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NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS OF THE TRANSITION ELEMENTS

(IUPAC Recommendations 1999)

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Nomenclature of organometallic compounds of the transition elements (IUPAC Recommendations 1999)

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Organometallic compounds are defined as containing at least one metal-carbon bond between an organic molecule, ion, or radical and a metal. Organometallic nomenclature therefore usually combines the nomenclature of organic chemistry and that of coordination chemistry. Provisional rules outlining nomenclature for such compounds are found both in *Nomenclature of Organic Chemistry*, 1979 and in *Nomenclature of Inorganic Chemistry*, 1990.

This document describes the nomenclature for organometallic compounds of the transition elements, that is compounds with metal-carbon single bonds, metal-carbon multiple bonds as well as complexes with unsaturated molecules (metal- π -complexes).

Organometallic compounds are considered to be produced by addition reactions and so they are named on an addition principle. The name therefore is built around the central metal atom name. Organic ligand names are derived according to the rules of organic chemistry with appropriate endings to indicate the different bonding modes. To designate the points of attachment of ligands in more complicated structures, the η , κ , and μ -notations are used. The final section deals with the abbreviated nomenclature for metallocenes and their derivatives.

1 INTRODUCTION

In this document, the general and fundamental concepts for naming organometallic compounds of the transition elements are outlined. With the enormous growth that this field has experienced within the last forty years and in view of the fact that new classes of compounds with unprecedented bonding modes have been discovered, it has become necessary to formulate additional nomenclature rules. Furthermore, the advent of new techniques for computer storage and retrieval of chemical information as well as legal and commercial requirements have placed a special emphasis on finding unique names for every new material prepared.

An organometallic compound is defined as any chemical species containing at least one bond between a carbon atom in an organic molecule, ion, or radical and a metal. By their very nature, the names of organometallic compounds should therefore incorporate the rules of organic chemistry as well as those of coordination chemistry. In general, however, these belong to two different nomenclature systems that have evolved separately. It is the aim of this Section to define a system of organometallic nomenclature that, while being principally based on the additive system of coordination nomenclature (*Nomenclature of Inorganic Chemistry, Recommendations 1990*, [1]), still incorporates the rules for naming organic groups and substituents (*A Guide to IUPAC Nomenclature of Organic Compounds, Recommendations 1993* [2]) as far as possible. In addition, further rules are formulated that unambiguously designate the special bonding modes of organometallic compounds.

It should be emphasized that the aim of nomenclature is confined to the precise description of the composition of a compound as well as the connectivity of atoms within a molecule or ion. Nomenclature should not attempt to convey details about the polarity of bonds, patterns of reactivity or methods of synthesis. The historical perspective on these may change with the advent of better theoretical models or the increase in chemical knowledge. This is particularly true in a relatively new field such as organometallic chemistry.

2 SYSTEMS OF NOMENCLATURE

Three general types of nomenclature for inorganic compounds have developed historically, each used for a specific type of chemical entity.

2.1 Binary type nomenclature

This type of nomenclature is widely in use for salt-like ionic species. The classification 'binary' derives from its predominant use for simple salts consisting of cation and anion, but it may be extended to more complicated compositions.

The components have to be in a specified order and a modification of the element name is sometimes necessary, e.g. bromide, telluride, etc. It is especially appropriate and commonly used, when the composition of a material is indicated, but information on the exact structure is not known or not required.

This system has also been extended to the more simple type of organometallic species that may be regarded as derivatives of inorganic salts or molecules and is most often used in designations of commercial products.

1. diethylaluminium bromide
2. phenylmercury acetate
3. methylmagnesium chloride
4. sodium cyclopentadienide

2.2 Substitutive nomenclature

This system has its origin in organic nomenclature and has been extended to the naming of organometallic compounds of some main-group elements, which in their bonding modes and properties closely resemble organic molecules. The system is based on the concept of a parent hydride (an alkane in organic nomenclature), e.g. SiH_4 = silane, AsH_3 = arsane etc., whose hydrogen atoms have partially or completely been replaced by organic groups (substituents). This system is used for naming compounds of group 13, 14, 15, and 16.

1. dicyclohexylborane $\text{B}(\text{C}_6\text{H}_{11})_2\text{H}$
2. chlorotrimethylsilane $\text{Si}(\text{CH}_3)_3\text{Cl}$
3. triethylarsane $\text{As}(\text{C}_2\text{H}_5)_3$
4. diphenylselane $\text{Se}(\text{C}_6\text{H}_5)_2$

Organometallic compounds with double bonds between the main-group elements may also be similarly named to alkenes, e.g. tetramesityldisilene for $[\text{2,4,6}-(\text{CH}_3)_3\text{C}_6\text{H}_2]_2\text{Si}=\text{Si}[\text{2,4,6}-(\text{CH}_3)_3\text{C}_6\text{H}_2]_2$.

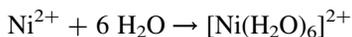
For details, see *Nomenclature of Organic Chemistry*, 1979 edition (*Blue Book '79*) [3], Rules D-3 and: *A Guide to IUPAC Nomenclature of Organic Compounds, Recommendations 1993* (*Blue Book '93*) [4].

2.3 Coordination nomenclature

According to a useful, historically-based formalism, coordination compounds are considered to be produced by addition reactions and so they were named on an addition principle. The name is built around the central atom name, just as the coordination entity is built around the central atom.

Example:

Addition of ligands to a central atom:



Addition of ligand names to a central atom name:

hexaaquanickel(II) ion

This nomenclature extends to more complicated structures where central atoms form dinuclear, trinuclear or even polynuclear species from mononuclear building blocks. The persistent centrality of the central atom is emphasized by the root 'nuclear'.

As coordination nomenclature is also the central core for the system presented here for naming organometallic complexes, a condensed outline of the general definitions and rules of coordination nomenclature is given in the following section.

3 COORDINATION NOMENCLATURE

3.1 General definitions of coordination chemistry

The additive system for naming inorganic coordination compounds regards a compound as a combination of a *central atom*, usually that of a metal, to which a surrounding array of other atoms or groups of atoms is attached, each of which is called a *ligand*. A coordination entity may be a neutral molecule, a cation or an anion. The ligands may be viewed as neutral or ionic entities or groups that are bonded (*ligated*) to an appropriately charged central atom.

It is standard practice to think of the ligand atoms that are directly attached to the central atom as defining a *coordination polyhedron (or polygon)* about the central atom. The *coordination number* is defined as being equal to the number of σ -bonds between the central atom and ligands. In this way, the coordination number may equal the number of vertices in the coordination polyhedron. This also applies to ligands such as CN^- , CO, N_2 , and $\text{P}(\text{CH}_3)_3$, whose bonding may involve a combination of σ - and π -bonding between the ligating atom and the central atom; the π -bonds are not considered in determining the coordination number. Thus, $[\text{W}(\text{CO})_6]$ has a coordination number of six and is an octahedral complex, while $[\text{Pb}(\text{C}_2\text{H}_5)_4]$ has a coordination number of 4 and is a tetrahedral complex.

This concept of coordination chemistry was unambiguous for a long time, but complications have arisen with the advent of new classes of complexes and ligands. According to tradition, every ligating atom or group was recognized as bringing a *lone pair of electrons* to the central atom in the coordination entity. This sharing of ligand electron pairs became synonymous with the verb '*to coordinate*'. Furthermore, in the inevitable electron book-keeping that ensues upon consideration of a chemical compound, the coordination entity was dissected (in thought) by removing each ligand in such a way that each ligating atom or group took two electrons with it. This definition is now no longer appropriate in all those areas of coordination chemistry and particularly organometallic chemistry, where the bonding through several adjacent atoms of a ligand to the central atom is often better described as a combination of σ , π and δ bonds (the label σ , π or δ referring to the symmetry of the orbital interactions between ligand and central atom).

A ligand such as ethene, consisting of two ligating carbon atoms, nevertheless brings only one pair of electrons to the central atom. Likewise, ethyne, coordinated *via* both carbon atoms, can be thought to bring either one or two pairs of electrons to one central atom, depending on the type of coordination involved. Both ligands are normally regarded as monodentate ligands. This changes when ethene or ethyne is considered to 'add oxidatively' to a central atom; they are then considered to be *didentate chelating ligands* which, on electron counting and dissection of the coordination entity to determine oxidation numbers, are assumed to take two pairs of electrons with them. This different view can be expressed by referring to such compounds as metallacyclopropanes or metallacycloprenes rather than alkene or alkyne complexes.

Chelation traditionally involves coordination of more than one σ -electron-pair donor group from the same ligand to the same central atom. The number of such ligating groups in a single chelating ligand is indicated by the adjectives didentate, tridentate, tetradentate, etc. The number of donor groups from a given ligand attached to the same central atom is called the *denticity*. This concept can again be applied strictly only to the more conventional types of coordination compounds of the 'Werner-type' and to those classes of organometallic complexes involving only σ -bonds. It will lead to ambiguities, as outlined above, even with a simple ligand such as ethene. Butadiene and benzene supply two and three pairs of electrons upon coordination and are therefore regarded as di- and tridentate ligands, respectively. In stereochemistry, however, such ligands are often treated as if they were monodentate (see section I-10.7.1 of the *Red Book* [1]).

A *bridging ligand* binds to two or more central atoms simultaneously, thereby linking them together to produce coordination entities having more than one central atom; complex polynuclear entities (involving a number of central atoms) are called *clusters*. The number of central atoms joined into a single coordination entity by bridging ligands or metal-metal bonds is indicated by dinuclear, trinuclear, tetranuclear, etc. The *bridge index* is the number of central atoms linked by a particular bridging ligand. Bridging can be through one or more atoms.

3.2 Oxidation numbers and net charges

The *oxidation number* of a central atom in a coordination entity is defined as the charge it would bear if all ligands were removed along with the electron pairs that were shared with the central atom. It may be represented by a Roman numeral.

The general and systematic treatment of oxidation numbers follows from the application of the classical definition of coordination numbers. This concept is therefore difficult to apply to compounds of which the coordination number cannot be unequivocally assigned. It must be emphasized that oxidation number is an index derived from a formal set of rules (Section I-5.5.2.2 of the *Red Book* [1]) and that it does not indicate electron distribution. In certain cases, the formalism does not give acceptable central atom oxidation numbers. This is especially true when it cannot be determined whether the addition of a ligand is better regarded as a Lewis-acid or -base association or as an oxidative addition. In such ambiguous cases, the *net charge* of the coordination entity is preferred in most nomenclature practices.

In the examples that follow, the relation of formal oxidation number to coordination number and net charge is illustrated for some simple coordination compounds (*en* = *ethane-1,2-diamine*) (Table 1).

Table 1 Oxidation number and net charge

Complex	Ligand list	Central atom oxidation number	Net charge
[CoCl(NO ₂)(NH ₃) ₄]	1 Cl ⁻ , 1 NO ₂ ⁻ , 4 NH ₃	II	0
[Co(en) ₃]Cl ₃	3 NH ₂ CH ₂ CH ₂ NH ₂	III	3+
[PdCl ₄] ²⁻	4 Cl ⁻	II	2-
[Fe(CO) ₄] ²⁻	4 CO	-II	2-
[FeH(CO) ₄] ⁻	4 CO, 1 H ⁻	0	1-
[FeH ₂ (CO) ₄]	4 CO, 2 H ⁻	II	0

As oxidation numbers cannot be assigned unambiguously to many organometallic compounds, no formal oxidation numbers will be attributed to the central atoms in the following section on organometallic nomenclature. However, this does not imply that the oxidation state of a metal or a ligand is not important when discussing reaction mechanisms, the polarity of bonds or the results of spectroscopic or structural studies. Oxidation numbers also have to be assigned, if only arbitrarily, when establishing the number of valence electrons.

3.3 Formulae and names for coordination compounds

In a *coordination formula*, the central atom is listed first. The formally anionic ligands appear next, listed

in alphabetical order according to the first symbols of their formulae. The neutral ligands follow, also in alphabetical order, according to the same principle. The formula of the entire coordination entity, whether charged or not, is enclosed in square brackets. If the coordination entity is negatively charged, the formula is preceded by the cation formula.

When ligands are polyatomic, their formulae are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses. In the special case of coordination entities, the nesting order of enclosing marks is given in Sections I-2.2 and I-4.6.7 of *Red Book I* [1]. There should be no space between representations of ionic species within a coordination formula (*en* = ethane-1,2-diamine).

Examples:

1. $\text{K}_2[\text{PdCl}_4]$
2. $[\text{Co}(\text{en})_3]\text{Cl}_3$
3. $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]$
4. $[\text{IrClH}_2(\text{CO})\{\text{P}(\text{CH}_3)_3\}_2]$
5. $[\text{CuCl}_2\{\text{OC}(\text{NH}_2)_2\}_2]$

In a *coordination name*, the ligands are listed in alphabetical order, regardless of their charge, before the name of the central atom. Numerical prefixes indicating the number of ligands are not considered in determining that order. In ionic species, the cations are listed first, then the anions. The stoichiometric proportions of ionic entities may be given by using numerical prefixes on both ions, as necessary.

Alternatively, the charge on a coordination entity may be indicated. The net charge is then written in Arabic numerals on the line, with the number preceding the charge sign, and enclosed in parentheses. It follows the name of the central atom without the intervention of a space. All anionic coordination entities take the ending -ate, whereas no distinguishing termination is used for cationic or neutral coordination entities. The use of parentheses in coordination names is outlined in *Red Book I-2.2.3.2*.

Examples:

1. $\text{K}_2[\text{PdCl}_4]$
potassium tetrachloropalladate(2-)
dipotassium tetrachloropalladate
2. $[\text{Co}(\text{en})_3]\text{Cl}_3$
tris(ethane-1,2-diamine)cobalt trichloride
tris(ethane-1,2-diamine)cobalt(3+) chloride
3. $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]$
tetraamminechloronitrito-*N*-cobalt
4. $[\text{IrClH}_2(\text{CO})\{\text{P}(\text{CH}_3)_3\}_2]$
carbonylchlorodihydridobis(trimethylphosphane)iridium
5. $[\text{CuCl}_2\{\text{OC}(\text{NH}_2)_2\}_2]$
dichlorobis(urea)copper

For a complete outline of the general concepts and definitions of coordination nomenclature, the *Nomenclature of Inorganic Chemistry, Recommendations 1990*, Chapter 10 [1], should be consulted.

4 NOMENCLATURE FOR ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

4.1 Valence-electron numbers and the 18-valence-electron rule

While formal oxidation numbers will not be assigned to organometallic complexes in this document, it is nevertheless important to establish correctly the number of valence electrons associated with each complex as well as the net charge.

The 18-electron rule (Sidgwick, 1927) is based on the valence-bond formalism of localised metal-ligand bonds; it states that thermodynamically stable transition metal organometallics are formed when the sum of the metal *d* electrons plus the electrons conventionally regarded as supplied by the ligands

equals 18. In this way, the metal formally attains the electron configuration of the next higher noble gas. The 18-electron rule is also known as the 'noble-gas rule' or the 'effective atomic number (EAN) rule'.

In the following table, ligands commonly encountered in organometallic compounds of the transition elements are listed together with the numbers of electrons they are considered to supply. The oxidation number of the metal has to be adjusted in relation to the charge attributed to the various ligands to obtain the correct net charge (Table 2).

Table 2 Charge and bonding electrons of commonly encountered ligands

Neutral	Positive	Negative	Ligand
1	–	2	alkyl, aryl, hydride, halide, amide
2	–	–	η^2 -alkene, CO, CS, amine, nitrile, isocyanide, phosphane
2	–	4(2–)	alkylidene (CR_2) or alkylidide (CR_2^{2-})
2	–	4(2–)	nitrene (NR) or imide (NR^{2-})
–	–	4(2–)	oxide O^{2-}
3	–	6(3–)	alkylidyne (CR) or alkyltriide (CR^{3-})
3	–	4	η^3 -allyl, η^3 -enyl, η^3 -cyclopropenyl
1	–	–	NO (bent)
3	2	–	NO (linear)*
4	–	–	η^4 -diene, η^4 -cyclobutadiene
5	–	6	η^5 -cyclopentadienyl
6	–	–	η^6 -arene, η^6 -triene
7	6	–	η^7 -tropylium [†] or η^7 -cycloheptatrienyl
8	–	10(2–)	η^8 -cyclooctatetraene [‡]

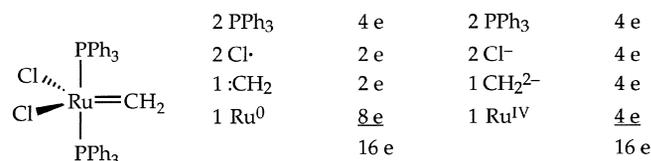
* NO^+ is isoelectronic with CO and as such acts as a two-electron ligand in substitution reactions.

[†]The name 'tropylium' designates the monocation C_7H_7^+ .

[‡]The coordinated C_8H_8 ligand may also be regarded as a dianion.

When determining valence electron numbers, the following conventions should be taken into account:

1. The intramolecular partitioning of electrons has to ensure that the total complex charge remains unchanged:



Scheme 1

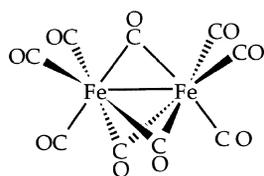
2. A metal-metal bond contributes one electron to the count on each metal. Metal-metal double or triple bonds supply 2 and 3 electrons, respectively, to each metal:



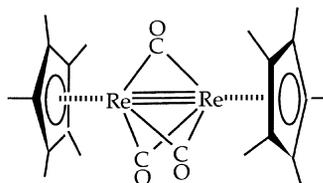
Scheme 2

3. The electron pair of a bridging ligand such as CO donates one electron to each of the bridged metals, as in the following two examples:

The 18 electron rule has considerable predictive value in that the composition of many transition-metal



3 CO	6 e
3 (μ-CO)	3 e
Fe ⁰	8 e
Fe—Fe	<u>1 e</u>
	18 e



1 C ₅ Me ₅ ⁻	6 e
3 (μ-CO)	3 e
Re ^I	6 e
Re≡Re	<u>3 e</u>
	18 e

Scheme 3

complexes may be predicted from combinations of sets of ligands with transition metals of appropriate *d* electron count. It is also relevant in establishing the existence and multiplicity of metal-metal bonds.

For organometallics of the *f* elements (lanthanoids and actinoids) this procedure is not applicable. Exceptions to this rule are also found in the early and late transition metals (see example 1) and in complexes with high formal oxidation states of the central atom, such as W(CH₃)₆ or CH₃ReO₃.

4.2 Ligand names

4.2.1 Ligands coordinating by one metal-carbon single bond

In coordination nomenclature, a ligand name for an anionic ligand ends in -o. If the anion name ends in -ide, -ite or -ate, the final -e is replaced by -o, giving -ido, -ito and -ato, respectively (see *Red Book* I-10.4.5 [1]). This is also the case if the ligand is organic but coordinates *via* an atom other than carbon. Thus, CH₃COO⁻ is called acetato and (CH₃)₂N⁻ is called dimethylamido. Neutral and cationic names are used without further modification. In the following table, names for the more common ligands not coordinating *via* carbon atoms are listed together with some ligands coordinating *via* carbon but not considered to be 'organic'. Enclosing marks are placed on ligand names as they are to be used in names of coordination entities (for a complete list, refer to *Red Book* I-10.4.5 [1]). The alternative name is often historically derived and therefore the one commonly used (Table 3).

If one regards organic ligands coordinating *via* one carbon atom as anions formed by removing one hydron from a carbon atom of an organic molecule, they are named by replacing the final -e of the parent compound name by -ide (*Blue Book* 79, C 84.3 [3]). The most common application of this rule is found in the binary type nomenclature for naming highly ionic organic compounds of the alkali and alkaline earth metals, such as sodium methanide or potassium cyclopentadienide.

In coordination nomenclature, the ending -ide has to be replaced by -ido. All names must have locants starting with propane, except monocyclic, unsubstituted rings.

Examples:

(CH ₃) ⁻	methanido
(CH ₃ CH ₂) ⁻	ethanido
(CH ₂ =CHCH ₂) ⁻	prop-2-en-1-ido
(C ₆ H ₅) ⁻	benzenido
(C ₅ H ₅) ⁻	cyclopentadienido

A transition metal compound such as [Ti(CH₃)Cl₃] would therefore be called trichlorido(methanido)titanium by systematic application of coordination nomenclature.

The alternative for naming an organic ligand attached *via* a single carbon atom is to regard it as a radical substituent, its name being derived from the parent hydrocarbon from which one hydrogen atom has been removed. This designation is somewhat arbitrary, as such ligands in organometallic chemistry

Table 3 Ligand names for ligands of Groups 15–17

Formula	Systematic ligand name	Alternative ligand name
Cl ⁻	chlorido	chloro
Br ⁻	bromido	bromo
I ⁻	iodido	iodo
O ²⁻	oxido	oxo
S ²⁻	sulfido	thio
H ₂ O	oxidane	aqua
OH ⁻	hydroxido	hydroxo
(CH ₃ O) ⁻	(methanolato)	methoxido
(C ₂ H ₅ O) ⁻	(ethanolato)	ethoxido
(C ₆ H ₅ O) ⁻	(phenolato)	phenoxido
(C ₆ H ₅ S) ⁻	(benzenethiolato)	(phenylsulfido)
(HCO ₂) ⁻	(methanoato)	(formato)
(CH ₃ CO ₂) ⁻	(ethanoato)	(acetato)
N ₂	(dinitrogen)	
N ³⁻	nitrido	
P ³⁻	phosphido	
NH ₃	(azane)	ammine
PH ₃	(phosphane)	(phosphine)
(NH ₂) ⁻	azanido	amido
(NH) ²⁻	azanediiido	imido
CH ₃ NH ₂	(methanamine)	(methylamine)
(CH ₃) ₂ NH	(<i>N</i> -methylmethanamine)	(dimethylamine)
(CH ₃) ₃ N	(<i>N,N</i> -dimethylmethanamine)	(trimethylamine)
CH ₃ PH ₂	(methylphosphane)	(methylphosphine)
(CH ₃) ₂ PH	(dimethylphosphane)	(dimethylphosphine)
(CH ₃) ₃ P	(trimethylphosphane)	(trimethylphosphine)
(CH ₃ N) ²⁻	[methanaminato(2-)]	(methylimido)
[(CH ₃) ₂ N] ⁻	(<i>N</i> -methylmethanaminato)	(dimethylamido)
[(CH ₃) ₂ P] ⁻	(dimethylphosphanido)	(dimethylphosphanyl)
(CH ₃ P) ²⁻	(methylphosphanediiido)	(methylphosphanediyil)
(CH ₃ PH) ⁻	(methylphosphanido)	(methylphosphino)
(NO ₂) ⁻	[dioxonitrato(1-)- <i>kO</i>]	nitrito- <i>O</i>
	[dioxonitrato(1-)- <i>kN</i>]	nitrito- <i>N</i> , nitro
(NO ₃) ⁻	[trioxonitrato(1-)]	nitrato
NO	(nitrogen monoxide)	nitrosyl
<i>Ligand names of 'inorganic' ligands of Group 14</i>		
CO	(carbon monoxide)	carbonyl
CO ₂	(carbon dioxide)	
CS	(carbon monosulfide)	(thiocarbonyl)
CN ⁻	cyanido	cyano

are generally treated as anions when calculating oxidation states (see 3.2), although the bonding in reality may be highly covalent. This system of nomenclature has a long tradition in organic and organometallic chemistry (see *Blue Guide 93*, section R-2.5 [2]). Its major advantage is that established 'trivial' names for organic groups can be used unchanged.

Suffixes are used according to two methods as follows:

(a) The suffix -yl replaces the ending -ane of the parent hydride name. The atom with the free valence terminates the chain and always has the locant '1', which is omitted from the name. This method is recommended only for saturated acyclic and monocyclic hydrocarbon substituent groups and for the mononuclear parent hydrides of silicon, germanium, tin, lead and boron.

Examples:

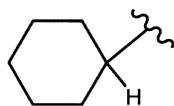
CH_3-	methyl
CH_3-CH_2-	ethyl
$\text{CH}_2=\text{CHCH}_2-$	allyl
$\text{C}_6\text{H}_{11}-$	cyclohexyl
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)\text{H}-$	1-methylbutyl
$(\text{CH}_3)_3\text{Si}-$	trimethylsilyl

The aforementioned compound $[\text{Ti}(\text{CH}_3)\text{Cl}_3]$ would therefore be called trichloro(methyl)titanium by this method.

(b) In a more general method, the suffix -yl is added to the name of the parent hydride with removal of the terminal -e, if present. The atom with the free valence is given a number as low as is consistent with any established numbering of the parent hydride. The locant number, including '1', must always be cited.

Examples:

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	pentan-1-yl
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)\text{H}-$	pentan-2-yl



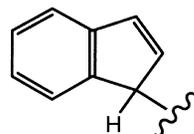
cyclohexan-1-yl

Scheme 4

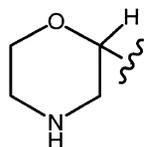
For a more complete discussion of substituent prefix names, it is recommended to refer to *Blue Guide 93*, section R-2.5 [2].

In fused polycyclic hydrocarbons as well as in heterocyclic systems, the special numbering schemes outlined in the *Blue Guide 93* [2] and *Nomenclature of fused and bridged fused ring systems (IUPAC Recommendations 1998)* [5], are adopted. The atom of attachment is then also indicated before the ending -yl.

Examples:



inden-1-yl



morpholin-2-yl

Scheme 5

In the following tables, organic ligand names are listed by their '*systematic additive name*' and their '*systematic substitutive name*'. In some cases an alternative name that is generally preferable for either historical reasons or reasons of brevity is also included. The currently **preferred name** is printed in bold. This preferred name will also be used in the examples following each table of ligand names (Table 4; Fig. 1).

4.2.2 Ligands coordinating by several metal-carbon single bonds

The ligand names are derived from the parent hydrocarbon, from which one or more hydrogen atoms have been removed. In the systematic substitutive name, a suffix -diyl or -triyl is attached to the name of the parent hydrocarbon, if two or three hydrogen atoms are replaced by metal atoms. The locant number must always be cited, except for ligands derived from methane. Alternatively, when using the additive

Table 4 Organic ligand names

Ligand formula	Systematic additive name	Systematic substitutive name	Alternative name
$\text{H}_3\text{C}-$	methanido	methyl	
CH_3CH_2-		ethyl	
$\text{CH}_3\text{CH}_2\text{CH}_2-$	(propan-1-ido)	propyl	
$(\text{CH}_3)_2\text{CH}-$	(propan-2-ido)	(propan-2-yl)	isopropyl
$\text{CH}_2=\text{CHCH}_2-$	(prop-2-en-1-ido)	(prop-2-en-1-yl)	allyl
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	(butan-1-ido)	butyl	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}- \\ \\ \text{H} \end{array}$	(butan-2-ido)	(butan-2-yl)	sec-butyl
$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{CH}-\text{CH}_2- \\ \diagup \\ \text{H}_3\text{C} \end{array}$	(2-methylpropan-1-ido)	(2-methylpropyl)	isobutyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}- \\ \\ \text{CH}_3 \end{array}$	(1,1-dimethylethanido)	(1,1-dimethylethyl)	tert-butyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	(2,2-dimethylpropanido)	(2,2-dimethylpropyl)	neopentyl
$\begin{array}{c} \text{H}_2\text{C} \\ \diagdown \quad \diagup \\ \quad \quad \text{CH}- \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \end{array}$	cyclopropanido	cyclopropyl	
$\begin{array}{c} \text{H}_2 \\ \diagdown \quad \diagup \\ \text{C} \quad \quad \text{CH}- \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \quad \text{C} \\ \diagdown \quad \diagup \\ \quad \quad \text{H}_2 \end{array}$	cyclobutanido	cyclobutyl	

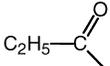
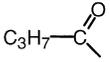
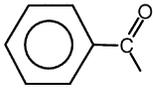
nomenclature as discussed before, the endings -diido and -triido should be used. This nomenclature also applies to hypervalent coordination modes, e.g. for bridging methyl groups.

Organic ligands can be either chelating, if coordinating to one metal atom, or bridging, if coordinating to several metal atoms.

The name methylene for CH_2 can only be used in connection with a bridging bonding mode. A CH_2 ligand bonding to one metal should be called methyldene (see 4.2.3). Likewise, the ligand HC will have at least three different bonding modes: bridging three metals (μ_3 -methanetriyl), bridging two metals (μ -methanylylidene) and coordinating to one metal (methyldyne) (see 4.2.3) (Scheme 6).

CH_2CH_2 in a bridging mode should be called μ -ethan-1,2-diyl, while the same ligand coordinating

Table 4 *Continued*

Ligand formula	Systematic additive name	Systematic substitutive name	Alternative name
C_5H_5-	cyclopentadienido	cyclopentadienyl	
C_6H_5-	benzenido		phenyl
$C_6H_5CH_2-$	(phenylmethanido)	(phenylmethyl)	benzyl
	(1-oxoethanido)	ethanoyl	acetyl
	(1-oxopropanido)	propanoyl	propionyl
	(1-oxobutanido)	butanoyl	butyryl
	(oxophenylmethanido)	phenylcarbonyl	benzoyl
$H_2C=CH-$	ethenido	ethenyl	vinyl
$HC\equiv C-$	ethynido	ethynyl	
H_3Si-	silanido	silyl	
H_3Ge-	germanido	germyl	
H_3Sn-	stannanido	stannyl	

with both carbon atoms to one metal should be called η^2 -ethene (see 4.2.4). A similar situation arises with CHCH, which, when bridging with one atom to each of two metals should be called μ -ethene-1,2-diyl or μ -ethanediyldiene (4.2.3). The same ligand coordinating with both carbons to two metals should be called μ -ethyne; when coordinated to one metal, it is named η^2 -ethyne (4.3.4).

The chelating atoms should be indicated either by specifying the coordinating atoms within the ligand name (such as butane-1,4-diyl) or by applying the italicized donor atom symbols of the κ notation (butanediyl- κ^2C^1, C^4) (*Red Book* I-10.6.2.2 [1]).

For ligands coordinating only via carbon atoms, it is generally preferable to specify the ligating atoms within the ligand name and not with the κ -notation. Number 1 is assigned in such a way as to create the longest chain of carbon atoms. In a metallacycle, the direction of numbering is so chosen as to give the

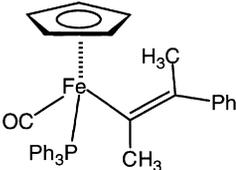
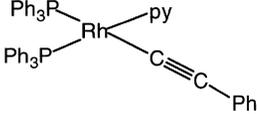
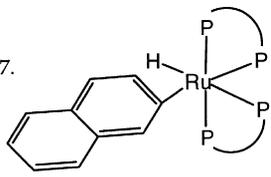
1. $[\text{Os}(\text{C}_2\text{H}_5)(\text{NH}_3)_5]\text{Cl}$ pentaammine(ethyl)osmium(1+) chloride
2. $\text{Li}[\text{Cu}(\text{CH}_3)_2]$ lithium dimethylcuprate(1-)
3. CrR_4 (R = ) tetrakis(bicyclo[2.2.1]heptan-1-yl)chromium
4. $[\text{Pt}(\text{CH}_3)(\text{CH}_3\text{CO})(\text{PEt}_3)_2]$ acetyl(methyl)bis(triethylphosphane)platinum
5.  carbonyl(cyclopentadienyl)(3-phenylbut-2-en-2-yl)-(triphenylphosphane)iron
6.  (phenylethynyl)(pyridine)bis(triphenylphosphane)rhodium
7.  bis{1,2-bis(dimethylphosphanyl-κP)ethane}-hydrido(naphthalen-2-yl)ruthenium*
 $\text{P} \quad \text{P} = (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2 = 1,2\text{-bis}(\text{dimethylphosphanyl-}\kappa\text{P})\text{ethane}$

Fig. 1 *The kappa nomenclature is outlined in Section 4.2.2.

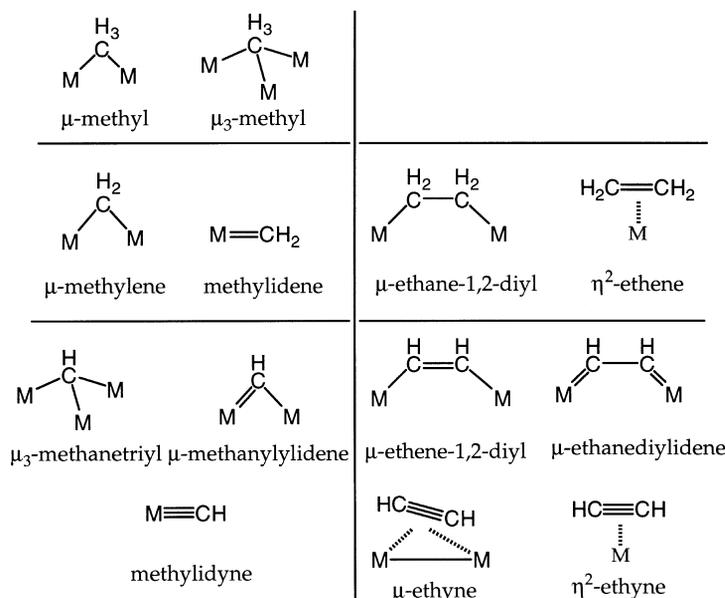
lowest numbers possible to side chains or substituents (see examples in Fig. 2). Special numbering schemes for the organic moiety are again found in heterocyclic or polycyclic systems (see *Blue Guide 93* [2] and *Nomenclature of fused and bridged fused ring systems (IUPAC Recommendations 1998)* [5]).

The κ notation becomes necessary to indicate the attachment of heteroatoms and also for unsymmetrical bridging modes in polynuclear complexes in conjunction with the numerical locant of the central atom (see examples in Fig. 3).

The bridging mode is indicated by the Greek letter μ (*Red Book I-10.8.1* [1]) (Table 5).

The kappa (κ) convention

As the complexity of the name and bonding mode of the ligand increases, a general system is needed to indicate the points of ligation. In the nomenclature of polydentate chelate complexes, single-ligand-atom attachments of a polyatomic ligand to a coordination centre are indicated by the italicized element symbol preceded by a Greek kappa, κ .



Scheme 6

Table 5 Organic ligand names used for ligands forming several metal-carbon single bonds*

Ligand formula	Systematic additive name	Systematic substitutive name	Alternative name
$-\text{CH}_2-$	μ -methanediido	μ -methanediyl	μ-methylene
$-\text{CH}_2\text{CH}_2-$	μ -ethane-1,2-diido	μ-ethane-1,2-diyl	μ -ethylene
$-\text{CH}_2\text{CH}_2\text{CH}_2-$	propane-1,3-diido	propane-1,3-diyl	
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	butane-1,4-diido	butane-1,4-diyl	
	μ_3 -methanetriido	μ_3-methanetriyl	
$\text{CH}_3 \text{ HC} <$	μ -ethane-1,1-diido	μ-ethane-1,1-diyl	
	μ_3 -ethane-1,1,1-triido	μ_3-ethane-1,1,1-triyl	
$-\text{CH}=\text{CH}-$	μ -ethene-1,2-diido	μ-ethene-1,2-diyl	μ -vinylene
$\text{CH}_2=\text{C} <$	μ -ethene-1,1-diido	μ-ethene-1,1-diyl	
$-\text{C}\equiv\text{C}-$	μ -ethyne-1,2-diido	μ-ethyne-1,2-diyl	

*The prefix μ - is attached to those ligands where the name given in Table 5 can only be used for the bridging mode.

In the case of more complicated ligand names, the ligand locant is placed after that portion of the ligand name which denotes the particular function, ring, chain, or radical in which the ligating atom is found. Ligating atoms occurring in functions, chains, rings, and radicals which contain other donor atoms are uniquely indicated by a superscript numeral, letter or prime on the element symbol. These indices denote the position of the ligating atom in the function, chain, ring, or radical.

For a polydentate ligand, a right superscript numeral is added to the symbol κ in order to indicate the number of identically bound ligating atoms in the *flexidentate* ligand. When a polydentate ligand contains several nonequivalent ligating atoms, each is indicated by its italicized element symbol preceded by κ .

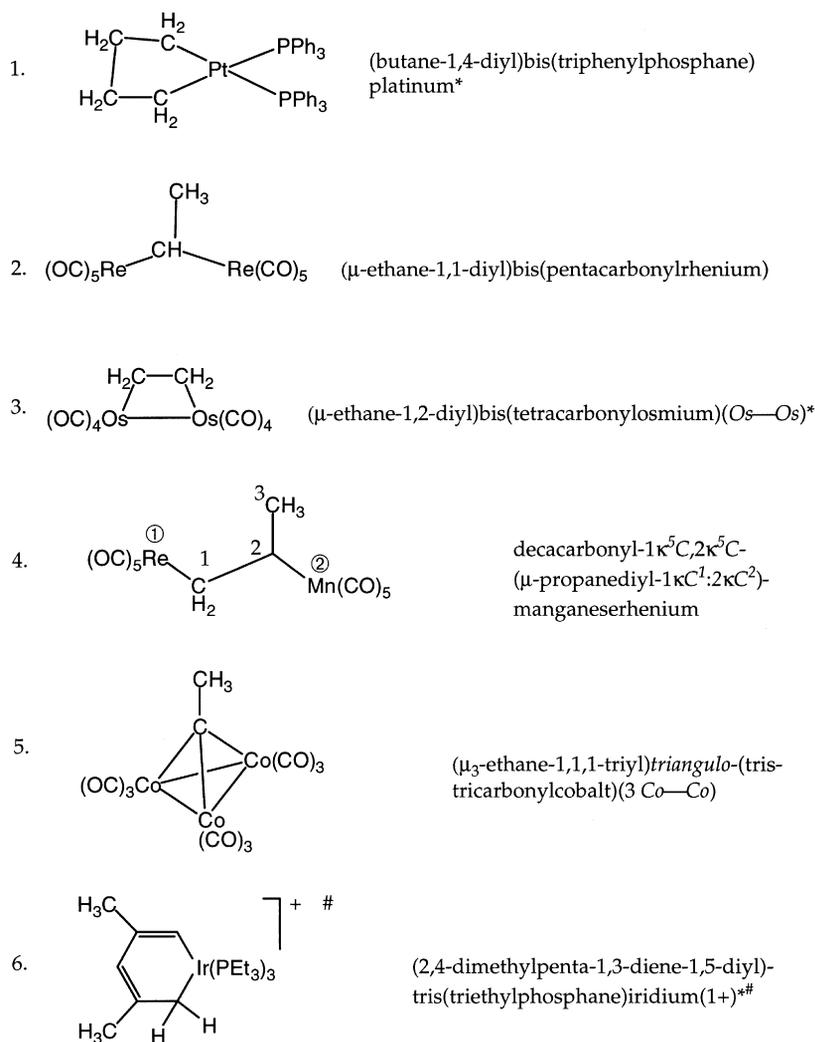


Fig. 2 *An alternative name describing this and similar compounds as metallacycles will be outlined in a separate document. # The half-bracket with the + sign indicates that this is a complex cation with a 1+ charge. This is an abbreviated form for []⁺.

The mu (μ) convention

Bridging ligands are indicated by the Greek letter μ appearing before the ligand name and separated by a hyphen. The whole term, e.g. μ -chloro, is separated from the rest of the name by hyphens, or by parentheses if more complex ligands are involved. If the bridging ligand occurs more than once and multiplicative prefixes are employed, the presentation is modified as in tri- μ -chloro-chloro, etc., or as in bis(μ -diphenylphosphido), etc., if more complex ligands are involved. The *bridging index*, the number of coordination centres connected by a bridging ligand, is indicated by a right subscript, μ_n , where $n \geq 2$. The bridging index 2 is usually omitted. Bridging ligands are listed in alphabetical order along with the other ligands, but a bridging ligand is cited before a corresponding non-bridging ligand, as with di- μ -chloro-tetrachloro.... Multiple bridging is listed in descending order of complexity, as shown by μ_3 -oxo-di- μ -oxo-trioxo.... For ligand names requiring enclosing marks, μ is contained within those enclosing marks.

Metal-metal bonding

Metal-metal bonding may be indicated in names by italicized atomic symbols of the appropriate metal atoms, separated by a long dash and enclosed in parentheses, placed after the list of central atoms and before the ionic charge. For the purpose of nomenclature, no distinction is made between different bond orders of metal-metal bonding.

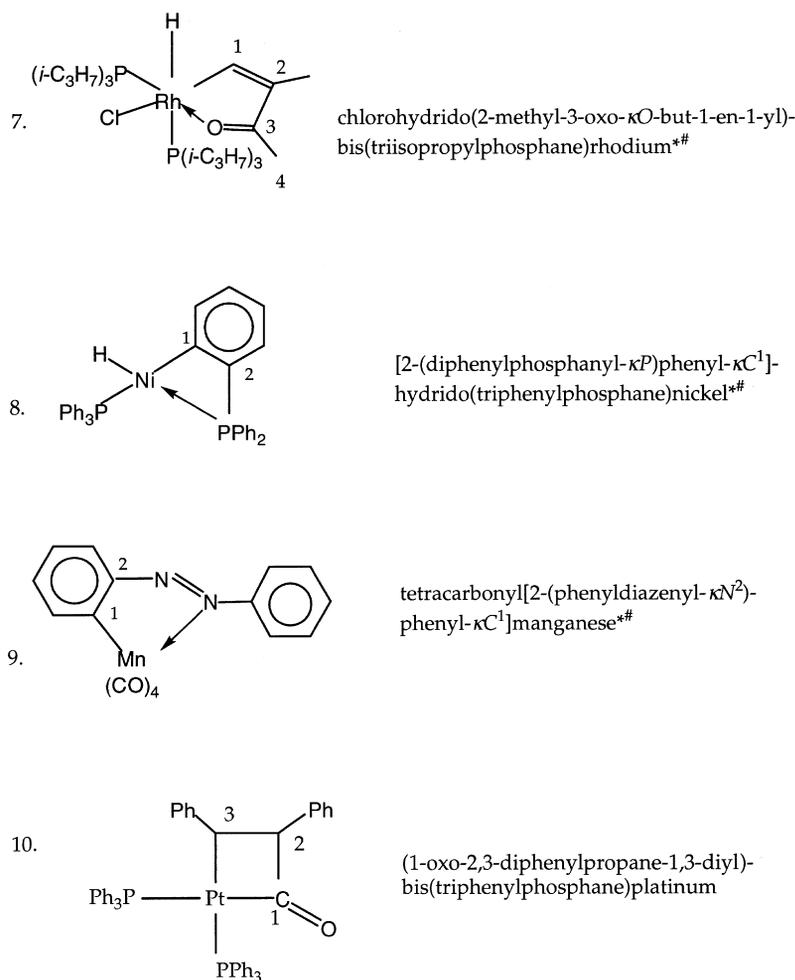


Fig. 3 *κC¹ is carried here for clarity, although the coordinate carbon is automatically labelled 1. # Arrows can be systematically used to indicate a coordinate dative bond and straight line can be used to indicate covalent bonding. This symbolism has been used explicitly in the Figure for demonstration purposes only. In other Figures, this symbolism is usually omitted!

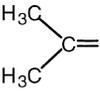
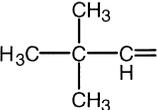
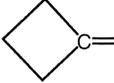
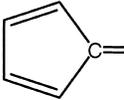
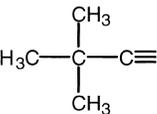
Dinuclear coordination entities may be unsymmetrical, because different types of metal atom are present, because of different patterns of ligation on similar metal atoms or for both reasons. Heterodinuclear entities (see I-2.15.4. and I-10.8.3.2) are numbered based on the priorities of the central elements listed in Table IV, *Red Book I* [1], the higher priority central atom being numbered 1, even though such elements are cited in alphabetical order. For monodinuclear entities, further rules are outlined in I-10.8.3.2.

Where necessary, the symbol kappa, κ, with the italicized atomic symbol(s) of the donor(s) is employed to indicate the ligating atom(s) and their distribution. Bridging and unsymmetrical distribution of ligands is shown by the numerical locant of the central atom to which the ligand is bonded. The numerical locant of the central atom is placed before the κ. Thus (benzenethiolato-1κS) indicates that the sulfur atom of benzenethiolate is bonded to central atom number 1. A right superscript numeral is employed to denote the number of equivalent ligating atoms bonded to the specified central atom.

Bridging is indicated by the μ prefix; where bridging is accomplished by different atoms of the same group, the ligating locants and symbols are separated by a colon, e.g., μ-propanediyl-1κC¹:2κC². The colon in this context is used only to indicate bridging (see Example 4 in Fig. 2).

For a more detailed discussion of dinuclear and larger clusters, Chapter 10, section 8 in *Red Book I* [1] should be consulted.

Table 6 Ligands coordinating under formation of metal-carbon multiple bonds

<i>Ligand formula</i>	<i>Systematic name</i>	<i>Alternative name</i>
$\text{H}_2\text{C}=\text{C}=\text{M}$	methylidene	
$\text{H}_3\text{CCH}=\text{C}=\text{M}$	ethylidene	
$\text{H}_2\text{C}=\text{C}=\text{C}=\text{M}$	ethenylidene	vinylidene
$\text{H}_2\text{C}=\text{HC}-\text{HC}=\text{M}$	(prop-2-enylidene)	allylidene
$\text{H}_2\text{C}=\text{C}=\text{C}=\text{M}$	(propa-1,2-dienylidene)	allenylidene
	(propan-2-ylidene)	isopropylidene
	(2,2-dimethylpropylidene)	neopentylidene
	cyclopropylidene	
	cyclobutylidene	
	cyclopenta-2,4-dienylidene	
$\text{C}_6\text{H}_5\text{HC}=\text{C}=\text{M}$	(phenylmethylidene)	benzylidene
	methanylylidene	
$\text{HC}\equiv\text{C}\equiv\text{M}$	methylidyne	
$\text{CH}_3\text{C}\equiv\text{C}\equiv\text{M}$	ethylidyne	
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}\equiv\text{M}$	propylidyne	
	(2,2-dimethylpropylidyne)	neopentylidyne
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}\equiv\text{M}$	(phenylmethylidyne)	benzylidyne

Ligands that bind to metals through a neutral heteroatom and a carbon atom are also given the customary substituent or additive names; the heteroatom bonding must be indicated by the italicized donor atom symbols of the κ -notation (see examples in Fig. 3).

4.2.3 Ligands coordinating by metal-carbon multiple bonds

Ligands regarded as having metal-carbon double or triple bonds are also given substituent group names, the ligand names ending with -ylidene for a double bond and with -ylidyne for a triple bond. These suffixes are used according to two methods as follows (see *Blue Guide 93*, section R-2.5 [2]):

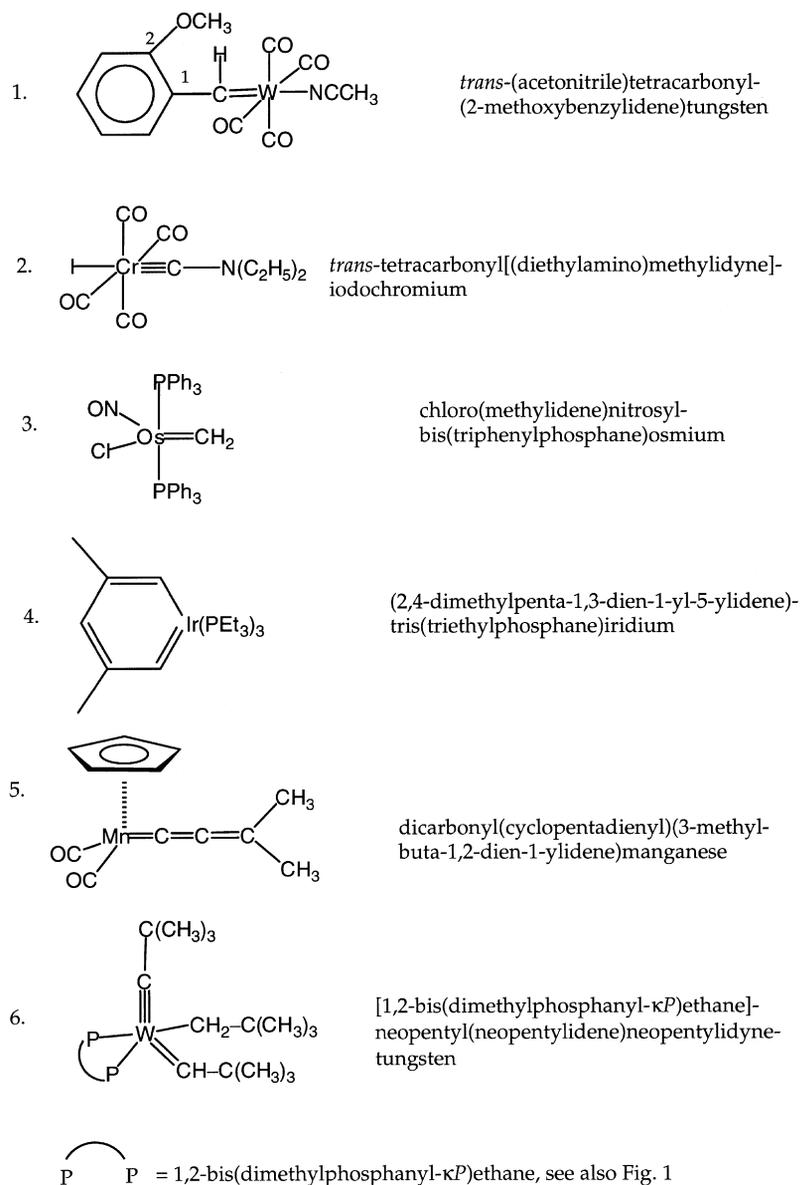
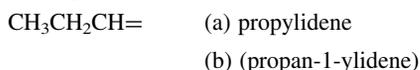


Fig. 4

(a) The suffix ylidene or ylidene replaces the ending -ane of the parent hydride name. The atom with the free valence terminates the chain and always has the locant '1', which is omitted from the name. This method is recommended only for saturated acyclic and monocyclic hydrocarbon substituent groups and for the mononuclear parent hydrides of silicon, germanium tin, lead and boron [6].

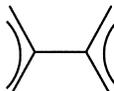
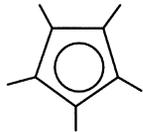
(b) More general method. The suffixes -ylidene or -ylidene is added to the name of the parent hydride with removal of the terminal -e, if present. The atoms with free valences are given numbers as low as consistent with any established numbering of the parent hydride. Except for unambiguous ligands and the suffix ylidene, the locant '1' must always be used.

Example:



Special numbering schemes again apply to heterocyclic and polycyclic systems (see *Blue Guide 93* [2] and *Nomenclature of fused and bridged fused ring systems (IUPAC Recommendations 1998)* [5]).

Table 7 Organic ligand names for unsaturated groups and molecules

	<i>Systematic additive name</i>	<i>Systematic substitutive name</i>	<i>Alternative name</i>
	η^3 -propenido	η^3 -propenyl	η^3 -allyl
	η^3 -(Z)-butenido	η^3 -(Z)-butenyl	
	(η^3 -2-methylpropenido)	(η^3 -2-methylpropenyl)	(η^3 -2-methylallyl)
	(η^4 -2-methylidene-propane-1,3-diido)	(η^4 -2-methylidene-propane-1,3-diyl)	
	(η^6 -2,3-dimethylidene-butane-1,4-diido)	(η^6 -2,3-dimethylidene-butane-1,4-diyl)	η^6 -2,2'-bialllyl
	η^5 -(Z,Z)-pentadienido	η^5 -(Z,Z)-pentadienyl	
	η^5 -cyclopentadienido	η^5 -cyclopentadienyl	
	pentamethyl- η^5 -cyclopentadienido	pentamethyl- η^5 -cyclopentadienyl	
	η^5 -cyclohexadienido	η^5 -cyclohexadienyl	

If a ligand has several points of attachment, the number 1 is assigned in such a way as to create the longest chain of carbon atoms. In a metallacycle, the direction is so chosen as to give the lowest numbers possible to side chains or substituents.

In a ligand containing both metal-carbon single bonds as well as metal-carbon multiple bonds, the order of endings is -yl, -ylidene, -ylidyne. Method (b) should then be used to give the lowest possible set of locants for free valencies. If a choice remains, low numbers are selected for -yl positions before -ylidene positions and then for side chains or substituents (Table 6; Fig. 4).

Example:

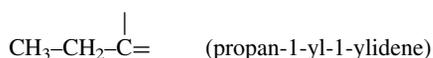


Table 7 Continued

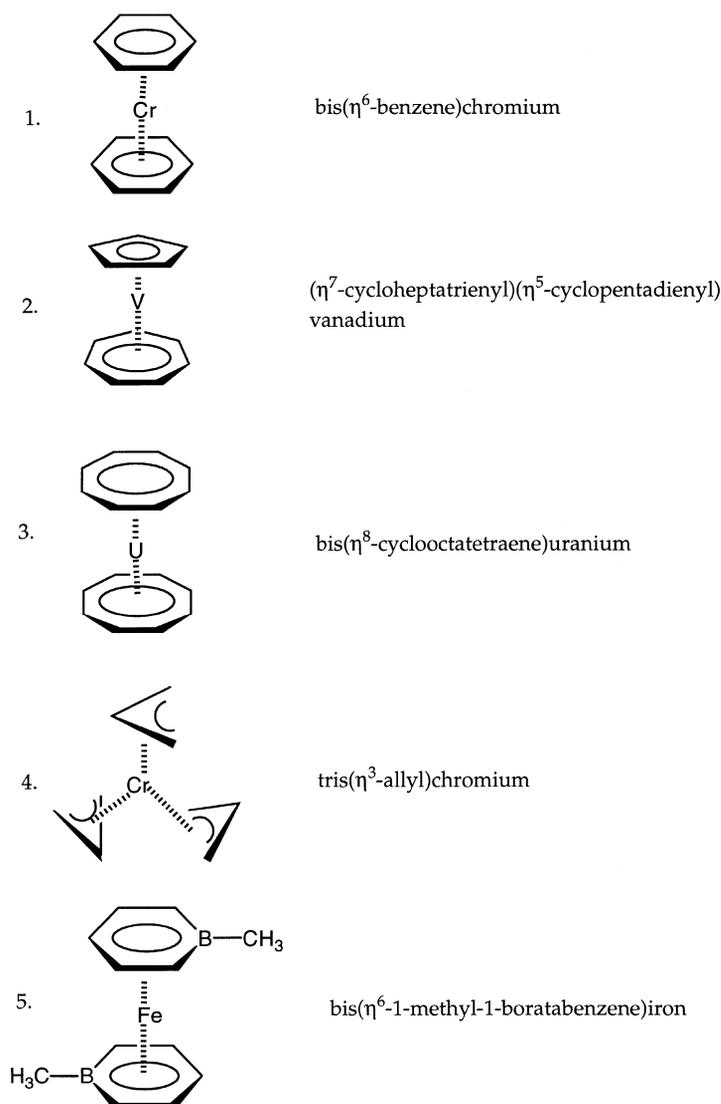
	Systematic additive name	Systematic substitutive name	Alternative name
	η^7 -cycloheptatrienido	η^7 -cycloheptatrienyl	η^7 -tropyyl*
	η^7 -cyclooctatrienido	η^7 -cyclooctatrienyl	η^7 -homotropyyl*
	1-methyl-η^5-borole		
	η^5 -azacyclo- pentadienido	η^5 -pyrrolyl	η^5 -azacyclo- pentadienyl
	η^5 -phosphacyclo- pentadienido	η^5 -phospholyl	η^5 -phosphacyclo- pentadienyl
	η^5 -arsacyclo- pentadienido	η^5 -arsolyl	η^5 -arsacyclo- pentadienyl
	η^6 -borinin-1-uido		η^6 -boratabenzene
	η^6 -1,4-diborinine-1-4-diuido		η^6 -1,4-diboratabenzene

Note: The arc used in this and later drawings indicates delocalized charges by analogy with the circle in benzene.
*If these ligands are regarded as cations, they receive the ending -ium.

4.2.4 Complexes with unsaturated molecules or groups

Since the discovery of 'Zeise's Salt', $K[Pt(C_2H_4)Cl_3]$, the first organometallic complex of a transition metal, and particularly since the first reported synthesis of 'ferrocene', $[Fe(C_5H_5)_2]$, the number and variety of organometallic compounds with unsaturated organic ligands has increased enormously.

Complexes containing ligands which coordinate to a central atom with at least two adjacent atoms in a 'side-on' fashion require a special nomenclature. The ligands are normally groups coordinating *via* the



Note: The symbolism η has been used to indicate the η -coordination of an extended π -system.

Fig. 5

π -electrons of their multiple bonds, such as alkenes, alkynes and aromatic compounds, but they may also be carbon-free entities containing heteroelement-multiple bonds. Such compounds are generally referred to as ' π -complexes'. However, the expression ' π -coordinated' is too imprecise, since the exact nature of the bonding (σ , π , δ) often is uncertain. Therefore, the atoms bonded to the metal atom are indicated in a manner completely independent of theoretical implications [7].

From the view of oxidation states, ligands such as alkenes, alkynes, nitriles, diazenes and other systems such as allyl (C_3H_5), butadiene (C_4H_6), cyclopentadienyl (C_5H_5), cycloheptatrienyl (C_7H_7) and cyclooctatetraene (C_8H_8) may formally be regarded as anionic, neutral or cationic (see 4.1). The structure and bonding in their complexes may also be complicated or ill-defined. Names for such ligands are therefore chosen that indicate stoichiometric composition and are derived in a similar way to those for the ligands discussed in preceding sections.

Neutral ligands are given a name in which that part of the molecule that is attached to the metal becomes the principal group. All other characteristic groups are then cited as suffixes. Other ligands are given the substituent

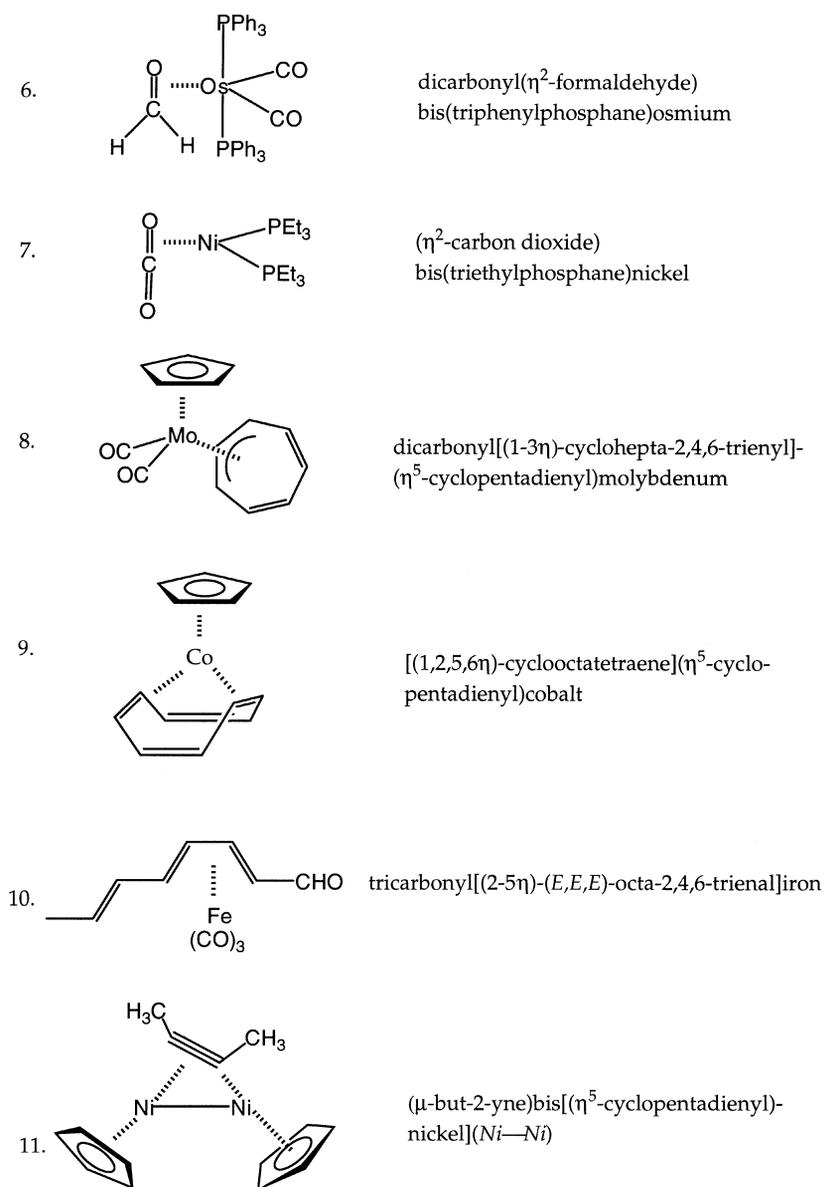


Fig. 5

names ending in -yl, -diyl, -ylidene, etc. depending on the number of hydrogen atoms removed and the type of bonding (as discussed in sections 4.1–4.3). Alternatively, the endings -ido, -diido, etc. can be used. A special nomenclature applies to fused polycyclic or unsaturated heterocyclic ligands, as mentioned before.

The point of attachment of the odd carbon in an allylic system such as an -enyl or a -dienyl ligand has to be localized in such a way as to create the longest chain.

The ligand names are again arranged in alphabetical order, followed by central atom names and the charge number of the complex, where necessary.

The following stoichiometric names illustrate this:

Examples:

1. $K[PtCl_3(C_2H_4)]$ potassium trichloro(ethene)platinate
2. $[Ni(C_5H_5)_2]$ bis(cyclopentadienyl)nickel (nickelocene) [8]
3. $[FeC_4H_6(CO)_3]$ (butadiene)tricarbonyliron
4. $[Cr(C_3H_5)_3]$ tris(allyl)chromium

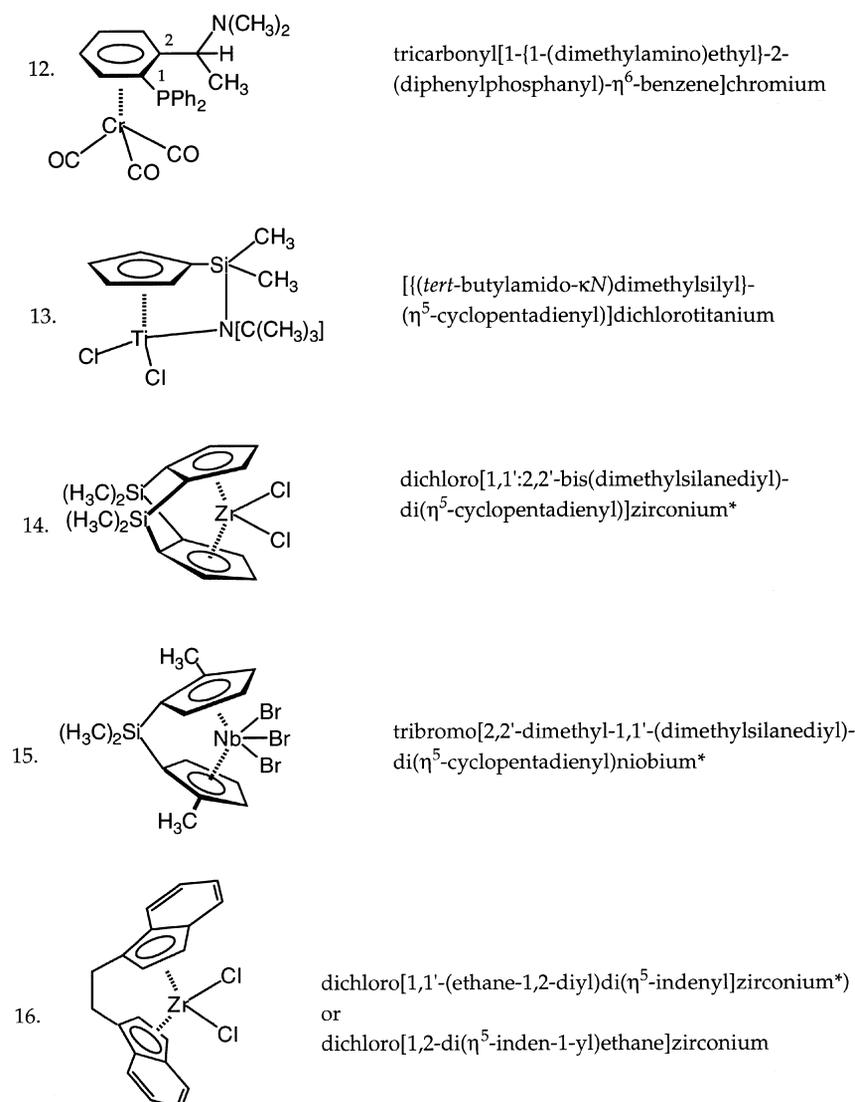
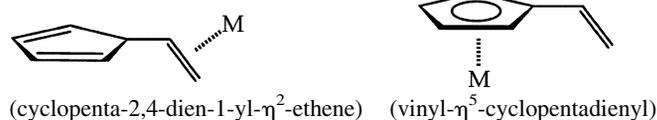


Fig. 5 *Additional rules and comments on the nomenclature of bi(cyclopentadienyl)compounds are given in Section 4.3.

The special nature of the bonding of unsaturated hydrocarbons to metals via their π -electrons has called for a special nomenclature to designate unambiguously the unique bonding modes of these compounds. Therefore, the 'hapto'-nomenclature has been developed [9]. The η -symbol (pronounced *eta*, see below) provides a topological description by indicating the connectivity between the ligand and the central atom.

If all unsaturated carbon atoms are coordinated to the metal, the name of the ligand is preceded by η . The number of coordinated carbon atoms is indicated by a numerical superscript (e.g. η^3 = eta three or trihapto, η^4 = eta four or tetrahapto, η^5 = eta five or pentahapto, etc.) [8].

Complexes of unsaturated systems incorporating heteroatoms may be designated in the same manner, if both the carbon atoms and adjacent heteroatoms are coordinated (see examples in Fig. 5; Table 7).



Scheme 7

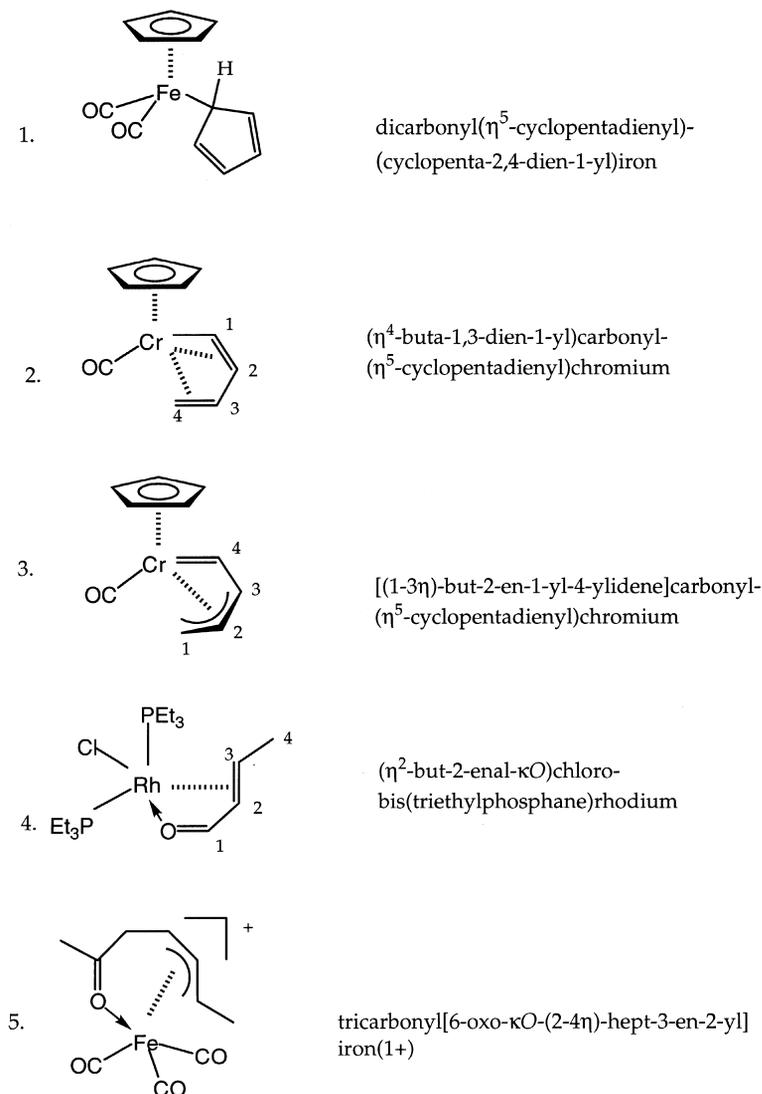


Fig. 6

The symbol η is prefixed to the ligand name or to that portion of the ligand name most appropriate to indicate the connectivity, as in (cyclopenta-2,4-dien-1-yl- η^2 -ethene) vs. (vinyl- η^5 -cyclopentadienyl).

If not all unsaturated atoms of a ligand are involved in bonding, if a ligand possesses several bonding modes, or if a ligand bridges several metal atoms, the locations of the ligating atoms appear in a numerical sequence before the haptic symbol η . Extended coordinations over more than two carbon atoms should be indicated by (1-4 η) rather than by (1,2,3,4 η). The locants and η are enclosed in parentheses. No superscript is necessary then.

Substituents are given lowest numerical locants in the usual manner. The η symbol can be combined with the κ symbol, if necessary. The symbol η then precedes the ligand name while the κ symbol is either placed at the end of the ligand name or, for more complicated structures, after that portion of the ligand name which denotes the particular function in which the ligating atom is found [10] (see examples 1, 4, 5 in Fig. 6).

If unsaturated hydrocarbons serve as bridging ligands, the prefix μ is used as outlined in *Red Book I-10.8* and in section 4.2.2. It is combined with both η and κ , where necessary. The colon is used to separate locants of the bridging ligands which indicate binding to different metal atoms. The priority numbers of the metal atoms in multinuclear compounds are placed before the η and κ symbols, which for η are then enclosed in parentheses, where necessary, as in 1(2-4 η) (see Fig. 7).

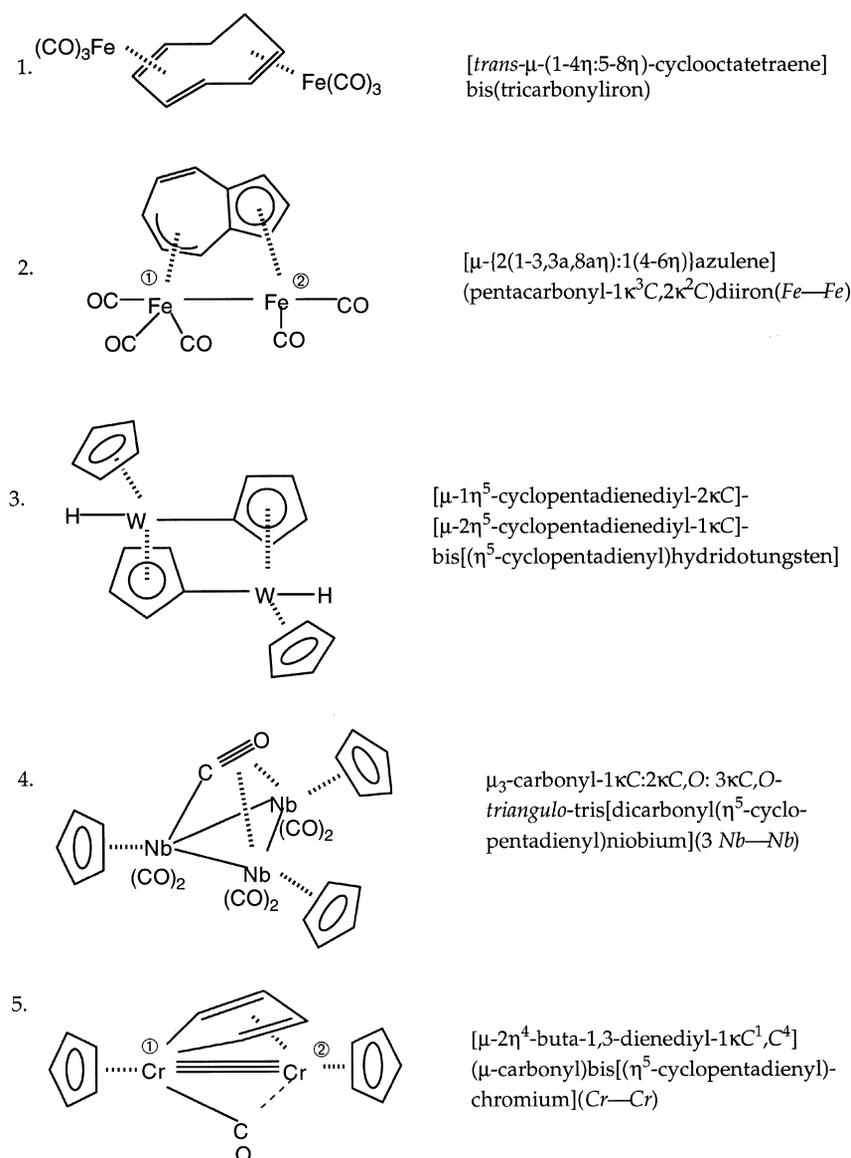


Fig. 7

The η-nomenclature can also be extended to π-coordinated ligands not containing any carbon atoms, such as borazines and pentaphospholyl. It may also be used for ligands in which σ-bonds are coordinated in a side-on fashion, such as the H-H bond in complexes of dihydrogen (η²-H₂) [11] (see example 4, Fig. 8) or saturated C-H bonds in 'agostic' interactions [12]. Locants for agostic interactions are placed separately from other locants at the end of the ligand name (see example 3, Fig. 8).

For zwitterionic complexes, in which a non-coordinated atom of the ligand carries a charge which is offset by the opposite charge at the metal atom, the charge of the ligand is indicated by the appropriate ligand name ending, while the charge of the central atom is not indicated (see example 5, Fig. 8).

4.3 Metallocene nomenclature

The first transition metal compound containing only carbocyclic rings as ligands was bis(cyclopentadienyl)iron, [Fe(η⁵-C₅H₅)₂], which was shown to have a 'sandwich' structure with two parallel η⁵- or p-bonded rings. The recognition that this compound was amenable to electrophilic substitution, similar to the aromatic behaviour of benzene, led to the suggestion of *ferrocene* as a trivial name for the compound.

The *metallocene* nomenclature has also been used extensively in discussion of ferrocene analogues

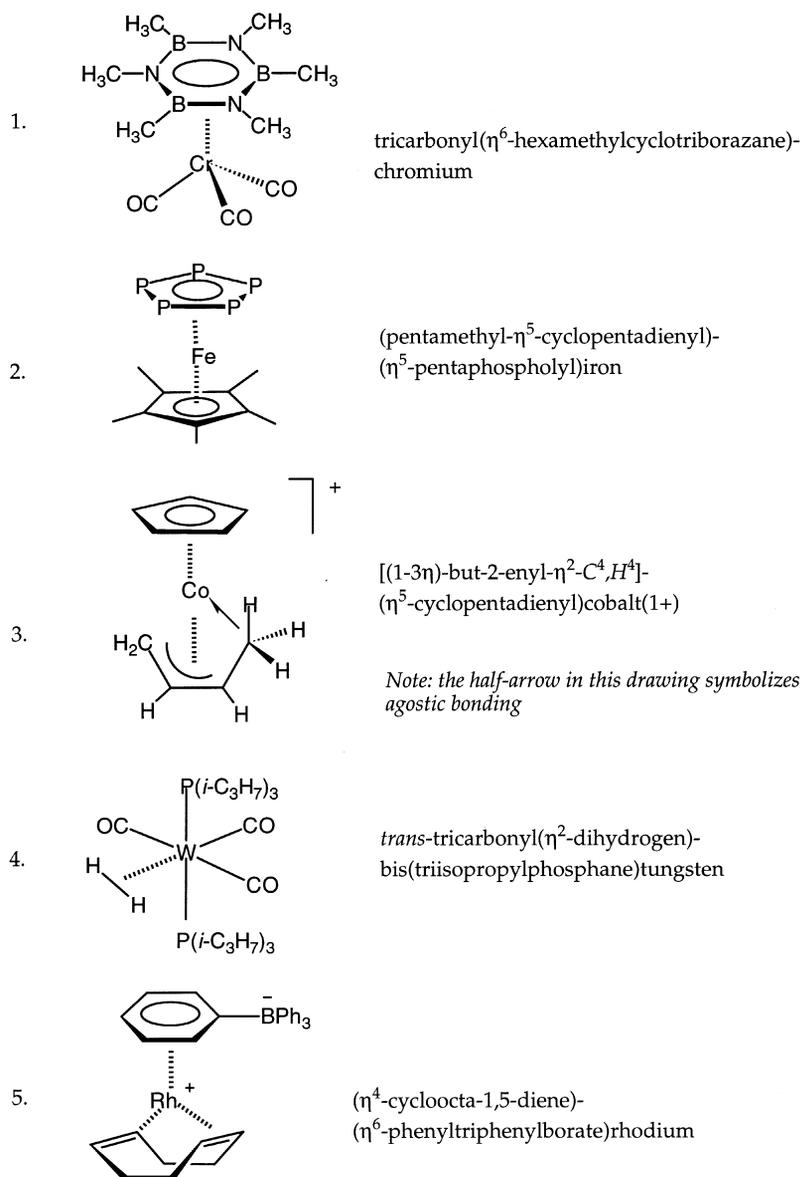


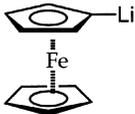
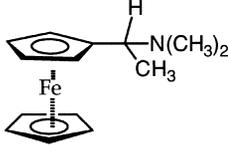
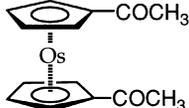
Fig. 8

containing the vertical congener metals Ru (*ruthenocene*), and Os (*osmocene*). Metallocene derivatives of Fe, Ru and Os may be named by either standard organic suffix (functional) nomenclature or by prefix nomenclature. The organic functional suffix system is described in *Blue Book 93*, R-3.2. Substituents on the equivalent cyclopentadienyl rings of the metallocene entity are given lowest numerical locants in the usual manner. The first ring is numbered 1–5 and the second ring 1'–5'. The substituent group names -ocenyl, -ocenediyl, -ocenetriyl, etc., are used.

Examples:

1. [Fe(η⁵-C₅H₄CH₃)₂] 1,1'-dimethylferrocene or
bis(methyl-η⁵-cyclopentadienyl)iron
2. [Ru{η⁵-C₅(CH₃)₅}₂] decamethylruthenocene or
bis(pentamethyl-η⁵-cyclopentadienyl)ruthenium

The use of metallocene nomenclature has spread to other metal-containing analogues of the general formula [M(C₅H₅)₂], e.g. V (*vanadocene*), Cr (*chromocene*), Co (*cobaltocene*) and Ni (*nickelocene*) as well as their substituted derivatives.

3. $[\text{Ni}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2]$ 1,1'-dimethylnickelocene
4. $[\text{Cr}\{\eta^5\text{-C}_5(\text{CH}_3)_4\text{C}_2\text{H}_5\}_2]$ 1,1'-diethyloctamethylchromocene or
bis(1-ethyl-2,3,4,5-tetramethyl- η^5 -cyclopentadienyl)-
chromium
5. $[\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ 1,1'-bis(diphenylphosphanyl)cobaltocene
6.  lithioferrocene or ferrocenyllithium
7.  [1-(dimethylamino)ethyl]ferrocene or
1-ferrocenyl-*N,N*-dimethylethan-1-amine
8.  1,1'-diacetylosmocene

Scheme 8

The use of the term *titanocene* is misleading, since there are at least two isomers which have the empirical formula $\text{TiC}_{10}\text{H}_{10}$, neither having the 'regular' sandwich structure $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]$. Instead, their structures involve $\eta^5:\eta^5$ -fulvalenediyl rings (see below) and bridging hydride atoms. These isomers therefore cannot correctly be named *titanocene*. *Manganocene* in the solid state has a chain structure, without individual 'sandwich' entities, although *decamethylmanganocene*, $[\text{Mn}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}_2]$, has a 'normal' sandwich structure as does *decamethylrhencene*, $[\text{Re}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}_2]$. With heavier elements, the occurrence of sandwich structures is rare, and compounds having the empirical formula $\text{MC}_{10}\text{H}_{10}$ occur as dimers, e.g., $[\text{M}_2(\eta^5\text{-C}_5\text{H}_5)_4]^z$ ($z = 0$, $\text{M} = \text{Re}$; $z = 1+$, $\text{M} = \text{Os}$) or possess $\eta^1:\eta^5$ -cyclopentadienediyl bridges or $\eta^5:\eta^5$ -fulvalenediyl bridges as well as terminal hydride ligands (see $[\text{W}_2(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_4)_2\text{H}_2]$ in Fig. 7).

Consequently, the name-ending *-ocene* should be confined to molecules of the form bis(η^5 -cyclopentadienyl)metal, where the metal is in the *d*-block [*i.e.* the terminology does not apply to compounds of the *s* or *p*-block elements such as $\text{Ba}(\text{C}_5\text{H}_5)_2$ or $\text{Sn}(\text{C}_5\text{H}_5)_2$], and where the rings are essentially coplanar to each other.

The oxidized species may be referred to as *metallocenium*(*n*+) salts, although it should be noted that the *-ium* ending does not carry the usual meaning that it has in substitutive nomenclature, *i.e.* the addition of a proton to a neutral parent compound. Substituted derivatives are named in a similar manner as described before. To avoid this ambiguity, the alternative *bis*(η^5 -cyclopentadienyl)iron(*l*+), instead of *ferrocenium*(*l*+) should be employed.

9. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{BF}_4]$ ferrocenium tetrafluoroborate or
bis(η^5 -cyclopentadienyl)iron(*l*+) tetrafluoroborate
10. $[\text{Fe}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}_2]\text{Cl}_2$ decamethylferrocenium dichloride or
bis(pentamethyl- η^5 -cyclopentadienyl)iron(*2+*) chloride

Further examples:

11. $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2]$ vanadocene $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ vanadocenium(*l*+)

12. $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2]$ chromocene $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ chromocenium(*l*+)

13. $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]$ ruthenocene $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ ruthenocenium(*l*+)

14. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$ cobaltocene $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cobaltocenium(*l*+)

15. $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ nickelocene $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ nickelocenium(*l*+)

16. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{COCH}_3)][\text{BF}_4]$ acetylcobaltocenium tetrafluoroborate

The oxidized form of osmocene, the osmocenium cation, is dinuclear in the solid state, with a long Os–Os bond, so should not be referred to by the -ocenium nomenclature. However, $[\text{Os}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}_2]^+$ has a mononuclear ‘sandwich’ structure and may be described as the decamethylsoscenium ion, but bis(pentamethylcyclopentadienyl)osmium cation is equally acceptable.

A number of metal complexes derived from ligands with additional rings fused to the cyclopentadienyl rings are known. The names of the transition metal compounds are derived from the trivial names of the hydrocarbon ligands, e.g. inden-1-yl (C_9H_7), fluoren-9-yl (C_{13}H_8), and azulene (C_{10}H_8). Thus, $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)_2]$ is to be named bis(η^5 -indenyl)iron. The use of fusion nomenclature, such as benzoferrrocene, is strongly discouraged.

In strong protic acid media, ferrocene is protonated to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}]^+$. To avoid ambiguities, this should be named by the additive procedure, viz. bis(η^5 -cyclopentadienyl)hydridoiron(1+).

There are a considerable number of other compounds which carry ligands other than two η^5 -cyclopentadienyl rings. They are often referred to as metallocene di(ligand) species. A well-known example is $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, frequently known as ‘titanocene dichloride’. This practice is discouraged, since the metallocene nomenclature is defined above as relating only to compounds carrying two η^5 -cyclopentadienyl (or ring-substituted cyclopentadienyl) ligands in a parallel arrangement and no other ligands. The compound $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ should be named dichlorobis(η^5 -cyclopentadienyl)titanium. Similarly, species such as $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$, $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2]$ and $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$ should be named bis(η^5 -cyclopentadienyl)dihydridotungsten (not tungstenocene dihydride), dicarbonylbis(η^5 -cyclopentadienyl)titanium, and bis(η^5 -cyclopentadienyl)dimethylzirconium.

The compound $[\text{U}(\eta^8\text{-C}_8\text{H}_8)_2]$, has been described in the literature as *uranocene*. Related species are obtained from the lanthanoids, e.g. $[\text{Ce}(\eta^8\text{-C}_8\text{H}_8)_2]^-$, and zirconium, $[\text{Zr}(\eta^8\text{-C}_8\text{H}_8)_2]$. In these complexes, the carbocyclic rings are parallel and there are certain molecular orbital similarities to ferrocene. However, it should be noted that some lanthanides also form metal(II) cyclopentadienyl complexes, such as $[\text{Sm}\{\text{C}_5(\text{CH}_3)_5\}_2]$. Extension of the -ocene nomenclature to $[\text{U}(\text{C}_8\text{H}_8)_2]$ and similar compounds can therefore only lead to confusion and is strongly discouraged. The cyclooctatetraene ring system can also function as an η^4 -ligand, as in $[\text{Ti}(\eta^8\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)]$. Compounds of cyclooctatetraene should therefore be named using standard organometallic nomenclature, as bis(η^8 -cyclooctatetraene)uranium or (η^8 -cyclooctatetraene)[(1-4 η)-cyclooctatetraene]-titanium [13].

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- 2 R. Panico, W. H. Powell, J.-C. Richer, eds. *A Guide to IUPAC Nomenclature of Organic Compounds, Recommendations 1993 (The Blue Book '93)*. Blackwell Scientific Publications, Oxford, UK (1993).
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- 4 A separate document on nomenclature of main-group organometallics is currently in preparation.
- 5 Commission on Nomenclature of Organic Chemistry (G. P. Moss). Nomenclature of fused and bridged fused ring systems (IUPAC Recommendations 1998). *Pure Appl. Chem.* **70**, 143 (1998).
- 6 The suffix -ylene (‘methylene’, ‘ethylene’ etc) should only be used in conjunction with μ to designate $-\text{CH}_2-$ (methanediyl) and $-\text{CH}_2\text{-CH}_2-$ (ethane-1,2-diyl) etc. (see 4.2.2).
- 7 The use of the prefixes σ and π is therefore not recommended for nomenclature use; they refer to the symmetry of orbitals and their interaction, which is irrelevant for nomenclature purposes.
- 8 A special simplified nomenclature applying to bis(cyclopentadienyl) complexes, the so-called ‘metallocenes’, is outlined in section 4.3.
- 9 F. A. Cotton. *J. Am. Chem. Soc.* **90**, 6230 (1968).
- 10 The use of η^1 for a ligand coordinating via one carbon atom is not generally recommended for nomenclature purposes (see III-4.3). A cyclopentadienyl ligand bonded by only one σ -bond (see example Fig. 6) is frequently called σ -cyclopentadienyl or η^1 -cyclopentadienyl, but cyclopenta-2,4-dien-1-yl or cyclopenta-2,4-dienyl- κC^1 are more appropriate.

- 11 D. J. Heinekey, W. J. Oldham, Jr. *Chem. Rev.* **93**, 913 (1993).
- 12 M. Brookhart, M. L. H. Green, L. Wong. *Prog. Inorg. Chem.* **36**, 1 (1988).
- 13 The ligand $C_8H_8^{2-}$ is occasionally referred to as 'cyclooctatetraenyl'. This name is incorrect, as it can only be used for an (as yet hypothetical) ligand C_8H_7 .