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COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

*The Synthesis, Reactions and Structures of
Organometallic Compounds*

Volume 6



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COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

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 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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37.1

Nickel: Introduction

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The following Chapters (37.2–37.9) are an essentially descriptive treatment of the synthesis, structure and reactions of the organonickel complexes. We have been greatly helped by the existence of earlier accounts of the topic which cover the literature up to 1974^{1,2} and although over 2000 additional publications have appeared in the six years following, the growth has been more in girth than in stature and this has allowed us to maintain practically the same lay-out as that used in ref. 1. In a few cases the opportunity has been taken to include short essays on topics which were either not included in the earlier volumes, or the significance of which escaped us.

The first two Chapters are devoted to nickel tetracarbonyl and the Lewis-base substituted nickel carbonyl complexes and are followed by discussions of the nickel hydride and alkyl complexes, the alkene and alkyne complexes and the η^3 -allyl, η -cyclobutadiene, η -cyclopentadienyl and η -arene complexes. An account of the use of nickel in organic synthesis has been reserved for Volume 8, Chapters 56.1–56.6.

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37.2

Nickel Tetracarbonyl

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37.2.1 INTRODUCTION

Nickel tetracarbonyl was discovered in 1890 by Mond, Langer and Quincke while investigating the feasibility of using nickel to remove carbon monoxide from gas mixtures. The observation that nickel tetracarbonyl is formed extremely readily became the basis of what is still one of the important industrial processes for preparing pure nickel. In this process the impure metal, generated either by hydrogen reduction of the oxide or by roasting the sulphide, is purified by conversion into the tetracarbonyl which is then decomposed at 200–300 °C; high-purity nickel (99.97+%) is deposited as a powder or as pellets and the CO liberated is recycled. In the original process, which is still operated in Wales, the reaction with CO is carried out at atmospheric pressure. A more recently developed medium-pressure process is operated in Canada in which the carbonylation is carried out at *ca.* 70 atm and the resulting mixture of iron pentacarbonyl and nickel tetracarbonyl is either separated by fractional distillation or decomposed directly to give an iron–nickel alloy.

Detailed accounts of earlier work on the preparation and reactions of nickel tetracarbonyl are to be found in refs. 1 and 2.

37.2.2 PREPARATION

The reader is referred to the handbooks of the Gmelin Institut² for a complete documentation concerning the preparation of nickel tetracarbonyl. All of the synthetically important procedures have in common the reaction of carbon monoxide with a reduced form of nickel, whereby the reduction step can be carried out prior to or during the reaction.

37.2.2.1 Reaction with Metallic Nickel

Nickel is the only metal which reacts readily with CO at room temperature and atmospheric pressure. Finely divided and activated nickel can be prepared by reducing the oxide, oxalate or formate (a convenient small scale synthesis is described in ref. 119). The presence of sulphide has a marked catalytic effect³ while tribomechanical activation causes a dramatic increase in the reaction rate.⁴ The much publicized oscillatory dependence of the rate of formation of nickel tetracarbonyl from a single nickel crystal in a magnetic field⁵ has proved to be an artefact.⁶ The rate of reaction is, however, dependent upon the crystallographic orientation of the surface.¹³³

The initial stages in the reaction between metallic nickel and CO have been followed by reacting atomic nickel with carbon monoxide in an argon matrix at low temperature (*e.g.* 4.2 K); IR evidence indicates not only the step-wise formation of $[\text{Ni}(\text{CO})_4]$ but also the generation of nickel cluster species containing up to three nickel atoms and linear, bridging and face-bridging CO groups.^{7,8}

37.2.2.2 Preparation in Solution

The mechanism of the reduction of nickel salts in the presence of carbon monoxide is frequently complex and seldom completely understood. The more important reactions are discussed in refs. 1 and 2. The reduction of nickel sulphate with dithionite has been recommended as a laboratory procedure; the dithionite is oxidized to sulphite (equation 1).⁹ An electrolytic cell for preparing nickel tetracarbonyl at atmospheric pressure has also been described.¹⁰



Ligand-free zerovalent nickel complexes such as $[\text{Ni}(\eta^3\text{-allyl})_2]$, $[\text{Ni}(\text{cod})_2]$ and $[\text{Ni}(\text{cdt})]$, as well as the product of the co-condensation of nickel vapour with organic substrates, react rapidly and quantitatively with carbon monoxide to give the tetracarbonyl.^{11,12}

37.2.3 PHYSICAL DATA AND BONDING

Nickel tetracarbonyl is a colourless, volatile liquid. A selection of physical data is given in Table 1. The highest published value for the melting point is -17.2°C but values of around -18 to -19°C are commonly observed for samples of normal purity. Nickel tetracarbonyl begins to decompose above 35°C and the boiling point of 42.2°C has been estimated by extrapolating the vapour pressure relationship $\log P = 7.8843 - 1578/T$ to 760 mmHg.

Table 1 Selected Physical Data for Nickel Tetracarbonyl

Property	Value	Remarks
M.p. ($^\circ\text{C}$)	-17.2^{13}	
B.p. ($^\circ\text{C}$)	42.2 (760 mmHg) ¹³	extrapolated from v.p. data
Density (g cm^{-3})	1.30 (25°C) ¹⁵	extrapolated from lit. values
	1.3103 (20°C) ¹⁴	
V.p. (mmHg)	128.05 (0°C), 271.40 (16.1°C), 332.32 (21.1°C)	
	450.0 (28.5°C), 582.65 (35.1°C) ¹³	

The mean dissociation energy $[\bar{D}(\text{M}-\text{CO})]$ for the process $[\text{Ni}(\text{CO})_4(\text{g})] \rightarrow \text{Ni}(\text{g}) + 4\text{CO}(\text{g})$ determined calorimetrically is $146.9 \text{ kJ mol}^{-1}$. The values obtained for the mononuclear metal

carbonyls of Cr, Mn, Fe, Co and Ni are found to correlate with the enthalpy of sublimation (ΔH°_f) such that $\bar{D} \approx (0.28 \pm 0.04) \times \Delta H^\circ_f[M(g)]$.^{16,17}

The structure of nickel tetracarbonyl has been determined by gas-phase electron diffraction at room temperature.¹⁸ The bond distances shown below have been derived assuming that the molecule is tetrahedral:

$$\text{Ni—C } 1.838(2) \text{ \AA}$$

$$\text{C—O } 1.141(2) \text{ \AA}$$

Nickel tetracarbonyl is a popular model for testing various semi-empirical and non-empirical molecular orbital calculations. An *ab-initio* all-electron SCF calculation approximates closely the experimentally determined order and energy of the highest filled molecular orbitals.^{19,20,111,112} Typical results are shown in Table 2 and these should be compared with those obtained for the corresponding palladium and platinum complexes, for which significant differences in the order and energy of the orbitals are observed. The nickel atom bears a small positive charge (+0.24e), indicative of a slight overall transfer of electrons from the nickel to the carbon monoxide molecules. A modification in which the core electrons have been neglected correlates well with the SCF results.²¹ Other calculations which have been reported are based upon the $X\alpha$ method, an INDO scheme, a CNDO scheme and a one-electron orbital procedure.^{22–25,113,122,134,135}

Table 2 Valence Orbital Energies for Nickel Tetracarbonyl²⁰

Molecular orbital	Orbital energy (a.u.)	Character	Ni—C overlap population
9t ₂	−0.400	d, p (2%)	−0.271
2e	−0.470	d	+0.016
8t ₂	−0.648	σ	+0.219
1t ₁	−0.650	π	—
7t ₂	−0.661	π	+0.004
1e	−0.664	π	+0.010
8a ₁	−0.697	σ	−0.030

The bonding and geometry in the coordinatively unsaturated $[\text{Ni}(\text{CO})_3]$ and $[\text{Ni}(\text{CO})_2]$ species have also been subjected to MO treatments of varying sophistication.^{26,27} $[\text{Ni}(\text{CO})_3]$ and $[\text{Ni}(\text{CO})_2]$ are predicted to have respectively D_{3h} and $D_{\infty h}$ symmetry, in agreement with IR data.²⁶ A generalized valence bond description of the low-lying energy states of $[\text{Ni}(\text{CO})]$ has also been published.²⁸

37.2.4 SPECTROSCOPIC PROPERTIES

37.2.4.1 Photoelectron Spectra

The ionization potentials (eV) in the He(I) photoelectron spectrum²⁹ and their provisional assignment are shown below:

$$8.90 (5t_2); 9.77 (2e); 14.12, 14.95 (4t_2 + 1t_1 + 1e + 3t_2); \\ 15.7 (3a_1); 18.25 (2t_2 + 2a_1)$$

The relative intensities of the first two absorptions (3:2) supports their assignment as t₂ and e orbitals having predominantly d-character. The discrepancy between the experimentally obtained values for these two absorptions and those derived theoretically (10.88 and 12.79 eV, see above) is an indication of the difficulty of applying Koopmans' theorem to zerovalent transition metal complexes.

The core electron ionization potentials for $[\text{Ni}(\text{CO})_4]$ (C 1s 294.0, O 1s 539.9 and Ni 2p_{3/2} 860.6 eV) have been discussed in relation to other simple metal carbonyls;^{30,132} back donation leads in all cases to a decrease, upon complexation, of the carbon and oxygen ionization potentials.

It has been pointed out¹⁰⁹ that the trend in the stability of the zerovalent metal complexes of nickel, palladium and platinum, which in the case of the tetracarbonyl complexes is reflected in the order of the metal-carbon force constants ($F_{\text{Ni—C}} > F_{\text{Pt—C}} > F_{\text{Pd—C}}$), parallels the trend

in the difference between the electron affinity and ionization potential for the metal in its d^{10} valence state.

37.2.4.2 Infrared and Raman Spectra

Nickel tetracarbonyl has tetrahedral symmetry (T_d) and nine fundamental vibrations ($2A_1$, $2E$, $4T_2$ and $1T_1$), eight of which are Raman active (A_1 , E and T_2), four IR active (T_2) and one inactive (T_1). Complete spectra have been reported frequently and a selection of reliable results is shown in Table 3. In addition, the IR spectrum of matrix-isolated $[\text{Ni}(\text{CO})_4]$ has been studied at 14 K: the Ni—C stretching frequency is assigned to a band at *ca.* 430 cm^{-1} and the Ni—C—O stretching mode to one at *ca.* 464 cm^{-1} . The former exhibits fine structure which has been attributed to the four nickel isotopes 58, 60, 62 and 64 in their natural abundance.³⁵

Table 3 Vibrational Spectra of Nickel Tetracarbonyl

Assignment	Symmetry	Activity	Description	IR(g) ³¹	IR(s) ³²	R(g) ³³	R(l) ³⁴
ν_1	A_1	R	$\nu(\text{CO})$	—	2123	2131	2128
ν_5	T_2	IR, R	$\nu(\text{CO})$	2057.8	2022–2038	2056	2037–2053
ν_6	T_2	IR, R	$\delta(\text{M—C—O})$	458.9	464	—	461
ν_7	T_2	IR, R	$\nu(\text{M—C})$	423.1	419–429	—	421
ν_2	A_1	R	$\nu(\text{M—C})$	—	391	367.5	381
ν_3	E	R	$\delta(\text{M—C—O})$	—	?	?	?
ν_9	T_1	inactive	$\delta(\text{M—C—O})$	—	303	300	300
ν_8	T_2	IR, R	$\delta(\text{C—M—C})$	80	97	69	78
ν_4	E	R	$\delta(\text{C—M—C})$	64–68	86	63	78

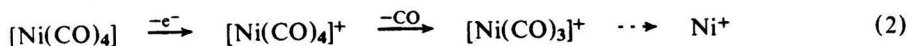
The Raman and IR spectra of nickel tetracarbonyl containing isotopically labelled carbon monoxide have been reported in detail and complete spectra have been recorded for $[\text{Ni}(\text{C}^{18}\text{O})_4]$ and $[\text{Ni}(\text{C}^{13}\text{O})_4]$.^{36,37} The characteristic frequency and intensity patterns for C^{18}O enriched $[\text{Ni}(\text{CO})_n]$ ($n = 1\text{--}4$) species — generated under matrix conditions — have also been analyzed.³⁸

Force constant calculations based upon these assignments have been carried out by a great many authors (see ref. 1, p. 12 and refs. 2, 18, 39). Typical values³¹ for gaseous nickel tetracarbonyl are $F_{\text{CO}} 17.85(09)$, $F_{\text{MC}} 2.08(10)$ and $F_{\text{CO}} 0.12(04) \times 10^{-8}\text{ N \AA}^{-1}$.

Two attempts have been made to calculate the dipole moment derivatives and to estimate the atomic charges in nickel tetracarbonyl using absolute integrated IR band intensity measurements.⁴⁰

37.2.4.3 Ionization Spectroscopy

The mass spectrum of nickel tetracarbonyl has historic interest since it was used in 1935 to determine the isotopic constitution of nickel. Fragmentation in the mass spectrometer occurs by the successive loss of neutral CO molecules (equation 2). High ionization potential is found to favour low mass ions while lower potentials favour high mass ions. For example, the most prominent ion at 75.8 eV is the Ni^+ cation while the $[\text{NiCO}]^+$ species predominates at 50 eV.^{47,48} The nickel ions generated by electron impact have been shown to react with further nickel tetracarbonyl to give $[\text{Ni}_2(\text{CO})_3]^+$ and $[\text{Ni}_2(\text{CO})_2]^+$ in addition to mononuclear species.¹¹⁴



A reliable set of appearance potentials and calculated heats of formation are listed in Table 4. The discrepancy between the values for the heat of formation obtained calorimetrically (see Section 37.2.3) and from spectral data (*ca.* $10\text{--}30\text{ kJ mol}^{-1}$) has not been convincingly explained. Calculations using the 'quasi-equilibrium theory' suggest that the excess energy found in the mass spectral determination represents a kinetic shift and does not indicate that the metal ion is generated in an excited valence state.⁴⁹

The negative ion mass spectrum has been generated using both electrons and potassium ions: $[\text{Ni}(\text{CO})_3]^-$ is formed initially and decomposes by loss of CO molecules.^{50,103}