Ag-00001-Mn-00145

# Dictionary of Organometallic Compounds

CHAPMAN AND HALL

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VOLUME ONE

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# Dictionary of Organometallic Compounds

VOLUME ONE Ag-Mn Ag-00001 - Mn-00145

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Write to

The Editor

Dictionary of Organometallic Compounds

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Treat all organometallic compounds as if they have dangerous properties.

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The specific information in this publication on the hazardous and toxic properties of certain compounds is included to alert the reader to possible dangers associated with the use of these compounds. The absence of such information should not however be taken as an indication of safety in use or misuse.

# **Preface**

The publication of this Dictionary marks the recognition of the fact that organometallic chemistry has now come of age as a scientific discipline. Although the first organometallic compound, Zeise's salt, was discovered in 1827 and a number of types of organometallic compound (for example, the Grignard reagents) have been known for many years, the birth of modern organometallic chemistry is a relatively recent phenomenon: it can perhaps be traced back to the exploitation of the hydroformylation process by Reppe in the early 1940's and to the discovery of ferrocene in 1951. Subsequently the number of known compounds grew exponentially throughout the 1960's and 1970's.

These compounds have exhibited an extraordinary variety of structure, with the preparation not only of new compounds, but of new *types* of compound being a commonplace event during the period referred to. Many of the types of compound discovered contain forms of bonding previously unknown to either organic or inorganic chemistry and they undergo or catalyse an extremely wide range of reactions, making available to the organic chemist a cornucopia of new routes to hitherto unknown or difficultly accessible compounds.

The aim of this publication is to review the whole field of organometallic chemistry, to select those compounds which are in the opinion of the specialist Editors most typical, representative, interesting and useful or potentially useful, and to present their properties and selected bibliography in an orderly and systematically indexed fashion.

It is intended that this treatment will not only help to make quickly available the most relevant specific information about each compound but will make an important contribution to the development of organometallic chemistry by facilitating comparisons between different types of compound. It should also encourage browsing by non-specialists as well as by organometallic chemists themselves.

The information in these volumes is arranged in a manner familiar to users of the *Dictionary of Organic Compounds* and is stored in the form of a carefully structured database which can readily be kept up to date and expanded. Annual supplements to the *Dictionary* will keep the whole compilation topical and thus will reflect the continuing exciting development of organometallic chemistry in future years.

B.J. Aylett M.F. Lappert P.L. Pauson

# Introduction

### 1. Using the Dictionary

The *Dictionary* is divided into element sections: within each section the arrangement of entries is in order of molecular formula according to the Hill convention (ie. C, then H, then other elements in alphabetical sequence of element symbol; where no carbon is present, the elements including H are ordered strictly alphabetically).

There is a section for every element except for the halogens, the noble gases, unstable radioactive elements for which no organometallic compounds have been well characterised, and the following: H, C, N, O, P, S, Se and Te (Entries for organic compounds containing only these elements are included in the companion Heilbron's *Dictionary of Organic Compounds*.) The entries for compounds which contain more than one type of metal atom are printed in full in all relevant sections, thus obviating the need for cross-references.

Every entry is numbered to assist ready location. The entry number consists of a metal element symbol followed by a five-digit number. In these Main Work volumes the first digit is invariably 0; Entries in the supplements will have the supplement number as the first digit.

Volume 3 contains three indexes; a name index, which lists every compound name or synonym in alphabetical order: a molecular formula index, which lists all molecular formulae, including those of derivatives, in Hill convention order, and a CAS registry number index listing all CAS numbers included in the *Dictionary* in serial order.

All indexes refer to the entry number. Each index is described in detail at the beginning of the index section.

In addition to these three printed indexes, each element section (except where the section is very short) is preceded by a graphical structure index allowing the rapid visual location of compounds of interest. The structure index reproduces all structure diagrams present in that element section in reduced size and printed in entry-number order.

### 2. Compound Selection Policy

### 2.1 General

In compiling this *Dictionary* the aim has been to include:

- (1) Compounds representative of all important structural types (typically, the parent member of each series, where known, together with a selection of its homologues).
- (2) Any compound with an established use, such as in catalysis, as a synthetic reagent or starting material.
- (3) Other compounds of particular chemical, structural, biological or historical interest, especially those thought to exhibit unusual bonding characteristics.

### 2.2 Derivatives

Some compounds which are not considered sufficiently important to justify separate entries of their own have been included as derivatives in the entries of other compounds. These may include for example:

- (a) Organic derivatives in the classical sense, e.g. the various esters of ferrocenecarboxylic acids.
  - (b) Donor-acceptor complexes.
- (c) The various salts of an anion or cation (see below).

All names and molecular formulae recorded for derivatives occur in the Name and Molecular Formula Indexes respectively.

### 2.3 Isotopically Labelled Compounds

In general, the *Dictionary* does not include data on isotopic variants.

### 2.4 Dimeric and Oligomeric Substances

Where a compound is known in several states of molecular aggregation, these are all included in the one entry, which usually refers to the monomer. The molecular formulae of all of the oligomeric forms are given, as well as all appropriate synonyms, and the compound can therefore be readily traced through the indexes whether looked for as the monomer or as the oligomer.

Compounds such as those organoplatinum halides which are known only in dimeric form (under ambient conditions) are entered as such, but the hypothetical monomers are included as derivatives to ensure that the names and molecular formulae of the monomeric forms occur in the indexes.

### 2.5 Anions and Cations

In nearly every case, the entry for an ionic substance refers to the naked anion or cation, and the molecular formula, molecular weight and CAS registry number given for the main entry are those of the ion, in agreement with current CAS practice. Salts of the ion with various counterions are then treated as derivatives and the molecular formulae of all of these are given.

In a few exceptional cases, for example the tetraphenylborates, each salt is an important compound in its own right and there are thus separate entries for sodium tetraphenylborate, potassium tetraphenylborate, etc.

### 3. Literature Coverage

In compiling these volumes the primary literature has been surveyed to mid-1983 and some important information from the 1984 literature has been incorporated.

The first annual supplement will appear in late 1985 and will cover the literature to mid-1984.

### 4. Organization of Entries

Fig. 1. illustrates the format of a typical entry within which the individual types of data have been labelled. The range of information included within the Entries is described in detail below.

### 4.1 Chemical Names and Synonyms

The naming of organometallic compounds presents numerous problems ranging from the moderately difficult to the exceptionally difficult. In selecting the range of alternative names to present for each compound or derivative, we have been guided by the following principles:

- (1) The function of the *Dictionary* is to report names which are found in the literature, including *Chemical Abstracts*, and not to attempt to impose a system of nomenclature. Therefore the editorial generation of new names has been kept to the minimum required by consistency. The vast majority of names given in the *Dictionary* are those given in the original paper(s) and in *Chemical Abstracts*.
- (2) For compounds of complex structure, especially metal cluster derivatives where nomenclature is still evolving, only the *Chemical Abstracts* name is reported. Frequently, the authors of papers reporting such compounds do not attempt to name them and it is to be assumed that most users of the *Dictionary* wishing to locate such compounds will do so via the molecular formula.

- (3) There are many examples in the primary literature of the naming of organometallic compounds which is definitely incorrect according to IUPAC convention, especially in the non-alphabetical ordering of ligands in coordination compounds. Many of these incorrect forms are reported.
- (4) Trivial variations in nomenclature which do not materially affect the alphabetical ordering of the name are not included. Such minor variations are legion: a common example is cyclopentadienyl complexes, which may be named as  $\eta^5$ -cyclopentadienyl,  $\eta$ -cyclopentadienyl (Royal Society of Chemistry practice),  $\eta^5$ -2,4-cyclopentadien-1-yl (9CI and 10CI practice),  $\pi$ -cyclopentadienyl (8CI practice), or h<sup>5</sup>-cyclopentadienyl (older literature).

Certain problems relating to the nomenclature of the compounds of particular elements are described in the element introductory sections.

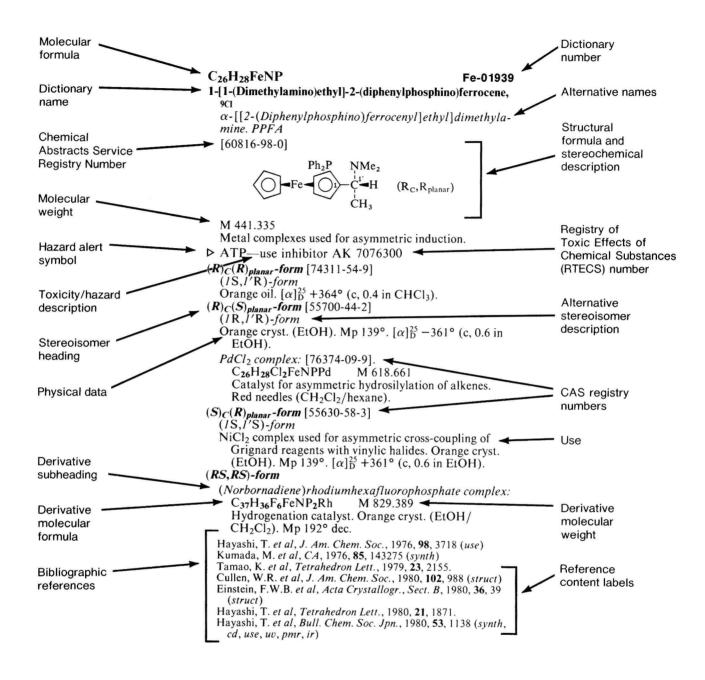
American spellings have been used for all chemical names, thus:

AmericanBritishSulfurSulphurCesiumCaesiumAluminumAluminium

CA names Names corresponding to those used by CAS during the 8th, 9th and 10th collective index periods (1967-71, 1972-6 and 1977-81 respectively) are labelled with the suffixes 8CI, 9CI and 10CI respectively. Names encountered in CA since 1981 are labelled 10CI although it is possible that some further changes may take place before the publication of the 11th Collective Index covering the period 1982-6. Whereas for the vast majority of organic compounds and for simple organometallic compounds such as metal alkyls the system of nomenclature brought in for the 9th Collective Index period, and referred to as 9CI nomenclature, is unchanged for the 10th and 11th Collective Index periods, this is not true for the more complex organometallic compounds where the nomenclature is still evolving. For such compounds there are also many examples of the same compound being registered more than once and being given two or more different names (and registry numbers) in CA.

The following suffixes which are to be found attached to CA names have been omitted:

(1) Stereochemical descriptors, for example, in dicarbonyldichlorobis(triphenylphosphine)ruthenium the CAS descriptor (OC-6-12) indicates the geometry shown below:



**Fig. 1.** Sample Entry. (Toxicity data indicated for illustrative purposes only.)

This is referred to in the dictionary as the *af*-dicarbonyl-*bd*-dichloro-*ce*-diphosphine form using IUPAC convention, *vide infra*.

(2) Bonding descriptors, for example (Fe-Fe) in hexacarbonylbis( $\eta^3$ -2-propenyl)diiron(Fe-Fe),9CI denotes the presence of an iron-iron bond.

For full details of these, see *Chemical Abstracts Index Guide*, 1984, appendix IV.

### 4.2 CAS Registry Numbers

CAS Registry Numbers are identifying numbers allocated to each distinctly definable chemical substance indexed by the Chemical Abstracts Service since 1965. The Numbers have no chemical significance but they provide a label for each substance independent of any system of nomenclature.

The following features of CAS Registry Numbers should, however, be noted:

- (1) Hydrates, salts, complexes, etc. have their own registry numbers.
- (2) Stereoisomeric forms also have their own Registry Numbers, usually in addition to the 'non-specific' Registry Number applicable to the generic substance.
- (3) Additional Registry Numbers may also be allocated to bonding isomers, etc., which are discussed in the literature but which have not been separately characterised (and which may not be capable of separate existence).

In this publication while every attempt has been made to achieve accuracy of the reported Registry Numbers, no guarantee can be provided as to the comprehensiveness of the range of numbers presented. Thus:

- (1) The absence of a Registry Number for a particular substance does not necessarily imply that one has not been allocated.
- (2) Where more than one Registry Number has been found, only one is quoted except for compounds existing in well-characterised stereoisomeric forms.
  - (3) Replaced Numbers are not quoted.

### 4.3 Structural Formulae

Very considerable variations in conventions for depicting organometallic compounds are to be met with in the literature. In preparing this Dictionary care has been taken to achieve as much consistency and clarity in the presentation of structural formulae as possible, according to best current practice and IUPAC recommendations. It must however be borne in mind at all times that the bonding situation in many transition metal complexes is more or less complex and subject to varying interpretations, and is therefore not amenable to accurate depiction by the conventions which serve reasonably well for

organic compounds. For example, the two following representations of the complex obtained from octacar-bonyldicobalt and acetylene refer to the same compound:

For sandwich complexes, the following convention, illustrated with ferrocene as an example, is used throughout.

$$\bigcirc$$
 Fe  $\bigcirc$   $\bigcirc$  or  $\bigcirc$  or  $\bigcirc$ 

Where no structure diagram is given for a particular entry, either the structure of the compound is unknown or it is an isomer of a compound immediately preceding and from which its structure can be readily inferred.

### 4.4 Stereochemical Conventions

Absolute and relative configurations are given according to the (R,S) and (E,Z)-conventions wherever feasible.

The (R,S)-system

In the simplest case, the four substituent atoms about a tetrahedral carbon atom are placed in order of increasing atomic number and the molecule is then viewed from the side remote from the substituent of lowest priority. The configuration is (R) (rectus) if the order of the three other groups from highest to lowest is clockwise, and (S) (sinister) is it is anticlockwise.

Extensions of the (R,S)-system refer to situations such as axial and planar chirality.

Where only the relative configuration of a compound containing more than one chiral centre is known, the symbols  $(R^*)$  and  $(S^*)$  are used, the lowest-numbered chiral centre being arbitrarily assigned the symbol  $(R^*)$ . For racemic modifications of compounds containing more than one chiral centre the symbols (RS) and (SR) are used, with the lowest-numbered chiral centre being arbitrarily assigned the symbol (RS).

For further information see Cahn, R.S. et al, J. Chem. Soc., 1951, 612; Experientia, 1956, 12, 81: Angew. Chem., Int. Ed. Engl., 1966, 5, 383.

The use of the (R,S)-system for chiral polyhaptocomplexes is not covered by the original Cahn-Ingold-Prelog rules and further specification of ligand priorities and bonding convention is required.

### (1) Chiral metallocenes and related complexes

The most widely employed system for specification of metallocene chirality is due to Schlögl. The bond from the central metal atom to the ring carbon atom under consideration is treated as a formal single bond. The carbon atom is then considered as a chiral centre and (R,S) nomenclature is applied in the usual way.

COOH
$$E = \frac{1}{Fe} = \frac{1}{COOH}$$

$$E = \frac{1}{Fe} = \frac{1}{COOH}$$

$$E = \frac{1}{S} = \frac{1}{S} = \frac{1}{COOH}$$
order of precedence Fe  $> C_1 > C_3 > CH_3$  chirality  $(2R)$ 

For further information see Schlögl, K., *Topics Stereochem.*, 1967, 39. In some older papers the molecule is considered overall as a case of planar chirality. However, this convention becomes ambiguous when applied to some more complex structures.

## (2) Polyhapto Ligand as a substituent on a chiral atom

Several conventions have been proposed for determining the order of priority of ligands where one or more is  $\pi$ -bonded. Probably the one most widely accepted and that given prominence in this *Dictionary*, is due to Stanley and Baird, in which the ligand is considered a pseudoatom of atomic weight equal to the sum of all of the  $\pi$ -bonded atoms.

Priority  $C_5H_5$  ("atomic weight" = 60) > Cl > PPh<sub>3</sub> > Me. Chirality (S)-at Fe.

For further information see Stanley, K. et al, J. Am. Chem. Soc., 1975, 97, 6598.

### The (E,Z)-system

This is an extension of the (R,S)-system for specifying configurations at alkene double bonds. The substituents are ordered as in the (R,S)-system and if the two of higher priority are on the same side of the double bond the configuration is (Z) (zusammen), while if they are on the opposite side it is (E) (entgegen).

$$Pt C = C H Pt C = C H$$

$$(E-) (Z-)$$

Note that (E)-does not always correspond to the *trans*- of the earlier literature.

### Octahedral Complexes

IUPAC convention is used to denote the stereochemistry at an octahedral site. In the case of complexes bearing two different types of substituents, for example, the stereochemistry is adequately defined using the terms cis, trans, mer, or fac.

In more complicated cases, italicized letters are used to designate the positions of ligands in various configurations. The letters are assigned thus;

$$e \stackrel{a}{\downarrow} b$$
 $d \stackrel{M}{\downarrow} c$ 

The first mentioned alphabetical ligand in the name is given the designator a, the second ligand the next lowest designator and the assignments to the remaining ligands then follow from this. An example is given above (Section 4.1).

### 4.5 Molecular Weights

Molecular weights given in the *Dictionary* are computer-calculated from the molecular formulae using the values for atomic weights of the elements published by the IUPAC Inorganic Chemistry Division, Commission on Atomic Weights and Isotopic Abundances, 1979.

Molecular weights are given to three decimal places, but it is important to note that the atomic weights of some elements are variable within much wider limits than is implied by the three decimal places. This applies not only to radioactive elements such as Tc and U but also to some non-radioactive elements, especially Pd which exhibits a wide natural variation.

### 4.6 Importance/Use

Information on the use of an organometallic compound is given when it has an established laboratory or industrial use or where it has been shown to undergo or catalyse reactions of potential usefulness.

### 4.7 Physical Data

### (1) Melting-points

The policy followed in the case of conflicting data is as follows:

- (a) Where the literature melting-points are closely similar, only one figure (the highest or most probable) is quoted.
- (b) Where two or more melting-points are recorded and differ by several degrees (the most likely explanation being that one sample was impure) the lower figure is given in parentheses, thus: 139° (135-6°).
- (c) Where quoted figures differ widely and some other explanation such as polymorphism or incorrect identity seems the most likely explanation, both figures are quoted without parentheses, thus: 142°, 205-6°.
- (d) Known cases of polymorphism or double melting-point are noted.

Many organometallic compounds do not melt sharply due to decomposition at or below the melting-point and to difficulties of complete purification. There are therefore numerous examples of wide discrepancies in melting-point, some of which may eventually be attributed to polymorphism, stereoisomerism or non-identity.

### (2) Boiling-points and sublimation-points

Sublimation-points are normally recorded as modified boiling-points, thus: Bp<sub>20</sub> 210° subl. It should be noted, however, that the boiling-point is a thermodynamic property of the compound whereas sublimation is not since it takes place under non-equilibrium conditions.

### (3) Spectroscopic data

Spectroscopic data such as ir maxima and uv wavelengths and extinction coefficients are given in many cases where spectroscopic identification has been important in characterisation, particularly for unstable compounds. In many other cases, spectroscopic data can be rapidly located through the references quoted.

### 4.8 Toxicity and Hazard Information

### (1) General

Toxicity and hazard information is highlighted by the sign  $\triangleright$  (which also appears in the indexes).

The field of safety testing is a complex, difficult and rapidly expanding one, and while as much care as possible has been taken to ensure the accuracy of reported data, the dictionary must not be considered a comprehensive source on hazard data. The function of the reported hazard data is to alert the user to possible hazards associated with the use of a particular compound, but the absence of such data cannot be taken as an indication of safety in use, and the publishers cannot be held responsible for any inaccuracies in the reported information.

Many organometallic compounds have not been evaluated toxicologically but it is to be assumed that all compounds of certain elements such as As, Be, Hg and Tl are toxic.

The handling of the majority of air-sensitive organometallic compounds is to be regarded as hazardous to a greater or lesser degree because of the risk of fire or explosion in contact with air. Not every such sensitive compound will be specially marked as hazardous.

### (2) RTECS Accession Numbers

Many Entries contain one or more RTECS Accession Numbers. Possession of these numbers allows users to locate toxicity information on relevant substances from the NIOSH Registry of Toxic Effects of Chemical Substances.

The Registry is a compendium of toxicity data extracted from the scientific literature and each substance is identified by a unique nine-character alphanumeric RTECS Accession Number.

For each RTECS Accession Number the RTECS database provides the following data when available: substance name and synonyms; update date; CAS Registry Number; molecular weight and formula; reproductive, tumorigenic, and toxic dose data; and citations to aquatic toxicity ratings, IARC reviews, ACGIH Threshold Limit Values, toxicological reviews, existing Federal standards, the NIOSH criteria document program for recommended standards, the NIOSH current intelligence program, the NCI Carcinogenesis Testing Program, and the EPA Toxic Substances Control Act inventory.

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- 2. Microfiche edition (published quarterly), also available from U.S. Government Printing Office.
- 3. RTECS on-line data base (updated quarterly), available from two sources: National Library of Medicine (NLM) Medical Literature Analysis and Retrieval System (MEDLARS), National Library of Medicine, 8600 Rockville Pike, Bethesda, Maryland 20209, and the National Institutes of Health/Environmental Protection Agency Chemical Information System (CIS), 2135 Wisconsin Avenue, N.W., Washington, D.C. 20007.
- 4. RTECS computer tape (produced annually), available from: National Technical Information Service (NTIS), Port Royal Road, Springfield, VA 22161.

# Bibliographic References 4.10 Journal Abbreviations

The selection of references is made with the aim of facilitating entry into the literature for the user who wishes to locate more detailed information about a particular compound. Thus in general, recent references are preferred to older ones. The number of references quoted cannot be taken as an indication of the relative importance of a compound.

The contents of many references are indicated by means of mnemonic suffixes, of which the following are the most important: In general these follow the practice of the *Chemical Abstracts Service Source Index* (CASSI) with one or two exceptions such as the *Chemical Communications* published by the Royal Society of Chemistry. This changed its name from *Chem. Commun.* to *J. Chem. Soc.* (D) in 1970, then again to *J. Chem. Soc. Chem. Commun.* in 1972. For consistency the latter form has been used throughout.

pharmacology

polarography

resolution

synthesis

toxicity

tautomerism

review

resonance spectrum

proton (1H) nuclear magnetic

properties (chemical or physical)

ultraviolet spectrum (includes

visible spectrum in the case of

coloured compounds)

In patent references, no distinction is made between patent applications and granted patents.

specific rotation

(abs config)	absolute configuration
(anal)	analysis
(bibl)	bibliography
(cd)	circular dichromism
(chromatog)	chromatography
(cmr)	carbon (13C) nuclear magnetic
()	resonance spectrum
(conformn)	conformation
(cryst struct)	X-ray crystal structure
	determination
(deriv)	reference referring to a derivative
(ed)	electron diffraction
(esr)	electron spin resonance spectrum
(glc)	gas-liquid chromatography
(haz)	hazard
(ir)	infrared spectrum
(isom)	isomerism
(mcd)	magnetic circular dichroism
(mord)	magnetic optical rotatory
	dispersion
(ms)	mass spectrum
(nd)	neutron diffraction
(nmr)	nuclear magnetic resonance
	spectrum

optical rotary dispersion

photoelectron spectrum

### 4.11 Abbreviations

 $[\alpha]$ 

(pharmacol)

(pmr)

(polarog)

(props)

(resoln)

(synth)

(tautom)

(rev)

(tox)

(uv)

abs. config.	absolute configuration
Ac	acetyl
AcOH	acetic acid
alk.	alkaline
amorph.	amorphous
anal.	analytical applications, analysis
	or detection
anhyd.	anhydrous
approx.	approximately
aq.	aqueous
asym.	asymmetrical, unsymmetrical
B.	base
bibl.	bibliography
biosynth.	biosynthesis
Bp	boiling point
B.P.	British Patent
c.	concentration
cmr	<sup>13</sup> C nuclear magnetic resonance
	spectrum
ca.	(circa) about
c.d.	circular dichromism
chromatog.	chromatography
col.	colour, coloration
comly.	commercially

compd. compound conc. concentrated config. configuration constit. constituent density d. dec. decomposes, decomposition deg. degree deriv(s). derivative(s) descr. described detn. detection dilute, dilution dil. dimorph. dimorphic diss. dissolves, dissolved distil, distillation dist. equilib. equilibrium especially esp. electron spin resonance spectrum esr Et ethyl **EtOAc** ethyl acetate evaporation evapn. exposure, experimental exp. flash point fl. p. fluoresces, fluorescence fluor. formn. formation Fp freezing point gas liquid chromatography glc haz. hazard high performance liquid hplc chromatography hydrol. hydrolyses, hydrolysed, hydrolysis insol. insoluble infrared spectrum ir. isol. isolated isom. isomerises lethal dose: LD<sub>50</sub>, a dose which is LD lethal to 50% of the animals tested manufacturer, manufactured manuf. max. maximum Me methyl metab. metabolite misc. miscible mixt. mixture moderately mod. melting point Mp ms mass spectrum index of refraction e.g. (n<sub>D</sub><sup>20</sup> for n 20° and sodium light) nuclear magnetic resonance nmr spectrum obtained obt. optical rotatory dispersion ord pet, ether petroleum ether (light petroleum)

Ph

pharmacol. pharmacology proton magnetic resonance pmr spectrum polarography polarog. precipitated ppd. probably prob. properties props. purifn. purification Py pyridine reference ref. resoln. resolution review rev. r.t. room temperature separation sepn. sl. slightly soluble sol. soln. solution solv. solvent spar. sparingly subl. sublimation synth. synthesis tautomerism tautom. thin layer chromatography tlc toxicity tox. TLV Threshold Limit Value

unsatd. unsaturated
U.S.P. United States Patent

v. very
var. variety
vis. visible
vol. volume

### 5. Sources of further information

The following books and review series provide more information about various aspects of organometallic chemistry. Lists of reviews specific to organic compounds of particular metals may be found in the introductory sections of the metals concerned.

ultraviolet spectrum

### General

uv

Comprehensive Organometallic Chemistry, Wilkinson, G. et al. Eds, Pergamon, Oxford, 1982. This book represents the most complete and up to date review of the whole subject. In addition to sections for each element there are chapters on the use of organometallics in organic synthesis and catalysis.

Comprehensive Inorganic Chemistry, Trotman-Dickenson, A.F. et al. Eds, Pergamon, Oxford, 1973. Con-

phenyl (C<sub>6</sub>H<sub>5</sub>)