COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

The Synthesis, Reactions and Structures of Organometallic Compounds

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Volume 8

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PERGAMON PRESS
OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT

U.K. Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
U.S.A. Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA Pergamon Press Canada Ltd., Suite 104, 150 Consumers Road, Willowdale, Ontario M2J 1P9, Canada
AUSTRALIA Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, NSW 2011, Australia
FRANCE Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
FEDERAL REPUBLIC OF GERMANY Pergamon Press GmbH, Hammerweg 6, 6242 Kronberg/Taunus, Federal Republic of Germany

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First edition 1982

Library of Congress Cataloging in Publication Data

Main entry under title:

Comprehensive organometallic chemistry.

Includes bibliographical references and indexes.
1. Organometallic compounds. I. Wilkinson, Geoffrey, 1921–
II. Stone, F. Gordon A. (Francis Gordon Albert), 1925–
III. Abel, Edward W.
QD411.C65 1982 547′.05 82-7595 AACR2

British Library Cataloguing in Publication Data

Comprehensive organometallic chemistry.
1. Organometallic compounds
I. Wilkinson, Geoffrey
547′.05 QD411

ISBN 0-08-025269-9

Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter

COMPREHENSIVE
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Preface

Although the discovery of the platinum complex that we now know to be the first π-alkene complex, $K[PtCl_3(C_2H_4)]$, by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethylplatinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related π-complexes, the synthesis of a plethora of organometallic compounds containing metal–metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl–titanium chloride systems by Ziegler and Natta and of the Wacker palladium–copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the elements individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon–metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal–metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

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50.1

Preparation and Purification of Carbon Dioxide and Carbon Monoxide

R. P. A. SNEEDEN
C.N.R.S., Villeurbanne

50.1.1 CARBON DIOXIDE

50.1.1.1 Occurrence and Preparation

Carbon dioxide occurs widely in nature both free and in the combined state (natural springs, carbonates, bicarbonates) and it is also a by-product of numerous industrial processes. Thus it is present in the flue gases resulting from the combustion of carbonaceous materials (coal, coke, distillation residues). The controlled combustion of coke has been used industrially for the production of CO_2: the flue gases contain CO_2 (15–20%), CO, N_2, O_2 and steam, together with sulphur and organic impurities. The kiln gases from the manufacture of cement and lime (carbonate decomposition) are also rich in carbon dioxide (32–42%) and constitute primary industrial sources of CO_2. The gaseous effluents from some industrial fermentation processes are extremely rich in CO_2. The fermentation of various agricultural products (grain, molasses and wood waste) towards *ethanol* gives essentially pure (99%) CO_2, whilst fermentation towards *acetone* and *1-butanol* gives an off-gas containing both CO_2 (60%) and H_2 (40%).[1]

50.1.1.2 Purification

The precise purification process employed will depend upon the origin of, and thus the impurities accompanying, the carbon dioxide. In general, with CO_2-rich streams the impurities are removed, whilst with dilute CO_2 streams the CO_2 is removed by absorption.[1,2]

In the case of the fermentation processes, the effluent is rich in CO_2 and the impurities consist of alcohols and other organic compounds. The purification therefore includes treatment with an oxidizing agent (dichromate or permanganate), treatment with a drying agent (sulphuric acid, calcium chloride, charcoal, molecular sieves, *etc.*), and compression to liquid (cylinder) or solid (block) carbon dioxide.

The flue and kiln gases consist of relatively dilute CO_2 streams with some solid and organic impurities as well as unwanted gaseous products. The gases are subjected to an initial water-wash to remove the solid matter and the CO_2 subsequently absorbed by an 'alkaline wash' (sodium or potassium carbonates, or alkanolamines). The release of relatively pure CO_2 is effected by heating the latter wash-solutions and the desorbed gas is treated with an oxidizing agent (to remove organic compounds), dried and compressed.

Several industrial processes exist for the recovery of CO_2 from other mixed gas streams (*e.g.* Syn-gas for NH_3 synthesis).[3–6] They all consist essentially of the use of a suitable 'solvent' for the absorption of CO_2 and eventually other acid gases; the separation and desorption are assured technically by changes in pressure and/or temperature, depending upon the nature of the adsorbent. The 'solvents' include: (i) simple physical adsorbents, *e.g.* water, methanol, propene carbonate; desorption is achieved by pressure changes; (ii) chemical solvents like alkanolamines, solutions of K_2CO_3 with and without activators (arsenic oxide, *etc.*), solutions of sodium phenoxide or solutions of salts of other weak organic acids; desorption is effected by variations in temperature and/or pressure.

The reactions and end uses of CO_2 are discussed in Chapter 50.4.

50.1.2 CARBON MONOXIDE

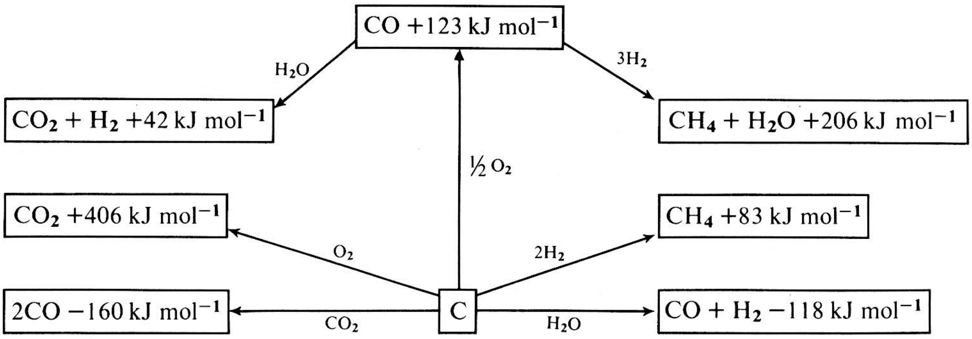
50.1.2.1 Synthesis

Carbon monoxide is a synthetic product obtained industrially by the transformation of various forms of fossilized carbon (lignites, coals, petroleum fractions, *etc.*). The history of its production[7–9] is intimately associated with developments in coal and petroleum technologies.

50.1.2.1.1 Coal-derived CO-containing mixtures

Originally, CO-containing gases were obtained by the gasification of coal or coke by means of air and/or steam and later by means of oxygen/steam, at times under pressure. The gasification is effected at high temperatures, of the order of 1000 °C, and a simplified form of the reactions involved (assuming that carbon is the active entity) is represented schematically in Scheme 1.[9]

The composition and the calorific value of the resulting gas vary according to the process used (see Table 1). Thus when the gasification is carried out with air, a mixture containing large proportions of nitrogen and other inert gases is obtained. With air/steam it is possible to obtain mixtures rich in CO/H_2; however, since the formation of the latter is endothermic (see Scheme 1) it is necessary to employ alternate blasts of air and steam; water gas, produced during the steam blast, is relatively free from N_2. The advent of cheap oxygen permitted the continuous production



Scheme 1 Schematic representation of coal gasification reactions

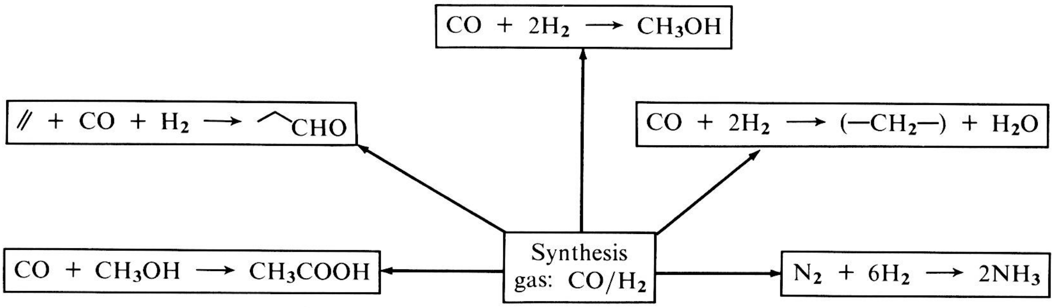
Table 1 Coal Gasification Characteristics of Various Gases[7–9]

Gasification method	*Name of gas*	CO (vol %)	CO_2 (vol %)	H_2 (vol %)	N_2 (vol %)	CH_4 (vol %)	*Calorific value* (kJ m^{-3})	*End use*	*Comments*
Air	Producer gas Generator gas	30	5–8	13	50–56	0.2	5000–7000	Industrial heating	Continuous
Air/Steam	Synthesis gas Water gas	40	2–4	50–55	3–7	0.5	10 400–11 600	After adjustment and CO_2 removal, organic syntheses and source of H_2 for NH_3 synthesis	Alternate
O_2/Steam	Synthesis gas Water gas	40–64	10–23	20–40	1–1.6	0.1–0.9	10 400–11 600		Continuous
O_2/Steam/20 bar	Town gas	17–23	27–32	34–50	0.7–1.4	9–16	12 800–18 700	Town gas	Pressurized

of CO/H_2 mixtures free from N_2. Pressure favours methane formation and the pressure gasification of coals with O_2/steam gives a product rich in methane. The increased calorific value of this gas predestined it for domestic heating in the form of town gas.

There are in principal two major types of gasification processes: the autothermic process, in which the requisite heat is obtained by the *in situ* combustion of part of the carbonaceous material, and the allothermic process, in which the heat for the reaction is brought to the reactor. The latter could be of importance in the exploitation of nuclear energy; however, the former is at the base of most current gasification technologies. The coal is fed in the form of fine powders or slurries and the production capacities of the reactors are in the order of 3000 m^3 gas m^{-2} shaft h^{-1} and productions correspond to 30 000 to 50 000 m^3 gas h^{-1}.[9]

The precise choice of process will clearly depend upon the end use of the gas (see Table 1) and the present discussion will only treat of CO/H_2 mixtures for syntheses purposes. Synthesis gas is at the base of many industrial syntheses (see Chapters 50.2 and 50.3). Some of the examples represented in Scheme 2 reveal that CO : H_2 compositions, varying from pure CO, CO/H_2 1 : 1, 1 : 2, *etc.*, to pure H_2, are in fact required.



Scheme 2 Synthesis gas based industrial processes

The composition of most coal-based feedstocks is such that the actual gases obtained by gasification, once cleaned of tars, oils, fly-ash, *etc.*, contain, besides the compounds listed in Table 1, various impurities together with H_2S and other sulphur compounds. These impurities are deleterious to many subsequent catalytic reactions and therefore the crude synthesis gas must be purified (see Section 50.1.2.2). The actual CO/H_2 ratio can be varied by modifying the conditions used in the gasification process;[7-9] however, it is almost always necessary to adjust this ratio in the final gas mixture by means of the water-gas-shift (WGS) reaction (equation 1). As will be discussed in Section 50.1.2, this reaction is catalyzed at high temperatures by Co/Mo and Fe/Cr catalysts. In the Lurgi pressure process the Co/Mo catalysts are used at 400–460 °C to effect the water-gas-shift in the moist crude synthesis gas. However, with iron-based contact masses the position of the equilibrium with the sulphide phase depends upon the partial pressure of H_2S (equation 2).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (1)$$

$$Fe_3O_4 + 3H_2S + H_2 \rightleftharpoons 3FeS + 4H_2O \quad (2)$$

Thus with concentrations of H_2S less than 75 p.p.m. the oxide is favoured thermodynamically and the contact mass is active in the catalysis of the WGS reaction. However, with 2000 p.p.m. H_2S the equilibrium lies on the side[10] of the sulphide, which results in a drastic reduction of the catalytic activity of the system. It follows therefore that for iron contact masses the coal-derived synthesis gases must be freed from sulphur before the water-gas-shift reaction, whilst with many petroleum-derived gases the sulphur content is such as to allow the water-gas-shift to be effected directly on the crude gas.[11]

Many processes are in use for the preparation of synthesis gas and these include the Lurgi, Koppers–Totzek, Winkler and Ruhrgas processes, and many new ones (COGAS, Hygas, Bigas, Synthane, *etc.*) are at the trial stages.[8,9,11,12]

50.1.2.1.2 Petroleum-derived CO-containing mixtures

CO-containing gases can also be obtained by the action of oxygen (air) and/or steam on petroleum products (methane, naphtha, crude oils, *etc.*) by methods analogous to those used in coal gasification.The principal reactions involved are respectively exothermic and endothermic, *e.g.* equations (3)–(5) for methane. As in the case of coal gasification, both autothermic and allothermic processes have been developed for the transformation of petroleum-based feedstocks into synthesis gas (Table 2).[6,12]

$$CH_4 + H_2O \longrightarrow CO + 3H_2 - 206\ \text{kJ mol}^{-1} \tag{3}$$

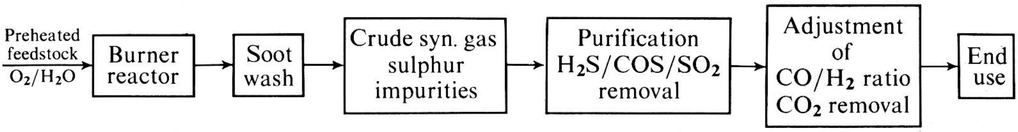
$$CH_4 + 0.5O_2 \longrightarrow CO + 2H_2 + 40\ \text{kJ mol}^{-1} \tag{4}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 798\ \text{kJ mol}^{-1} \tag{5}$$

Table 2 Synthesis Gas Compositions Obtained from Various Feedstocks[6]

	Composition of synthesis gas (vol %)					
Feedstock	CO	CO_2	H_2	CH_4	N_2	S
Natural gas	38	2.4	59.5	0.1	0.5	—
Heating oil	47.5	3.6	47.9	0.3	0.2	0.5
Tars	54	5.7	39	0.3	0.8	0.2
Heavy oils	47	4.3	44.7	1.4	0.3	2.3

The autothermic process requires no catalyst and thus no purification of the feedstock (desulphurization) and the heat required for the reaction comes from the combustion of part of the feedstock with oxygen. These processes, which operate under pressure (30–40 bar) and at high temperatures (1300–1500 °C) permit the use of almost any type of petroleum product from natural gas, light oils to bunker oils and tars; they have the disadvantage, however, of being soot-forming. As is illustrated schematically in Scheme 3, the feedstock, oxygen and steam are preheated and brought, under pressure (30–40 bar), to a burner in the reaction chamber.



Scheme 3 Schematic representation of autothermic generation of synthesis gas

The heat generated by the combustion of part of the fuel raises the temperature in the reactor to 1300–1500 °C, which engenders the steam cracking of the remainder. The crude synthesis gas is freed from soot by washing, however it still contains sulphur impurities, mostly as H_2S. The quantity of sulphur present (at times in the order of 250 mg S/m^3 gas) depends upon the composition of the original feedstock, but it must be eliminated in a subsequent purification step (see Section 50.1.2.2) before the synthesis gas can be exploited in catalytic processes.

The Shell, Texaco and BASF processes are amongst the autothermic processes currently in operation. Various feedstocks are used, however. Table 2 indicates that the composition of the final synthesis gas is virtually independent of the petroleum product used.[6,12,13]

In the allothermic process the steam cracking of the hydrocarbons is effected with a nickel catalyst at 700–900 °C/15–40 bar and the heat required for this endothermic reaction (equation 3) is brought to the reactor. The conditions (temperature and pressure) in this primary reformer are such that the effluent, obtained at the rate of 2000 m^3/m^3 catalyst volume, still contains some methane (7%). The methane content is reduced to the desired level (0.2%) by means of a second catalytic reaction, in the presence of air or oxygen, in a secondary reformer operating at 1000–1050 °C. The use of metal catalysts necessitates sulphur-free feedstocks; however, the disadvantage of this preliminary purification (desulphurization) stage is largely compensated by the purity of the product. The final synthesis gas obtained is free from soot and sulphur-containing impurities and is thus ready for exploitation.