover of the first d1111trogen complex (A. D. Allen, C. V. Senoff) 	у

ri Main source; .I. S. Thayer, Adv. Or1:annmetal. Chem.. 13, r (197S).

a gaseous compound under ordinary conditions, combine with platinum? When the synthesis of this compound, which is now called Zeise's salt, was first reported (in Latin at that time), Zeise was severely attacked by Liebig.² The compound was condemned as a fantasy by the renowned Liebig, the founder of Justus Liebig's *Annalen der Chemie*, the inventor of the Liebig condenser, and a celebrity regarded as the father of organic chemistry. However, the infallible Liebig was wrong on this occasion.

The analysis of this compound established the essential soundness of Zeise's formulation unequi vocally. Later, structural determination revealed a structure having ethylene combined with platinum through its double bond (see structure 1-1).

1-1

(The local transformation $h_{0,1}$) (The local

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rcaser, by mull or -bond between the platinum atom and the double bond of uc 1 a c cm ca bond the formation of which plays a key role m ethylene is now known as a rr 't' et I catalysts It was not of olef ms by trans1 10n m a catJytIc trans ormat1on ntur that the first theory satIsfactonly unt1J the middle of the twentieth ce b M J S Dewar4 and later by accounting for the rr bond was propose Y · · · · Chatt und Duncanson. d h , direct metal-to-alkyl *a* bond "Ih c f": organome t' IJ lc compoun E aving a was synthesized also acc ldentally, by f ran a In 1849. ry tself was f ry tself was f ran a chemist i m its m a