COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

The Synthesis, Reactions and Structures of Organometallic Compounds

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Volume 5

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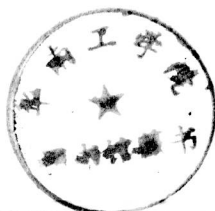*Imperial College of Science & Technology*
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Preface

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 ele-

ments 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 organo-metallic 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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Cobalt

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34.1 INTRODUCTION

Cobalt, the 27th element of the Periodic Table, constitutes about 0.001% of the Earth's crust, where it is widely distributed usually in association with nickel and arsenic. It is a hard bluish–white ferromagnetic metal, m.p. 1493 °C, b.p. 3100 °C. Cobalt is relatively unreactive. It dissolves slowly in dilute mineral acids but does not combine with hydrogen or nitrogen, probably because in air the metal is covered with a layer of CoO. However, finely divided Raney cobalt does have catalytic hydrogenation properties.[1] The conditions necessary for metal atom synthesis using cobalt have been described.[2]

Cobalt has a valence shell electron configuration of $(3d)^7 (4s)^2$, and there is a well established organometallic chemistry for all six oxidation states from −1 to +4. As cobalt has an odd number of electrons, a consequence of the 18-electron rule is that in the great majority of organocobalt compounds the metal is in an odd-numbered oxidation state; −1, +1 or +3. Even-numbered oxidation state cobalt compounds are either paramagnetic, or polynuclear with metal–metal bonds. Typical of these are the two principal homoleptic carbonyls of cobalt, $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$, which were the first organocobalt compounds to be prepared and characterized.[3] $[Co_2(CO)_8]$ is now of major economic importance: 25,000 tonnes are employed per annum in hydroformylation synthesis.[4]

The carbonyls apart, the organometallic chemistry of cobalt before 1950 was limited to some ill-defined alkyl- and aryl-cobalt compounds formed by the reaction of Grignard and other organometallic reagents with cobalt halides.[5] With the great expansion of organometallic chemistry in the 1950s initiated by the discovery of ferrocene, organocobalt chemistry was rapidly extended. The first sandwich complexes of cobalt, the cobalticinium ion[6,7] and cobaltocene itself,[8] alkylcobalt(I) carbonyls[9] and the first example of an η^3-allyl complex,[10] were important classes of compounds discovered in this period. Following the discovery that a naturally occurring molecule, vitamin B_{12} coenzyme, contains a cobalt(III)–carbon bond[11] very many related organocobalt(III) complexes have now been prepared and studied.

In addition to the cobalt(III) complexes there is an extensive organometallic chemistry of cobalt(I). Most cobalt(I) complexes contain π-acid ligands such as Cp, CO, RNC or R_3P.

The stable existence of two oxidation states, cobalt(I) (d^8) and cobalt(III) (d^6), which differ by two units, should allow cobalt(I) complexes to take part in oxidative addition reactions. This is certainly the case for the second- and third-row congeners; these are the typical reactions of the Vaska-type complexes of rhodium(I) and iridium(I). Cobalt(I) complexes are usually five-coordinate, *e.g.* $[CoX(CO)_2(PPh_3)_2]$ (X = halide), $[CoMe(PMe_3)_4]$ and $[CoL_2Cp]$ (L = CO, PR_3). These complexes undergo oxidative addition reactions, with elimination of one ligand.

Besides the obvious analogies that can be drawn between cobalt and the second and third row elements, rhodium and iridium, relationships also exist between isoelectronic species of neighbouring first row metals. Thus the two complexes $[Co_2(CO)_8]$ and $[Ni(CO)Cp]_2$ have many similar reactions; both form complexes with acetylene bridges for example, $[Co_2(CO)_6(\mu\text{-}RC_2R)]$ and $[Ni_2Cp_2(\mu\text{-}RC_2R)]$. The chemistry of $[Co(CO)_2Cp]$ has much in common with that of $[Fe(CO)_5]$, for example both react with CF_3I to give $[CoI(CF_3)(CO)Cp]$ and $[FeI(CF_3)-(CO)_4]$ respectively.

The aim of this chapter is to describe the chemistry of all compounds containing a cobalt–carbon bond, but with the following exceptions. Cyanide complexes where cyanide is the only carbon-bonded ligand present have not been included. We have not given a detailed discussion of the catalytic reactions of organocobalt compounds, nor the chemistry of vitamin B_{12} since these topics are discussed in other volumes of this work. Similarly, other chapters deal with heteronuclear cobalt-metal bonded compounds, and carborane compounds.

The literature has been searched up to the end of 1979 and we have also included references from 1980. Although we have included many examples of particular types of complexes in tables, these are not intended to be fully comprehensive. Very detailed information on organocobalt compounds can be found in two excellent Gmelin handbooks.[12,13]

34.2 COMPOUNDS WITHOUT HYDROCARBON LIGANDS

34.2.1 Carbonyls, Hydridocarbonyls and Related Compounds

Two very thorough reviews dealing with the structures[14] and synthesis and reactivity[15] of metal carbonyls refer to the early work on cobalt carbonyl chemistry. Detailed information on the preparation, structure and properties of cobalt carbonyl compounds is given in a general account of the use of metal carbonyls in organic synthesis.[16]

34.2.1.1 Mononuclear carbonyls

There are no stable mononuclear cobalt carbonyls, but cocondensation reactions of cobalt atoms with carbon monoxide at 6–15 K using very low cobalt atom concentrations (Co:CO < 1:10⁴) have allowed investigation of the unstable species $[Co(CO)_n]$ ($n = 1, 4$).[17] The extreme instability of these mononuclear species is demonstrated by the ready formation of binuclear carbonyls at concentrations ($1:10^4 <$ Co:CO $< 1:10^2$) where the statistical generation of dinuclear species would be negligibly small. The structures of these simple $[Co(CO)_n]$ open shell species apparently have less than the highest possible symmetry. According to vibrational and ESR spectroscopy $[Co(CO)_4]$ in CO matrices adopts a C_{3v} distortion from tetrahedral geometry, and $[Co(CO)_3]$ has a C_{3v} pyramidal structure. $\Delta H_f^\circ[Co(CO)_4, g]$ is -561 ± 12 kJ mol⁻¹.

34.2.1.2 *Dinuclear carbonyls,* [Co₂(CO)₈]

The only stable dinuclear cobalt carbonyl, octacarbonyldicobalt $[Co_2(CO)_8]$, was first prepared in 1910.[3] The species $[Co_2(CO)_7]$ has been proposed as an intermediate in the reactions of $[Co_2(CO)_8]$ with alkynes and with hydrogen. It also appears to be the major product of the photolytic decomposition of $[Co_2(CO)_8]$ in an argon matrix;[18] its IR spectrum is consistent with the formulation $(CO)_4Co$—$Co(CO)_3$. Earlier reports that an unstable species $[Co_2(CO)_9]$ was formed by the action of CO on $[Co_2(CO)_8]$ at high pressures have been discounted.[19]

(i) *Preparation of* [Co₂(CO)₈]

Methods of preparation of $[Co_2(CO)_8]$ have been reviewed,[16] and are summarized in Table 1. The original synthesis involved direct reaction between cobalt metal, prepared by the reduction of cobalt oxalate with hydrogen, and carbon monoxide at high temperature and pressure. By careful elimination of oxygen, carbon dioxide and water the yield can be made virtually quantitative.

The most convenient high pressure synthesis involves a one step process in which cobalt acetate suspended in acetic anhydride is treated with a 1:4 mixture of hydrogen and carbon monoxide at 160–180 °C. A systematic investigation of the synthesis of $[Co_2(CO)_8]$ from cobalt salts in organic solvents using hydrogen and carbon monoxide has been carried out.[20] The reaction is first order with respect to hydrogen but is retarded by CO pressures greater than 15 atm (1.5 MPa). $[Co_2(CO)_8]$ acts as an autocatalyst, but the Co(II) concentration has no kinetic effect on the reaction.

A convenient laboratory synthesis not requiring high pressure involves the initial preparation of $K[Co(CO)_4]$ by passing carbon monoxide through an alkaline suspension of cobalt(II) cyanide. On acidification the initially formed $[CoH(CO)_4]$ is allowed to decompose thermally to give $[Co_2(CO)_8]$. A low pressure direct synthesis using anhydrous cobalt(II) iodide and zinc powder has also been described.

(ii) *Properties and structure of* [Co₂(CO)₈]

Octacarbonyldicobalt is an orange crystalline solid (m.p. 51 °C) soluble in organic solvents and thermally unstable, slowly losing carbon monoxide at room temperature to give $[Co_4(CO)_{12}]$ and eventually cobalt metal. It is also oxidized on exposure to air to a purple Co(II) species, and is pyrophoric in microcrystalline form. $[Co_2(CO)_8]$ sublimes readily; its vapour pressure at 298.15 K is 0.078 Torr (10.4 Pa) and over the temperature range 288–298 K is given by $\log_e(p/\text{Torr}) = 23.83 - (7865/T)$. ΔH_{293}° (sublimation) = 65.3, ΔH_f° (c) = 1250.6, ΔH_f° (g) = −1172 kJ mol⁻¹.[21]

The crystal structure[22] of $[Co_2(CO)_8]$ shows that in the solid state the molecule has two bridging carbonyl groups (1). The Co—Co distance of 2.52 Å is taken to represent a single cobalt–cobalt bond, consistent with the diamagnetism of the compound.

Although the carbonyl-bridged structure persists in solution and in the gas phase, at least two other isomeric non-bridged forms coexist in equilibrium with it in these phases. IR spectra of matrix isolated $[Co_2(CO)_8]$ molecules condensed from the gas phase into an argon matrix show the presence of the three forms (1)–(3). The order of free energies below 77 K is (1) < (2) < (3), with

(1)   (2)   (3)
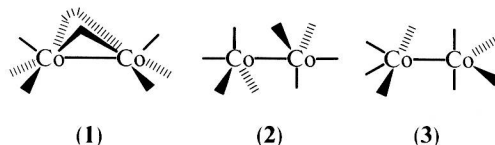
an estimated ΔG for (2) → (1) of 26 kJ mol⁻¹; conversion of (3) into (2) occurs very readily.[23] Hexane solution IR and Raman spectra, and gas phase IR spectra of $[Co_2(CO)_8]$ are all consistent with an increasing proportion of the non-bridged isomers (2) and (3) with increasing temperature. At 298 K, (3) is approximately 30% abundant and predominates at higher temperatures. An analysis of the intramolecular interaction in $[Co_2(CO)_8]$ has concluded that both electronic and steric factors are important in controlling the relative stabilities of these isomeric structures.[24] Extended Hückel Theory calculations have been carried out on structures (1), (2) and (3) to determine optimized geometries and investigate reaction pathways between the different forms.

Table 1 Methods of Preparation of [Co$_2$(CO)$_8$]

Starting material	Solvent	Gas (pressure/atm)	Temperature (°C)	Reaction time (h)	Yield (%)	Comments	Ref.
Co	—	CO(30–40)	150	—	—	Co from reduction of cobalt oxalate in H$_2$ at 5 atm, 300 °C	1
Co	—	CO(200)	150–170	—	99	Co from CoO + H$_2$ at 350 °C. H$_2$ and CO purified from CO$_2$, O$_2$, H$_2$O	2
CoS/Cu	—	CO(220)	200	12	100		3
CoI$_2$/Cu	—	CO(145)	160	12	100		3
CoO	—	CO(1900)	80		100		4
CoCO$_3$	pet. ether	H$_2$/CO 1:1 (200–300)	150–160	3	73–78	systematic study	5
Co(OAc)$_2$·4H$_2$O	(AcO)$_2$O	H$_2$/CO 1:4 (200)	160–180	2	60		6
Co(OH)$_2$	Bu^{t}OH/MePh	H$_2$/CO 1:2 (150)	60	1	97	catalysed by Pd; systematic study	7
CoI$_2$/Zn	Bu^{t}OH/MePh	CO(1)	r.t.	20	55–85		8
Co(CN)$_2$ + KOH	water	CO(1)	r.t.	36–100	45	K[Co(CO)$_4$] initially formed is acidified and [CoH(CO)$_4$] decomposes	9, 10

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Calculated Co—Co bond lengths are 2.56 Å (**1**), 2.88 Å (**2**) and 2.87 Å (**3**). In the case of (**3**), a slight preference for the eclipsed D_{4h} symmetry is found.[25]

NMR spectroscopy shows that carbonyl site exchange occurs very rapidly in $[Co_2(CO)_8]$ at 193 K ($k \gg 10^3$ s^{-1}), the ^{13}C spectrum at this temperature consisting of a single resonance (δ = 204 p.p.m., $\Delta\nu_{1/2}$ = 15 Hz) which broadens with increasing temperature due to quadrupole effects of the ^{59}Co nucleus.[26] The rate of ^{14}CO exchange with $[Co_2(CO)_8]$ is very rapid at room temperature.[27]

(iii)   Reactions of $[Co_2(CO)_8]$

Octacarbonyldicobalt is a very convenient starting material for the preparation of almost any cobalt compound as it is commercially available, is readily obtained pure and undergoes a wide range of reactions. The chemical reactions of $[Co_2(CO)_8]$ have been reviewed.[16,28] Some of the more important reactions not involving organic reagents are illustrated in Scheme 1.
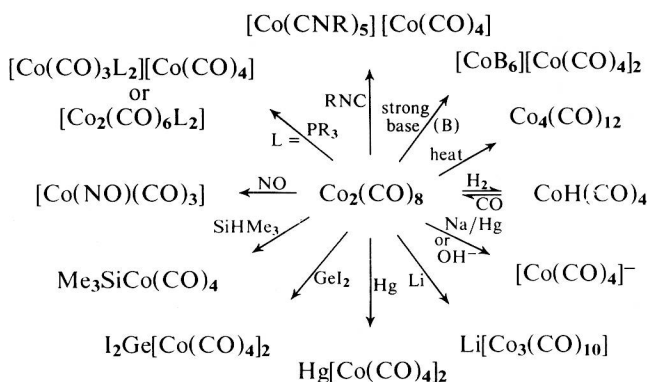
Scheme 1

Reactions may be classified into (a) oxidation, (b) reduction, (c) disproportionation and (d) substitution.

(*a*) *Oxidation reactions.* $[Co_2(CO)_8]$ is readily oxidized by air, halogens and oxidizing acids to give the corresponding cobalt(II) compounds and carbon monoxide. Although $[Co(CO)_5]^+$ is unknown, substituted cobalt(I) carbonyl cationic species are well known and are described in Section 34.2.4.1.

(*b*) *Reduction reactions.* $[Co_2(CO)_8]$ is readily reduced by metals, *e.g.* sodium amalgam in diethyl ether, to the $[Co(CO)_4]^-$ anion, and by hydrogen to $[CoH(CO)_4]$. The reaction of alkali metals with $[Co_2(CO)_8]$ in diethyl ether also yields the $[Co_3(CO)_{10}]^-$ anion.

(*c*) *Disproportionation reactions.* Reactions of $[Co_2(CO)_8]$ with bases such as tertiary phosphines, arsines and stibines under mild conditions and in polar solvents leads to complexes of the type $[Co(CO)_3L_2][Co(CO)_4]$. Isocyanides react to give complexes $[Co(CNR)_5][Co(CO)_4]$, although at higher temperatures, further substitution of CO occurs to give $[Co_2(CNR)_8]$. With more strongly basic oxygen- or nitrogen-donor ligands (B), disproportionation occurs to give cobalt(II) complex salts, $[CoB_6](Co(CO)_4)_2$.

(*d*) *Substitution reactions.* Reaction of $[Co_2(CO)_8]$ with phosphines in non-polar solvents or at high temperatures in polar solvents produces complexes of the type $[Co(CO)_3(PR_3)]_2$. The monosubstituted compounds $[Co_2(CO)_7(PR_3)]$ can also be prepared by direct reaction in Nujol solution, but direct substitution of more than two CO molecules does not readily occur unless potentially bridging phosphines such as $MeN(PF_2)_2$ are used.

The products of disproportionation and substitution reactions are discussed in more detail in Section 34.2.4.

34.2.1.3 [Co₄(CO)₁₂]

A general review of the preparations, structures, properties and reactions of tetranuclear carbonyl clusters contains many references to dodecacarbonyltetracobalt.[29]

(i) Preparation of [Co₄(CO)₁₂]

Dodecacarbonyltetracobalt, [Co₄(CO)₁₂], was discovered at the same time as octacarbonyldicobalt.[3] It is readily formed by the thermal decomposition of [Co₂(CO)₈] at 50 °C in an inert atmosphere. The kinetics of the decomposition have been studied,[30] the rate of [Co₄(CO)₁₂] formation suggesting a fast pre-equilibrium formation of [Co₂(CO)₇] (equation 1). The temperature dependence of K_D^1 agrees well with that derived from the reaction between [Co₂(CO)₈] and hydrogen which is thought to involve the same pre-equilibrium.

$$Co_2(CO)_8 \; \xrightleftharpoons{K_D^1} \; Co_2(CO)_7 \; + \; CO \qquad (1)$$

A more convenient synthesis has been described[31] based on the reduction of cobalt(II) 2-ethylhexanoate with hydrogen in the presence of octacarbonyldicobalt which is more suitable for the preparation of large quantities of the dodecacarbonyl.

(ii) Properties and structure of [Co₄(CO)₁₂]

Dodecacarbonyltetracobalt is a black crystalline solid which is only slightly soluble in organic solvents, melts with decomposition at 60 °C and sublimes with decomposition at 90 °C and 0.1 mmHg. It is slowly oxidized on exposure to the air. $\Delta H°$ (c) = −1843 kJ mol⁻¹, and from an estimate (105 kJ mol⁻¹) of the enthalpy of sublimation,[32] $\Delta H°$ (g) = −1749 kJ mol⁻¹.

The crystal structure of [Co₄(CO)₁₂] is difficult to determine accurately because of crystal disorder, but a recent X-ray study[33] confirms earlier interpretation that the solid state molecular structure corresponds to (4), a tetrahedron of cobalt atoms (av. Co—Co = 2.492 Å) with both terminal and bridging carbonyl groups and having approximate C_{3v} symmetry. An alternative description of this structure has been suggested by Johnson[34] as part of a new general approach to understanding the structures of polynuclear metal carbonyls. The structure is regarded as an icosahedron of 12 close-packed carbonyl groups into which is fitted a tetrahedron of cobalt atoms so oriented as to maximize metal–carbonyl interactions.

(4) (5)

The structure of [Co₄(CO)₁₂] in solution has been the subject of much controversy; the available evidence has been recently reviewed.[35] Early IR evidence suggested an alternative D_{2d} structure (5) to be present in solution, but later work using more concentrated solutions and with ¹³C isotopic substitution now favours the solid state C_{3v} structure (4). From NMR evidence it is clear that the molecule is fluxional in solution, and it has been proposed that rapid carbonyl exchange occurs *via* an unbridged intermediate of T_d symmetry (the [Ir₄(CO)₁₂] structure). The low temperature ¹³C NMR spectrum shows three equally intense resonances which is apparently incompatible with the C_{3v} structure, although the high ⁵⁹Co quadrupole moment may perturb the spectrum. The ⁵⁹Co NMR spectrum has two resonances with relative intensities 3:1, consistent with the C_{3v} structure. Unfortunately, sample decomposition sets in at higher temperatures precluding an analysis of the mechanism of the scrambling process from a fast-exchange spectrum. However, a promising new approach to the understanding of carbonyl scrambling processes in [M₄(CO)₁₂] compounds has been described.[35] The close-packed icosahedron of carbon monoxide ligands is