

IR-10 Organometallic Compounds (Draft March 2004)

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IR-10.1 INTRODUCTION

The enormous growth in organometallic chemistry over the last fifty years and the discovery of new classes of compounds with unprecedented bonding modes has resulted in the need for additional nomenclature rules for organometallic compounds. This Chapter is therefore

considerably expanded over Section I-10.9 of Ref. 1 and is largely based on the IUPAC recommendations published in 1999 for organometallic compounds of the transition elements.²

An organometallic compound is defined as any chemical species containing at least one bond between a metal and a carbon atom in an organic molecule, ion or substituent group. The names of organometallic compounds should therefore accord with the rules of both organic and coordination chemistry nomenclature (even though these have tended to evolve separately).

The major part of this Chapter presents a system of nomenclature for transition metal organometallic compounds, based on the additive nomenclature system (Section IR-4.3.4 and Chapter IR-7) that is applied to coordination compounds (Chapter IR-9) but incorporating, as far as possible, the rules for naming organic groups and substituents.³ In addition, further rules are formulated which unambiguously designate the special modes of bonding often found in organometallic compounds.

The latter part of this Chapter briefly describes aspects of the naming of main group organometallic compounds, where the substitutive system of nomenclature (Section IR-4.3.3 and Chapter IR-6) is applied by substituting the appropriate parent hydrides of the elements of groups 13-16. The names of organometallic compounds of the groups 1 and 2 elements are, on the other hand, based on the additive nomenclature system.

It should be emphasized that the aim of nomenclature is confined to the precise description of the composition of a compound and the connectivity of atoms within a molecule or ion. It is particularly true of organometallic chemistry that nomenclature should not attempt to convey details about the polarity of bonds, patterns of reactivity or methods of synthesis.

IR-10.2. NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS OF THE TRANSITION METALS

IR-10.2.1 **Concepts and conventions**

The (additive) nomenclature of coordination complexes, the general definitions and rules of which are given in Sections IR-9.1 and IR-9.2, provides the basis for the system presented here for naming organometallic compounds of the transition elements. The general concepts of coordination chemistry can be applied to organometallic compounds but need to be expanded to deal with the additional modes of connectivity afforded by the interaction of metals with, for example, organic ligands containing unsaturated groupings, such as alkenes,

alkynes and aromatic compounds. This section examines relevant concepts and conventions from coordination chemistry as they are applied to organometallic compounds, and indicates what new conventions need to be introduced in order to designate unambiguously the special bonding modes of organometallic compounds.

IR-10.2.1.1 *Coordination number*

The definition of coordination number as being equal to the number of σ -bonds between the ligands and the central atom (Section IR-9.1.2.6) also applies to ligands such as CN^- , CO , N_2 and PPh_3 , where the bonding of a single ligating atom to a metal may involve a combination of σ - and π -components. The π -bond components are not considered in determining the coordination number, and so $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $[\text{RhI}_2(\text{Me})(\text{PPh}_3)_2]$ and $[\text{W}(\text{CO})_6]$ have coordination numbers of four, five and six, respectively.

However, this definition cannot be applied to the many organometallic compounds in which two or more adjacent atoms of a ligand interact with the central metal atom through what is often a combination of σ , π and δ bonding (the labels σ , π or δ referring to the symmetry of the orbital interactions between ligand and central atom).

For example, a ligand such as ethene, consisting of two ligating carbon atoms, nevertheless brings only one pair of electrons to the central atom. Likewise, ethyne, coordinating *via* both carbon atoms, can be thought to bring either one or two pairs of electrons to a single metal atom, depending on the type of coordination involved. Both ligands are normally regarded as monodentate. This changes when ethene or ethyne is considered to add oxidatively to a central metal atom; they are then considered to be bidentate 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 compounds of such ligands as metallacyclopropanes or metallacycloprenes rather than alkene or alkyne complexes.

IR-10.2.1.2 *Chelation*

The concept of chelation (Section IR-9.1.2.7) can again be applied strictly only to those organometallic complexes in which the donor atoms of a ligand are attached to the central metal atom through σ -bonds alone. Otherwise, ambiguities will result, 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 bi- and tridentate ligands, respectively. In stereochemistry, however, such ligands are often treated as if they were monodentate.

IR-10.2.1.3 *Specifying connectivity*

In the event of a ligand containing several different donor atoms, particularly when not all are used, the point or points of attachment to the metal are specified using the kappa (κ) convention (see Sections IR-9.2.4.1 and IR-9.2.4.2). In organometallic nomenclature the ligating carbon atoms are usually sufficiently specified by the locants preceding the appropriate suffix within the ligand name, but use of the kappa notation becomes necessary to indicate the attachment of heteroatoms, and also to specify the particular points of attachment of a single ligand when bridging different metal centres in a polynuclear complex. The strength of the kappa convention is that its use completely avoids any ambiguities in describing the connectivities between a ligand and one or more metal centres. Its use in organometallic nomenclature is discussed further in Section IR-10.2.3.3.

A complementary notation, the eta (η) convention, is used to specify the number ('hapticity') of contiguous ligating atoms that are involved in bonding to one or more metals. The need for this convention arises from the special nature of the bonding of unsaturated hydrocarbons to metals *via* their π -electrons, and is required only when there are several contiguous atoms involved in the bond to the metal. The contiguous atoms of the π -coordinated ligand are often the same element, but they need not be, and they may also be atoms other than carbon. The eta convention is defined in Section IR-10.2.5.1, where its use is extensively illustrated (see also Section IR-9.2.4.3). While complicated structures will require use of both the kappa and eta conventions, these descriptors are complementary and should not be interchanged in usage.

Organic ligands with the ability to form more than one bond to a metal centre may be either chelating (if bonding to a single metal), bridging (if bonding to more than one metal), or sometimes even both chelating and bridging. As in coordination chemistry, the bridging bonding mode is indicated by the Greek letter μ (mu) prefixing the ligand name (Section IR-9.2.5.2). This convention is further exemplified for organometallic compounds in Sections IR-10.2.3.1 and IR-10.2.3.4.

IR-10.2.1.4 *Oxidation number and net charge*

The concept of oxidation number (see also Sections IR-4.6.1, IR-5.4.2.2 and IR-9.1.2.8) follows from the application of the classical definition of coordination number and is therefore difficult to apply to organometallic compounds where often the coordination number cannot be unequivocally assigned. This is especially true when it cannot be determined whether complexation by a ligand is better regarded as a Lewis-acid or -base

association or as an oxidative addition. In such ambiguous cases, the net charge on the coordination entity is preferred in most nomenclature practices.

Thus, no formal oxidation numbers will be attributed to the central metal atoms in the following sections. This does not mean, however, that the oxidation state of a metal or a ligand is unimportant 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.

IR-10.2.1.5 *Valence-electron numbers and the 18-valence-electron rule*

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

The 18-electron rule is based on the valence-bond formalism of localised metal-ligand bonds; it states that thermodynamically stable transition-metal organometallic compounds are formed when the sum of the number of metal d electrons plus the number of 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.

Table IR-10.1 lists ligands commonly encountered in organotransition metal compounds 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 IR-10.1 Number of bonding electrons of commonly encountered ligands

<i>Ligand</i> ^a	<i>Neutral</i>	<i>Positive</i>	<i>Negative</i>
alkyl, aryl, hydride, halide, amide	1	-	2
η^2 -alkene, CO, CS, amine, nitrile, isocyanide, phosphane	2	-	-
alkylidene (CR ₂) or alkanediide (CR ₂ ²⁻)	2	-	4 (2-)
azanylidene (nitrene, NR)	2	-	4 (2-)
azanediide, (imide, NR ²⁻)	-	-	4 (2-)
oxide O ²⁻	-	-	4 (2-)
alkylidyne (CR) or alkanetriide (CR ³⁻)	3	-	6 (3-)

η^3 -allyl, η^3 -enyl, <i>e.g.</i> η^3 -cyclopropenyl	3	-	4
NO (bent)	1	-	-
NO (linear) ^b	3	2	-
η^4 -diene, <i>e.g.</i> η^4 -cyclobutadiene	4	-	-
η^5 -cyclopentadienyl	5	-	6
η^6 -arene, η^6 -triene	6	-	-
η^7 -tropylium ^c or η^7 -cycloheptatrienyl	7	6	-
η^8 -cyclooctatetraene ^d	8	-	10 (2-)

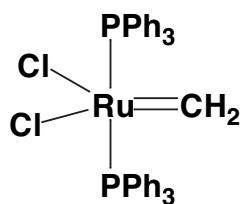
^a The η (eta) notation is described in Section IR-10.2.5.1. ^b NO⁺ is isoelectronic with CO and as such acts as a two-electron ligand. ^c The name 'tropylium' designates the monocation C₇H₇⁺. ^d The coordinated C₈H₈ ligand may also be regarded as a dianion.

When determining valence electron numbers, several conventions should be taken into account.

(a) The intramolecular partitioning of electrons is made so as to ensure that the total charge on the complex remains unchanged.

Example:

1.

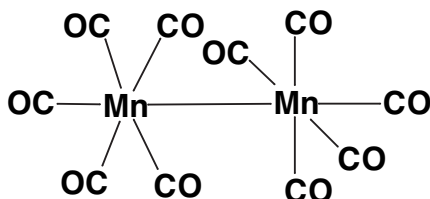


2 PPh ₃	4 e ⁻	or	2 PPh ₃	4 e ⁻
2 Cl	2 e ⁻		2 Cl ⁻	4 e ⁻
1 :CH ₂	2 e ⁻		1 CH ₂ ²⁻	4 e ⁻
1 Ru ⁰	8 e ⁻		1 Ru ^{IV}	4 e ⁻
Total	16 e ⁻			16 e ⁻

(b) A metal-metal bond contributes one electron to the count for each metal. Metal-metal double or triple bonds supply two and three electrons, respectively, to each metal.

Example:

2.

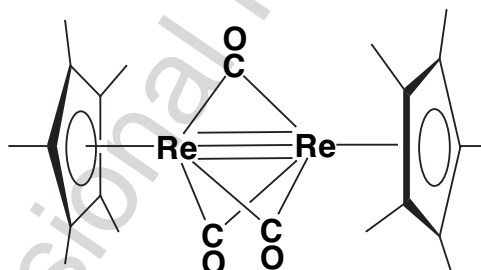


5 CO	10 e ⁻
Mn ⁰	7 e ⁻
Mn—Mn	1 e ⁻
Total	18 e ⁻

(c) The electron pair of a bridging ligand such as CO donates one electron to each of the bridged metals.

Example:

3.



1 C ₅ Me ₅ ⁻	6 e ⁻
3 (μ-CO)	3 e ⁻
Re ^I	6 e ⁻
Re≡Re	3 e ⁻
Total	18 e ⁻

For organometallic compounds of the f-block elements (lanthanoids and actinoids) this procedure is not applicable. Exceptions to the 18-electron rule are also found with the early and late-transition metals (see Example 1 above) and in complexes in which the central atom has a high formal oxidation state, *e.g.* [WMe₆] or [ReMe(O)₃].

IR-10.2.2 Compounds with one metal-carbon single bond

In naming organometallic compounds the usual rules for naming ligands in coordination entities are applied if the ligand is organic but coordinates *via* an atom other than carbon (Section IR-9.2.2.3). Thus, the ligand MeCOO^- is named acetato, Me_2N^- is named dimethylamido (or *N*-methylmethanaminido), and PPh_3 is named triphenylphosphane.

If organic ligands coordinating *via* one carbon atom are regarded as anions formed by the removal of one hydron from a carbon atom of an organic molecule, the anions are named by replacing the final 'e' of the parent compound name by 'ido' (see Section P-72.2.2 of Ref. 3). This rule is most commonly applied when using compositional nomenclature with highly ionic organic compounds of the alkali and alkaline earth metals, such as sodium methanide or potassium cyclopentadienide.

As in the nomenclature of coordination compounds, the ending 'ido' is replaced by 'ido' upon coordination of the ligand. All names must have locants, starting with propane (except monocyclic, unsubstituted rings).

Examples:

Me^-	methanido
Et^-	ethanido
$(\text{CH}_2=\text{CHCH}_2)^-$	prop-2-en-1-ido
Ph^-	benzenido
$(\text{C}_5\text{H}_5)^-$	cyclopentadienido

The compound $[\text{TiCl}_3\text{Me}]$ would therefore be called trichlorido(methanido)titanium by the systematic application of the additive nomenclature of coordination compounds.

The alternative for naming an organic ligand attached *via* a single carbon atom is to regard it as a substituent group, its name being derived from the parent hydride from which one hydrogen atom has been removed. This designation is somewhat arbitrary as such ligands in organometallic chemistry are generally treated as anions when deducing oxidation states, although the bonding in reality may be highly covalent. However, this system of nomenclature (see Section P-29.2 of Ref. 3) has a long tradition in organic and organometallic chemistry, and its major advantage is that names used in common practice for organic groups can be applied unchanged.

In this system suffixes are used according to two methods:

(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 best employed in simple cases like saturated acyclic and monocyclic hydrocarbon substituent groups and for the mononuclear parent hydrides of silicon, germanium, tin and lead. (See also Section P-29.2.1 of Ref. 3).

Examples:

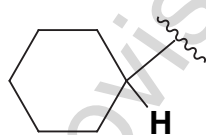
CH ₃ –	methyl
CH ₃ CH ₂ –	ethyl
C ₆ H ₁₁ –	cyclohexyl
CH ₃ CH ₂ CH ₂ C(Me)H–	1-methylbutyl
Me ₃ Si–	trimethylsilyl

Thus the compound [TiCl₃Me] would be called trichlorido(methyl)titanium by this method.

(b) In a more general method, the suffix 'yl' is added to the name of the parent hydride with elision 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. (See Section P-29.2.2 of Ref. 3 for a more complete discussion of substituent prefix names).

Examples:

CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ –	pentan-1-yl
CH ₃ CH ₂ CH ₂ C(Me)H–	pentan-2-yl

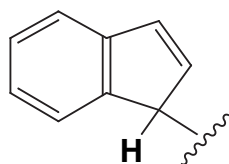


cyclohexan-1-yl

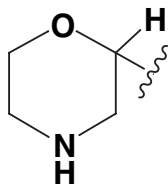
CH ₂ =CHCH ₂ –	prop-2-en-1-yl
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In fused polycyclic hydrocarbons as well as in heterocyclic systems, special numbering schemes are adopted. (See Ref. 4 and Sections P-29.3.3 and P-29.3.4 of Ref. 3). The locant of the ligating atom is then also indicated before the ending 'yl'.

Examples:



inden-1-yl



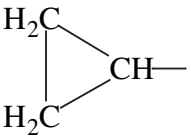
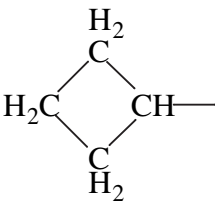
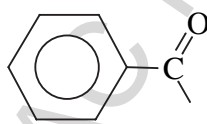
morpholin-2-yl

Table IR-10.2 gives the names used for ligands forming a single bond to a metal, and this is followed by examples illustrating the naming of compounds containing one metal-carbon single bond.

In Table IR-10.2 (as well as Tables IR-10.3 and IR-10.5) the organic ligands are listed by their systematic additive and systematic substitutive names. In all the Tables an alternative name is sometimes included that is generally preferred either for historical reasons or for reasons of brevity.

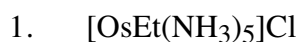
Table IR-10.2 Names for ligands forming a metal-carbon single bond

<i>Ligand formula</i>	<i>Systematic additive name</i>	<i>Systematic substitutive name</i>	<i>Alternative name</i>
$\text{H}_3\text{C}-$	methanido	methyl	
CH_3CH_2-	ethanido	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 or 1-methylpropyl	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

$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}- \\ \\ \text{CH}_3 \end{array}$	2-methylpropan-2-ido	2-methylpropan-2-yl or 1,1-dimethylethyl	<i>tert</i> -butyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	2,2-dimethylpropan-1-ido	2,2-dimethylpropyl	neopentyl
	cyclopropanido	cyclopropyl	
	cyclobutanido	cyclobutyl	
C_5H_5-	cyclopentadienido	cyclopentadienyl	
C_6H_5-	benzenido	phenyl	
$\text{C}_6\text{H}_5\text{CH}_2-$	phenylmethanido	phenylmethyl	benzyl
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$	1-oxoethanido	ethanoyl	acetyl
$\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-$	1-oxopropanido	propanoyl	propionyl
$\text{C}_3\text{H}_7-\overset{\text{O}}{\parallel}{\text{C}}-$	1-oxobutanido	butanoyl	butyryl
	oxo(phenyl)methanido	phenylcarbonyl	benzoyl
$\text{H}_2\text{C}=\text{CH}-$	ethenido	ethenyl	vinyl
$\text{HC}\equiv\text{C}-$	ethynido	ethynyl	
$\text{H}_3\text{Si}-$	silanido	silyl	
$\text{H}_3\text{Ge}-$	germanido	germyl	

$\text{H}_3\text{Sn}-$ stannanido stannyl

Examples:

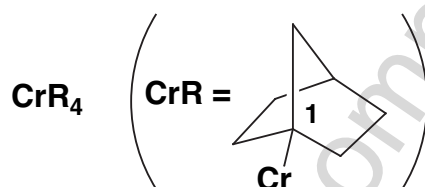


pentaammine(ethyl)osmium(1+) chloride



lithium dimethylcuprate(1-)

3.

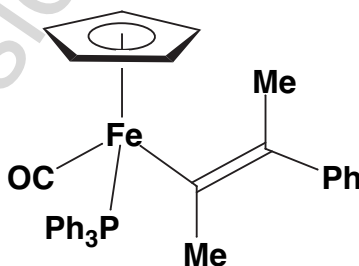


tetrakis(bicyclo[2.2.1]heptan-1-yl)chromium



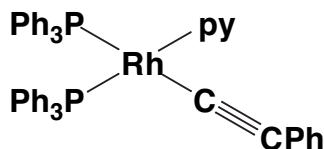
acetyl(methyl)bis(triethylphosphane)platinum

5.



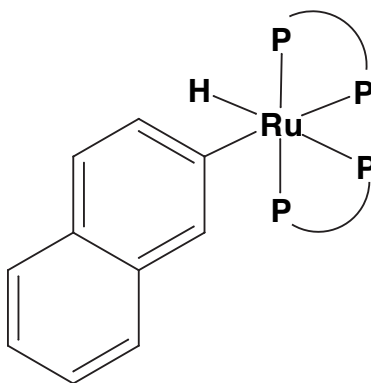
carbonyl(η^5 -cyclopentadienyl)[(2E)-3-phenylbut-2-en-2-yl](triphenylphosphane)iron

6.

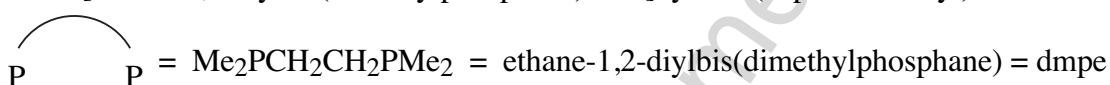


(phenylethynyl)(pyridine)bis(triphenylphosphane)rhodium

7.



bis[ethane-1,2-diylbis(dimethylphosphane)- κ^2P]hydrido(naphthalen-2-yl)ruthenium



IR-10.2.3 Compounds with several metal-carbon single bonds from one ligand

When an organic ligand forms more than one metal-carbon single bond (to one or more metal atoms), the ligand name is derived from the parent hydrocarbon from which the appropriate number of hydrogen atoms have been removed. In the systematic substitutive name, the suffix 'diyl' or 'triyl' is attached to the name of the parent hydrocarbon if two or three hydrogen atoms, respectively, are replaced by one or more metal atoms. There is no removal of the terminal 'e', such elision being required only before suffixes beginning with 'a', 'i', 'o', 'u' or 'y'. The locant number must always be cited, except for ligands derived from methane. Alternatively, when using additive nomenclature, the endings 'diido' and 'triido' should be used. This nomenclature also applies to hypervalent coordination modes, *e.g.* for bridging methyl groups. Typical ligands forming two or three metal-carbon single bonds are listed in Table IR-10.3.

Table IR-10.3 Names for ligands forming several metal-carbon single bonds

<i>Ligand formula</i>	<i>Systematic additive name</i>	<i>Systematic substitutive name</i>	<i>Alternative name</i>
$-\text{CH}_2-$	methanediido	methanediyl	methylene
$-\text{CH}_2\text{CH}_2-$	ethane-1,2-diido	ethane-1,2-diyl	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	
$\begin{array}{c} \\ \text{HC} - \\ \end{array}$	methanetriido	methanetriyl	

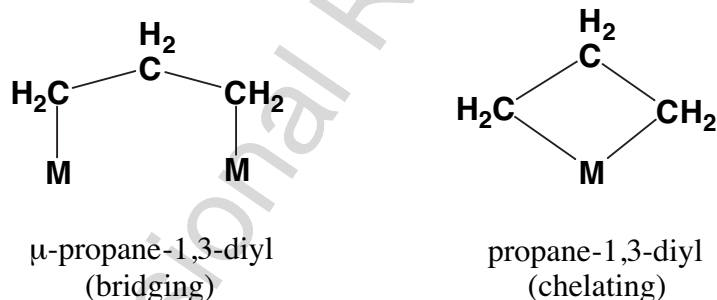
CH_3HC	ethane-1,1-diido	ethane-1,1-diyl
CH_3C	ethane-1,1,1-triido	ethane-1,1,1-triyl
$-\text{CH}=\text{CH}-$	ethene-1,2-diido	ethene-1,2-diyl
$\text{H}_2\text{C}=\text{C}$	ethene-1,1-diido	ethene-1,1-diyl
$-\text{C}\equiv\text{C}-$	ethyne-1,2-diido	ethyne-1,2-diyl

IR-10.2.3.1 The mu (μ) convention

Organic ligands forming more than one metal-carbon bond can be either chelating, if coordinating to one metal atom, or bridging, if coordinating to two or more metal atoms. A bridging bonding mode is indicated by the Greek letter μ (Sections IR-9.2.5.2 and IR-10.2.3.4).

Example:

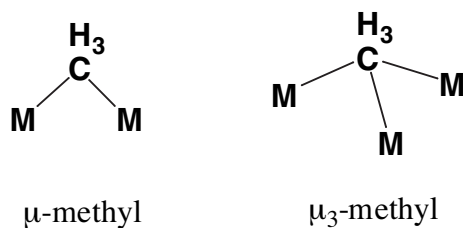
1.



The number of metal atoms connected by a bridging ligand is indicated by a right subscript, μ_n , where $n \geq 2$, though the bridging index 2 is not normally indicated.

Example:

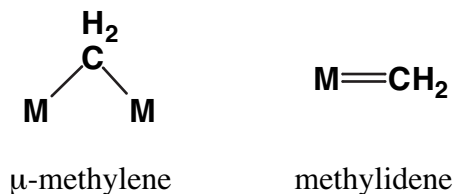
2.



The name methylene for CH₂ can only be used in connection with a bridging bonding mode (μ -methylene), whereas a CH₂ ligand bonding to one metal only has a metal-carbon double bond and should be named as methylidene (see Section IR-10.2.4).

Example:

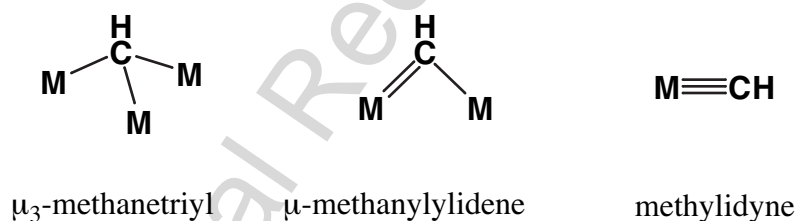
3.



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 (methylidyne, see Section IR-10.2.4).

Example:

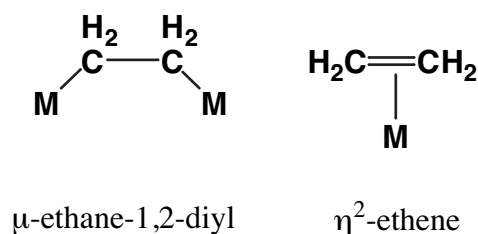
4.



In a bridging mode the ligand CH₂CH₂ should be called μ -ethane-1,2-diyl, while the same ligand coordinating through both carbon atoms to a single metal centre should be called η^2 -ethene (see Section IR-10.2.5).

Example:

5.

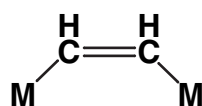


A similar situation arises with CHCH which, when bridging with the carbon atoms individually bonded to each of two metals, should be called μ -ethene-1,2-diyl or, when the metal-carbon bonds are double, μ -ethanediylidene (see Section IR-10.2.4). The same ligand coordinating through both carbon atoms to both metal centres should be called μ -ethyne;

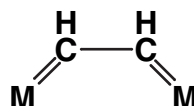
when coordinated through both carbons to one metal it is named η^2 -ethyne (see Section IR-10.2.5).

Example:

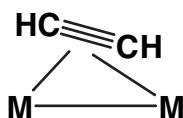
6.



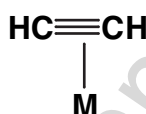
μ -ethene-1,2-diyl



μ -ethanedilydene



μ -ethyne



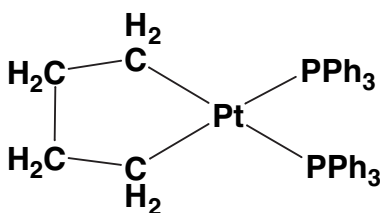
η^2 -ethyne

IR-10.2.3.2 *Chelating ligands*

Where a ligand is chelating, the coordinating atoms should be indicated either by specifying them within the ligand name (such as propane-1,3-diyl) or by applying the italicized donor atom symbols of the κ notation (propanediyl- κ^2C^1,C^3) (Sections IR-9.2.4.2 and IR-10.2.3.3). 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. The locant '1' is assigned so as to create the longest chain of carbon atoms, and the direction of numbering is chosen to give the lowest possible locants to side chains or substituents. For heterocyclic and polycyclic ligand systems special numbering schemes for the organic moieties are employed (see Ref. 4 and Sections P-29.3.3 and P-29.3.4 of Ref. 3). Note that an alternative nomenclature for metallacycles, *e.g.* Examples 1, 2 and 3, is currently being developed.

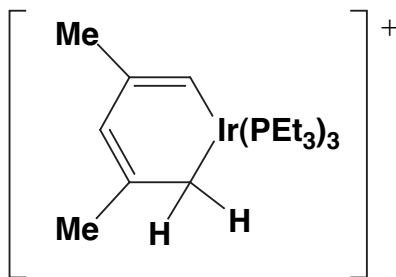
Examples:

1.



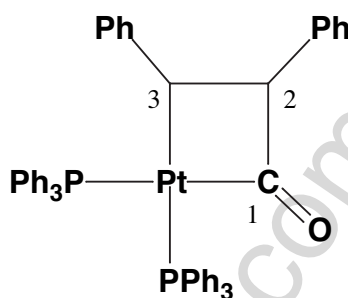
(butane-1,4-diyl)bis(triphenylphosphane)platinum

2.



(2,4-dimethylpenta-1,3-diene-1,5-diyl)tris(triethylphosphane)iridium(1+)

3.



(1-oxo-2,3-diphenylpropane-1,3-diyl)bis(triphenylphosphane)platinum

IR-10.2.3.3 *The kappa (κ) convention*

Chelate rings that contain a coordinate (dative) bond from a heteroatom in addition to a carbon attachment should be named using the κ convention. In this notation (see Section IR-9.2.4.2) the coordinating atoms of a polydentate ligand bonding to a metal centre are indicated by the Greek letter kappa, κ , preceding the italicized element symbol of each ligating atom. A right superscript numeral may be added to the symbol κ to indicate the number of identically bound ligating atoms; non-equivalent ligating atoms should each be indicated by an italicized element symbol preceded by κ .

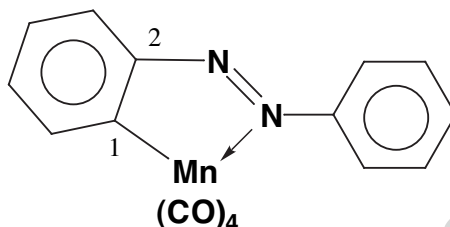
In simple cases one or more superscript primes on the element symbol may be used to differentiate between donor atoms of the same element. Otherwise a right superscript numeral corresponding to the conventional numbering of the atoms in the ligand is used to define unambiguously the identity of the ligating atom. These symbols are placed after that portion of the ligand name which represents the particular functionality, substituent group, ring or chain in which the ligating atom is found.

Often it is only necessary for the coordinating heteroatom to be specified using the κ convention, the ligating carbon atom being adequately specified by the appropriate

substitutive suffix. For illustrative purposes only, an arrow is used in the examples that follow to indicate a coordinate bond in the chelate ring. In Example 1 the κC^1 specification is included for clarity but is not strictly necessary as the ligating phenyl carbon atom, being bonded to the metal, is automatically labelled '1'.

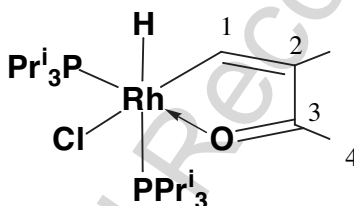
Examples:

1.



tetracarbonyl[2-(phenyldiazenyl- κN^2)phenyl- κC^1]manganese

2.



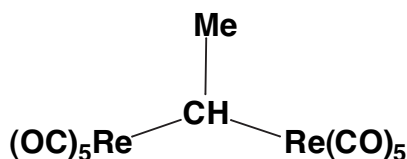
chloridohydrido(2-methyl-3-oxo- κO -but-1-en-1-yl)bis(triisopropylphosphane)rhodium

IR-10.2.3.4 Bridging ligands

Bridging ligands are indicated by the Greek letter μ (mu) prefixing the ligand name (see Sections IR-9.2.5.2 and IR-10.2.3.1). Bridging ligands are cited before terminal ligands, the ligands in each category being listed in alphabetical order, and multiple bridging is listed in descending order of complexity, *e.g.* μ_3 bridging before μ_2 bridging.

Example:

1.



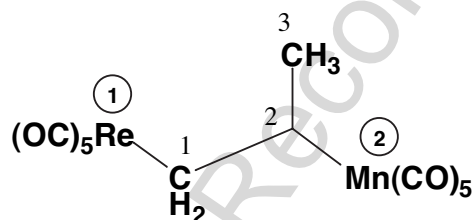
(μ -ethane-1,1-diyl)bis(pentacarbonylrhenium)

The metal centres in heterobinuclear molecules are numbered and listed according to the element priority sequence given in Table VI*, the higher priority central atom being numbered '1' and listed in the name first (see Sections IR-2.15.4 and IR-9.2.5.1).

The numerical locants of the central atoms are used in conjunction with the κ notation to indicate the distribution of the ligating atoms. Such locants are placed before the κ symbol, which, as before, may be followed by a right superscript numeral to denote the number of equivalent ligating atoms bonded to the central atom specified by the locant (see Section IR-9.2.5.5). Thus, decacarbonyl-1 $\kappa^5C,2\kappa^5C$ indicates that the carbon atoms of five carbonyl ligands are bonded to central atom number 1 and another five to central atom number 2. Where bridging is accomplished by different atoms of the same group, the ligating locants and symbols are separated by a colon, *e.g.* μ -propane-1,2-diyl-1 $\kappa C^1:2\kappa C^2$.

Example:

2.



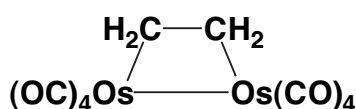
decacarbonyl-1 $\kappa^5C,2\kappa^5C$ -(μ -propane-1,2-diyl-1 $\kappa C^1:2\kappa C^2$)rheniummanganese

IR-10.2.3.5 *Metal-metal bonding*

Metal-metal bonding is indicated by the italicized element symbols of the appropriate metal atoms, separated by an 'em' dash and enclosed in parentheses, placed after the list of central atoms and before the ionic charge. The element symbols are placed in the same order as the central atoms appear in the name, *i.e.* with the higher priority element, as determined from Table VI, given first. The number of such metal-metal bonds is indicated by an arabic numeral placed before the first element symbol and separated from it by a space. For the purpose of nomenclature, no distinction is made between different metal-metal bond orders.

Examples:

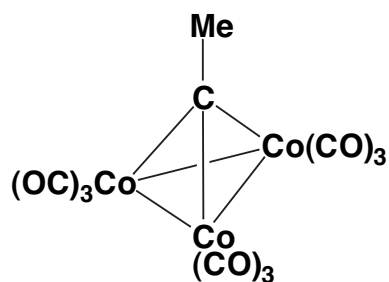
1.



* Tables numbered with a Roman numeral are collected together at the end of this book.

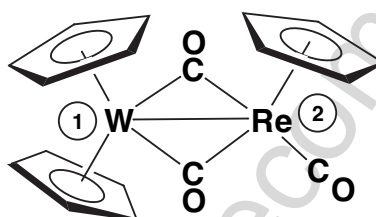
(μ -ethane-1,2-diyl)bis(tetracarbonylosmium)(Os—Os)

2.



(μ_3 -ethane-1,1,1-triyl)-*triangulo*-tris(tricarbonylcobalt)(3 Co—Co)

3.



di- μ -carbonyl-carbonyl-2 κ C-tris[1,1,2(η^5)-cyclopentadienyl]tungstenrhenium(W—Re)

For a more detailed discussion of binuclear compounds and larger polynuclear clusters, with further examples, see Section IR-9.2.5.

IR-10.2.4 Compounds with metal-carbon multiple bonds

Ligands regarded as forming metal-carbon double or triple bonds are also given substituent prefix names derived from the parent hydrides, 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 (see Sections P-29.2.1 and P-29.2.2 of Ref. 3).

(a) The suffix 'ylidene' or 'ylidyne' 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. Note that the suffix 'ylene' should only be used in conjunction with μ to designate bridging $-\text{CH}_2-$ (methylene) or $-\text{C}_6\text{H}_4-$ (phenylene) (see Section IR-10.2.3.1).

(b) In a more general method, the suffix 'ylidene' or 'ylidyne' is added to the name of the parent hydride with elision 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. Except for ligands which are bonded to a metal in an unambiguous fashion or when using the suffix 'ylidyne', the locant '1' must always be cited.

Example:

1. $\text{CH}_3\text{CH}_2\text{CH}=\text{}$ (a) propylidene, or
(b) propan-1-ylidene

Note that in numbering a ligand that has several points of attachment, the longest chain of carbon atoms is chosen as the parent chain before assigning the lowest possible locant to the atom with the free valence. In a metallacycle, the direction of numbering is chosen so as to give the lowest possible locants to side chains or substituents. Once again, special numbering schemes apply to heterocyclic and polycyclic systems (see Ref. 4 and Sections P-29.3.3 and P-29.3.4 of Ref. 3).

In a ligand containing one or more 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 the free valencies. If a choice remains, lower numbers are selected for the 'yl' positions before the 'ylidene' positions and then for any side chains or substituents.

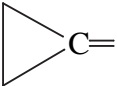
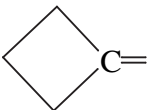
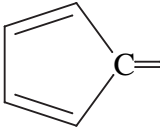
Example:

2. $\text{CH}_3-\text{CH}_2-\overset{|}{\text{C}}=\text{}$ propan-1-yl-1-ylidene

Typical ligands forming a metal-carbon double or triple bond are listed in Table IR-10.4, and this is followed by examples illustrating the naming of compounds containing one or more metal-carbon multiple bonds.

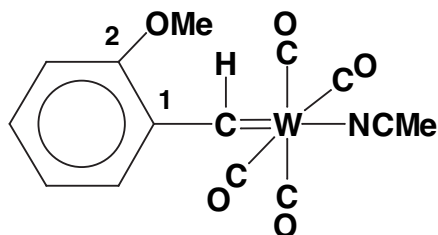
Table IR-10.4 Names for ligands forming metal-carbon multiple bonds

<i>Ligand formula</i>	<i>Systematic name</i>	<i>Alternative name</i>
$\text{H}_2\text{C}=\text{}$	methylidene	

$\text{H}_3\text{CCH=}$	ethylidene	
$\text{H}_2\text{C=C=}$	ethenylidene	vinylidene
$\text{H}_2\text{C=HC—HC=}$	prop-2-enylidene	allylidene
$\text{H}_2\text{C=C=C=}$	propa-1,2-dienylidene	allenylidene
$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C=} \\ \diagup \\ \text{H}_3\text{C} \end{array}$	propan-2-ylidene	isopropylidene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C—C—CH=} \\ \\ \text{CH}_3 \end{array}$	2,2-dimethylpropylidene	
	cyclopropylidene	
	cyclobutylidene	
	cyclopenta-2,4-dien-1-ylidene	
PhHC=	phenylmethylidene	benzylidene
HC=	methanylylidene	
$\text{HC}\equiv$	methylidyne	
$\text{MeC}\equiv$	ethylidyne	
$\text{EtC}\equiv$	propylidyne	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C—C—C}\equiv \\ \\ \text{CH}_3 \end{array}$	2,2-dimethylpropylidyne	
$\text{PhC}\equiv$	phenylmethylidyne	benzylidyne

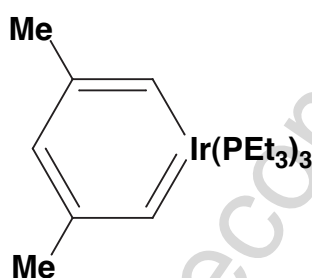
Examples:

1.



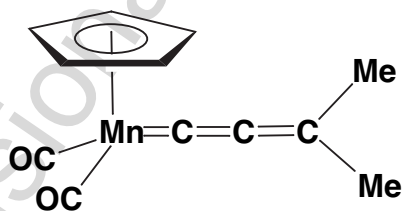
trans-(acetonitrile)tetracarbonyl(2-methoxybenzylidene)tungsten

2.



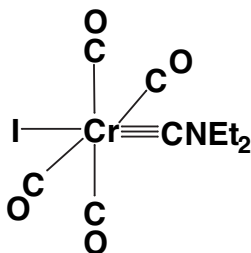
(2,4-dimethylpenta-1,3-dien-1-yl-5-ylidene)tris(triethylphosphane)iridium

3.



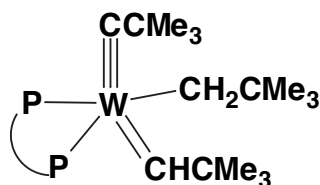
dicarbonyl(η^5 -cyclopentadienyl)(3-methylbuta-1,2-dien-1-ylidene)manganese

4.

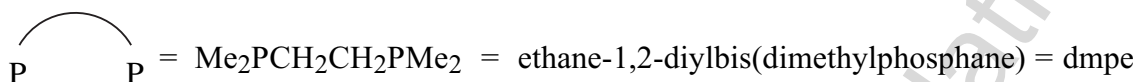


trans-tetracarbonyl[(diethylamino)methylidyne]iodidochromium

5.



[ethane-1,2-diylbis(dimethylphosphane)- κ^2P](neopentyl)(neopentylidene)(neopentylidyne)tungsten



IR-10.2.5 Compounds with bonds to unsaturated molecules or groups

Since the discovery of Zeise's salt, $\text{K}[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]$, the first organometallic complex of a transition metal, and particularly since the first reported synthesis of ferrocene, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$, 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. These ligands normally contain groups that coordinate *via* the π -electrons of their multiple bonds, such as alkenes, alkynes and aromatic compounds, but they may also be carbon-free entities containing bonds between heteroelements; 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) is often uncertain. The atoms bonded to the metal atom are therefore indicated in a manner independent of theoretical implications. Thus, the use of the prefixes σ and π is not recommended in nomenclature; these symbols refer to the symmetry of orbitals and their interactions, which are irrelevant for nomenclature purposes.

From the point of view of oxidation states, ligands such as alkenes, alkynes, nitriles, diazenes, and others such as allyl (C_3H_5), butadiene (C_4H_6), cyclopentadienyl (C_5H_5), cycloheptatrienyl (C_7H_7) and cyclooctatetraene (C_8H_8), may be formally regarded as anionic, neutral or cationic (see Section IR-10.2.1.5 and Table IR-10.1). The structures of, 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 prefixes. Other ligands are given the substituent names ending in 'yl', 'diyl', 'ylidene', etc., depending on the number of hydrogen atoms removed and the type of bonding (as

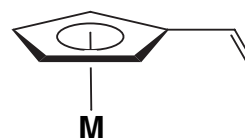
discussed in Sections IR-10.2.2, IR-10.2.3 and IR-10.2.4). Alternatively, the endings 'ido', 'diido', *etc.* can be used. As before, a special nomenclature applies to fused polycyclic or unsaturated heterocyclic ligands (see Ref. 4 and Sections P-29.3.3. and P-29.3.4 of Ref. 3).

IR-10.2.5.1 *The eta (η) convention*

The special nature of the bonding of unsaturated hydrocarbons to metals *via* their π -electrons has led to the development of the 'hapto' nomenclature to designate unambiguously the unique bonding modes of the compounds so formed.⁵ (See also Section IR-9.2.4.3). The Greek symbol η (eta) provides a topological description by indicating the connectivity between the ligand and the central atom. The number of contiguous atoms in the ligand coordinated to the metal is indicated by a right superscript numeral, *e.g.* η^3 ('eta three' or 'trihapto'), η^4 ('eta four' or 'tetrahapto'), η^5 ('eta five' or 'pentahapto'), *etc.* The symbol η is added as a prefix 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 *versus* vinyl- η^5 -cyclopentadienyl:



cyclopenta-2,4-dien-1-yl- η^2 -ethene



vinyl- η^5 -cyclopentadienyl

Complexes of unsaturated systems incorporating heteroatoms may be designated in the same manner if both the carbon atoms and adjacent heteroatoms are coordinated. Names for typical unsaturated molecules and groups acting as ligands are listed in Table IR-10.5, and this is followed by examples illustrating the naming of compounds containing such ligands.

Table IR-10.5 Ligand names for unsaturated molecules and groups

Ligand ^a	Systematic additive name	Systematic substitutive name	Alternative name
	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

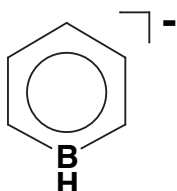
	η^4 -2-methylidenepropane-1,3-diido	η^4 -2-methylidenepropane-1,3-diyl	
	η^6 -2,3-dimethylidenebutane-1,4-diido	η^6 -2,3-dimethylidenebutane-1,4-diyl	η^6 -2,2'-biallyl
	η^5 -(Z,Z)-pentadienido	η^5 -(Z,Z)-pentadienyl	
	η^5 -cyclopentadienido	η^5 -cyclopentadienyl	
	pentamethyl- η^5 -cyclopentadienido	pentamethyl- η^5 -cyclopentadienyl	
	η^5 -cyclohexadienido	η^5 -cyclohexadienyl	
	η^7 -cycloheptatrienido	η^7 -cycloheptatrienyl	η^7 -tropyyl ^b
	η^7 -cyclooctatrienido	η^7 -cyclooctatrienyl	η^7 -homotropyyl ^b
			1-methyl- η^5 -borole
	η^5 -azacyclopentadienido	η^5 -azacyclopentadienyl	η^5 -pyrrolyl



η^5 -phosphacyclopentadienido η^5 -phosphacyclopentadienyl η^5 -phospholyl

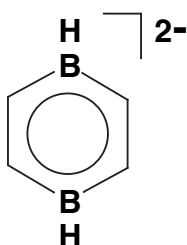


η^5 -arsacyclopentadienido η^5 -arsacyclopentadienyl η^5 -arsolyl



η^6 -borinin-1-ido

η^6 -boranuidabenzene ^c



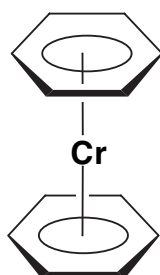
η^6 -1,4-diborinine-1,4-diido

η^6 -1,4-diboranuidabenzene ^d

^a The arcs used in these and later examples indicate delocalized charges (by analogy with the circle in benzene). ^b If these ligands are regarded as cations they take the ending 'ium'. ^c Previously named η^6 -boratabenzene. ^d Previously named η^6 -1,4-diboratabenzene.

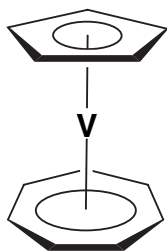
Examples:

1.



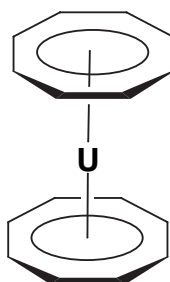
bis(η^6 -benzene)chromium

2.



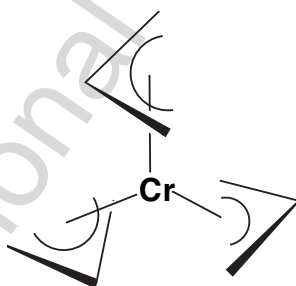
(η^7 -cycloheptatrienyl)(η^5 -cyclopentadienyl)vanadium

3.



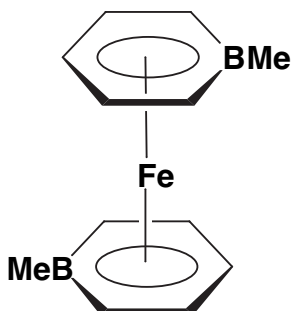
bis(η^8 -cyclooctatetraene)uranium

4.



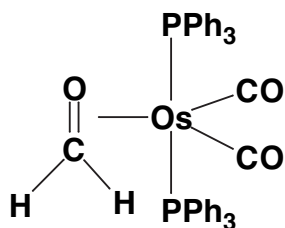
tris(η^3 -allyl)chromium

5.

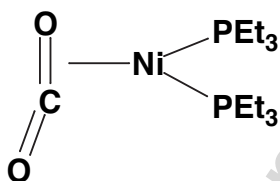


bis(η^6 -1-methyl-1-boranidabenzene)iron

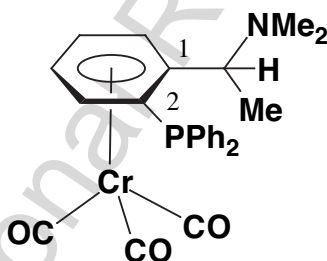
6.

dicarbonyl(η^2 -formaldehyde)bis(triphenylphosphane)osmium

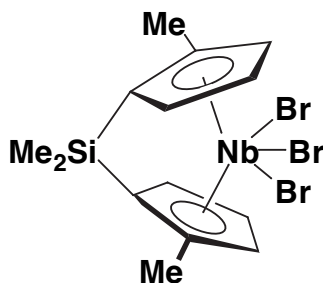
7.

(η^2 -carbon dioxide)bis(triethylphosphane)nickel

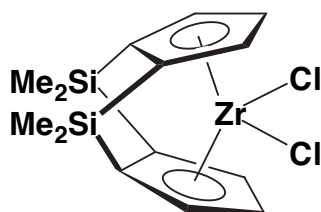
8.

tricarbonyl{1-[1-(dimethylamino)ethyl]-2-(diphenylphosphanyl)- η^6 -benzene}chromium

9.

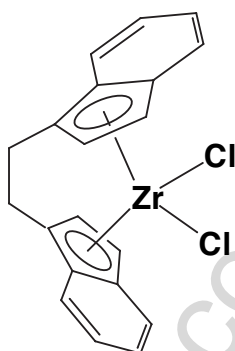
tribromido[1,1'-(dimethylsilanediyl)bis(2-methyl- η^5 -cyclopentadienyl)]niobium

10.



dichlorido[(1-3,3a,8a:4a,5-7,7a- η)-4,4,8,8-tetramethyl-1,4,5,8-tetrahydro-4,8-disila-s-indacenediyl]zirconium

11.

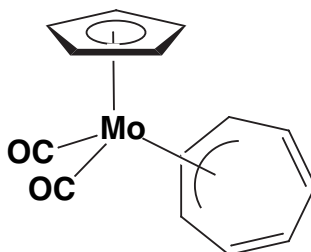


dichlorido[1,1'-(ethane-1,2-diyl)di(η^5 -indenyl)]zirconium

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

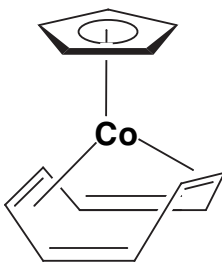
Examples:

12.



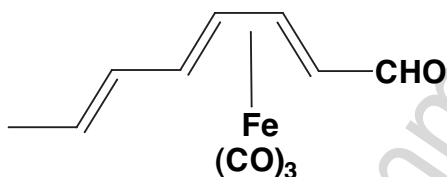
dicarbonyl[(1-3- η)-cyclohepta-2,4,6-trienyl](η^5 -cyclopentadienyl)molybdenum

13.



[(1,2,5,6-η)-cyclooctatetraene](η⁵-cyclopentadienyl)cobalt

14.

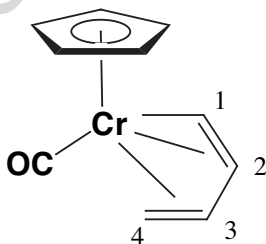


tricarbonyl[(2-5-η)-(E,E,E)-octa-2,4,6-trienal]iron

Substituents are given the lowest possible numerical locants in the usual manner. However, the point of attachment to the metal of the first carbon in an allylic system (such as an 'enyl' or a 'dienyl' ligand with an extended chain) has to be numbered in such a way as to create the longest chain, with the lowest possible locant for the 'yl' suffix.

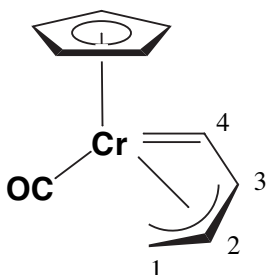
Examples:

15.



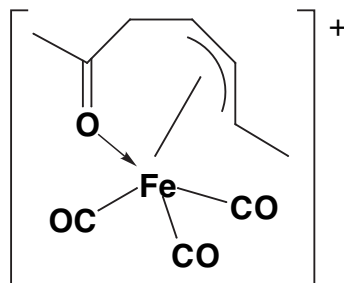
(η⁴-buta-1,3-dien-1-yl)carbonyl(η⁵-cyclopentadienyl)chromium

16.



[(1-3- η)-but-2-en-1-yl-4-ylidene]carbonyl(η^5 -cyclopentadienyl)chromium

17.

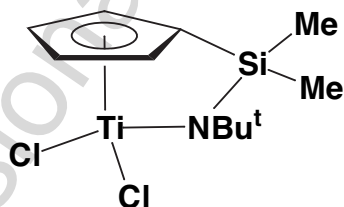


tricarbonyl[6-oxo- κ O-(2-4- η)-hept-3-en-2-yl]iron(1+)

As indicated in the previous example, the η symbol can, if necessary, be combined with the κ symbol (see Section IR-10.2.3.3). 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.

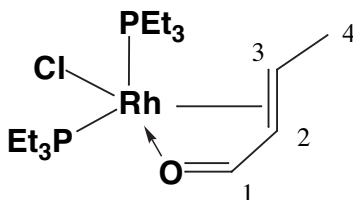
Examples:

18.



{[(η^5 -cyclopentadienyl)dimethylsilyl]-*tert*-butylaminido- κ N} dichloridotitanium

19.



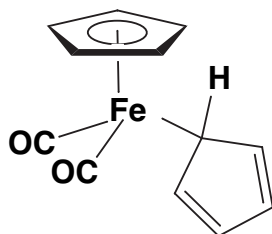
[(*E*)- η^2 -but-2-enal- κ O]chloridobis(triethylphosphane)rhodium

Use of the symbol η^1 for a ligand coordinating *via* one carbon atom is not generally recommended for nomenclature purposes. A cyclopentadienyl ligand bonded by only one

σ -bond is frequently called σ -cyclopentadienyl or η^1 -cyclopentadienyl, but cyclopenta-2,4-dien-1-yl or cyclopenta-2,4-dien-1-yl- κC^1 is more appropriate.

Example:

20.

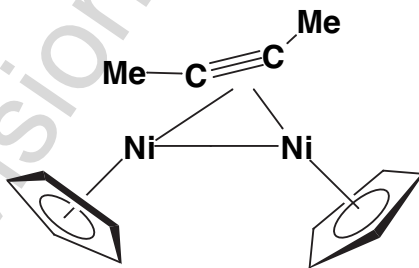


dicarbonyl(η^5 -cyclopentadienyl)(cyclopenta-2,4-dien-1-yl)iron

If an unsaturated hydrocarbon serves as a bridging ligand, the prefix μ (see Sections IR-10.2.3.1 and IR-10.2.3.4) is combined with both η and κ , where necessary. The colon is used to separate the locants of the bridging ligand which indicate binding to different metal atoms. The priority numbers (as determined from Table VI) of the metal atoms in polynuclear 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).

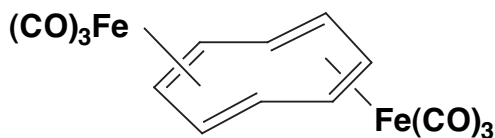
Examples:

21.



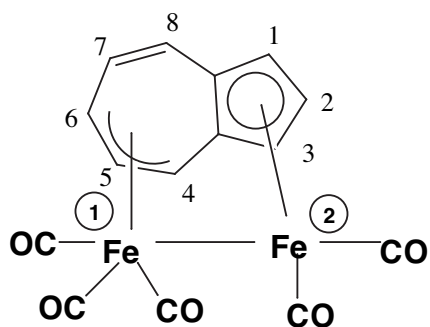
(μ -but-2-yne)bis[(η^5 -cyclopentadienyl)nickel](Ni—Ni)

22.



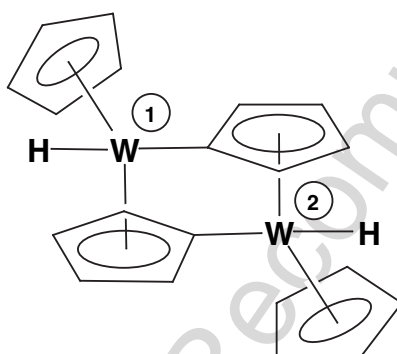
[*trans*- μ -(1-4- η :5-8- η)-cyclooctatetraene]bis(tricarbonyliron)

23.



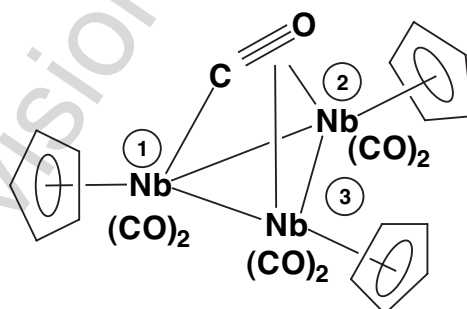
{ μ -[2(1-3,3a,8a- η):1(4-6- η)]azulene}(pentacarbonyl-1 κ^3 C,2 κ^2 C)diiron($Fe-Fe$)

24.



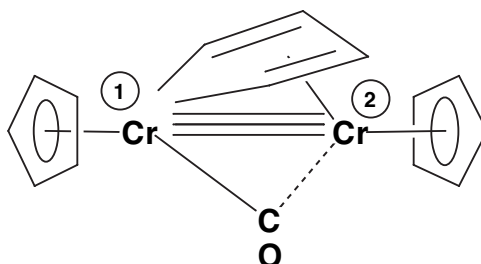
(μ -1 η^5 -cyclopentadienediyl-2 κ C)(μ -2 η^5 -cyclopentadienediyl-1 κ C)bis[(η^5 -cyclopentadienyl)hydridotungsten]

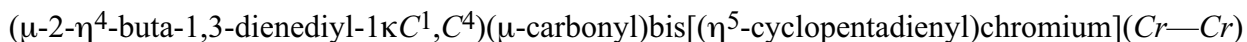
25.



μ_3 -carbonyl-1 κ C:2 κ C, O :3 κ C, O -triangulo-tris[dicarbonyl(η^5 -cyclopentadienyl)niobium](3 $Nb-Nb$)
or μ_3 -2- η^2 :3- η^2 -carbonyl-1 κ C-triangulo-tris[dicarbonyl(η^5 -cyclopentadienyl)niobium](3 $Nb-Nb$)

26.

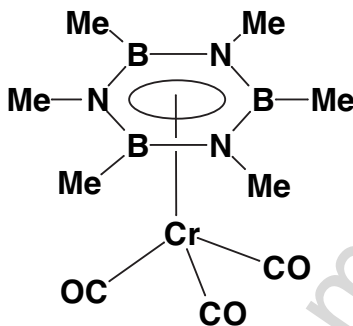




The η -nomenclature can also be extended to π -coordinated ligands containing no carbon atoms, such as the borazines and pentaphospholyl.

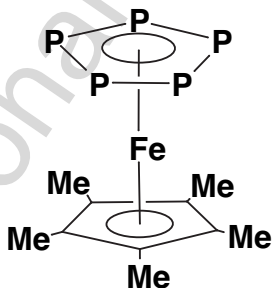
Examples:

27.



tricarbonyl(η^6 -hexamethyl-1,3,5,2,4,6-triazatriborinane)chromium,
or tricarbonyl(η^6 -hexamethylcyclotriborazane)chromium

28.

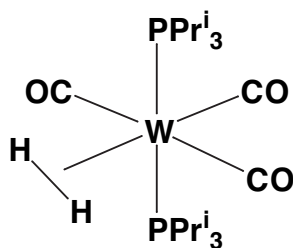


(pentamethyl- η^5 -cyclopentadienyl)(η^5 -pentaphospholyl)iron

This nomenclature 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 (*i.e.* $\eta^2\text{-H}_2$)⁶ or the saturated C–H bonds in 'agostic' interactions.⁷ The η symbol and locants for agostic interactions are placed separately from other locants at the end of the ligand name. In Example 30 the agostic bond is denoted by a half arrow.

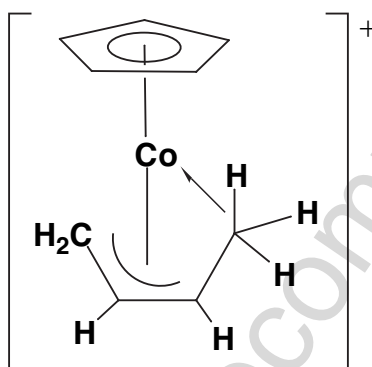
Examples:

29.



trans-tricarbonyl(η^2 -dihydrogen)bis(triisopropylphosphane)tungsten

30.

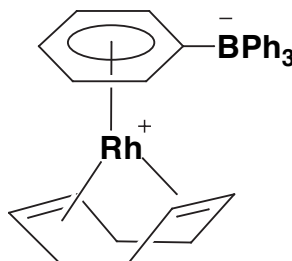


[(1-3- η)-but-2-enyl- η^2 -C⁴,H⁴](η^5 -cyclopentadienyl)cobalt(1+)

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 on the ligand is indicated by the appropriate ligand name ending, while the charge of the central atom is not indicated.

Example:

31.



(η^4 -cycloocta-1,5-diene)(η^6 -phenyltriphenylborate)rhodium, or
(η^4 -cycloocta-1,5-diene)(η^6 -phenyltriphenylboranuide)rhodium

The first transition metal compound containing only carbocyclic rings as ligands was bis(cyclopentadienyl)iron, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$, which has a 'sandwich' structure with two parallel η^5 - or π -bonded rings. The recognition that this compound was amenable to electrophilic substitution, similar to the aromatic behaviour of benzene, led to the suggestion of the non-systematic name 'ferrocene' and to similar names for other 'metallocenes'.

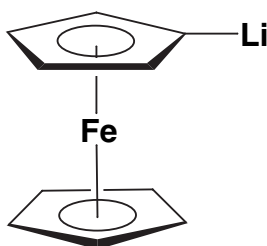
Examples:

1. $[\text{V}(\eta^5\text{-C}_5\text{H}_5)_2]$ vanadocene
2. $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2]$ chromocene
3. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$ cobaltocene
4. $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ nickelocene
5. $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]$ ruthenocene
6. $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)_2]$ osmocene

Metallocene derivatives may be named either by the standard organic suffix (functional) nomenclature or by prefix nomenclature. The organic functional suffix system is described in Section P-33 of Ref. 3. For metallocene derivatives the substituent group suffixes 'ocenyl', 'ocenediyl', 'ocenetriyl', *etc.*, are used.

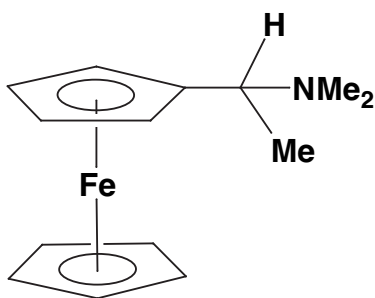
Examples:

7.

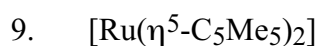


lithioferrocene or ferrocenyllithium

8.



1-[1-(dimethylamino)ethyl]ferrocene, or
1-ferrocen-1-yl-*N,N*-dimethylethan-1-amine

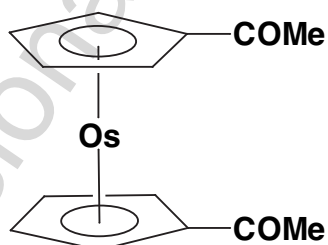


decamethylruthenocene, or
bis(pentamethyl- η^5 -cyclopentadienyl)ruthenium

Substituents on the equivalent cyclopentadienyl rings of the metallocene entity are given the lowest possible numerical locants in the usual manner. The first ring is numbered 1–5 and the second ring 1'–5'.

Examples:

10.



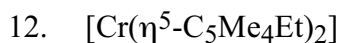
1,1'-diacetylosmocene, or
osmocene-1,1'-diylbis(ethan-1-one)

11.

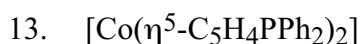


1,1'-(4-carboxybutane-1,3-diyl)ferrocene, or

3,5-(ferrocene-1,1'-diyl)pentanoic acid



1,1'-diethyloctamethylchromocene, or
bis(1-ethyl-2,3,4,5-tetramethyl- η^5 -cyclopentadienyl)chromium



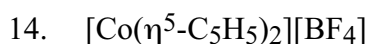
1,1'-bis(diphenylphosphanyl)cobaltocene, or
(cobaltocene-1,1'-diyl)bis(diphenylphosphane)

Metallocene nomenclature does not, however, apply to all transition metals. For example, there are at least two isomers with the empirical formula $\text{C}_{10}\text{H}_{10}\text{Ti}$ but neither has the regular sandwich structure analogous to that of ferrocene, and so none of these should be named 'titanocene'. Similarly, 'manganocene' is a misnomer since $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)_2]$ has a chain structure in the solid state, with no individual sandwich entities, although decamethylmanganocene, $[\text{Mn}(\eta^5\text{-C}_5\text{Me}_5)_2]$, has a normal sandwich structure, as does decamethylrhenocene, $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)_2]$. With the heavier metals, the occurrence of the classic ferrocene-type bis(η^5 -cyclopentadienyl) sandwich structure becomes rare.

The name-ending 'ocene' should therefore be confined to discrete molecules of the form bis(η^5 -cyclopentadienyl)metal (and ring-substituted analogues), where the cyclopentadienyl rings are essentially parallel, and 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 $\text{Sn}(\text{C}_5\text{H}_5)_2$].

The oxidized species may be referred to as metallocenium($n+$) salts, although it should be noted that in this case the ending 'ium' does not carry the usual meaning it has in substitutive nomenclature, *i.e.* the addition of a proton to a neutral parent compound. To avoid this ambiguity, the alternative bis(η^5 -cyclopentadienyl)iron(1+), for example, is preferred to ferrocenium(1+) for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$. Substituted derivatives are named in a similar manner, as described before.

Examples:



bis(η^5 -cyclopentadienyl)cobalt hexafluorophosphate, or
cobaltocenium hexafluorophosphate

15. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{COMe})][\text{BF}_4]$

(acetyl- η^5 -cyclopentadienyl)(η^5 -cyclopentadienyl)cobalt tetrafluoroborate,
or acetylcobaltocenium tetrafluoroborate

The oxidized form of osmocene is dinuclear in the solid state, with a long Os–Os bond, so should not be named using the 'ocenium' nomenclature. However, $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ has a mononuclear sandwich structure and may be described as the decamethylsmocenium(1+) ion, although bis(pentamethyl- η^5 -cyclopentadienyl)osmium(1+) cation is preferred.

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, *i.e.* bis(η^5 -cyclopentadienyl)hydridoiron(1+).

Transition metal complexes derived from ligands with additional rings fused to the cyclopentadienyl rings are also known. The names of these complexes are derived from the retained common or semisystematic names of the hydrocarbon ligands, *e.g.* inden-1-yl (C_9H_7), fluoren-9-yl (C_{13}H_9), and azulene (C_{10}H_8). Thus, $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)_2]$ is named bis(η^5 -indenyl)iron. To avoid possible ambiguities, the use of fusion nomenclature, such as 'benzoferrrocene', is strongly discouraged.

Many compounds have ligands in addition to two η^5 -cyclopentadienyl rings. They are often referred to as metallocene di(ligand) species, *e.g.* $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ is frequently named 'titanocene dichloride'. This practice is discouraged since metallocene nomenclature applies only to compounds in which the two rings are parallel. Thus, $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ is named dichloridobis(η^5 -cyclopentadienyl)titanium, and $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$, $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2]$ and $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{Me}_2]$ should be named bis(η^5 -cyclopentadienyl)dihydridotungsten, dicarbonylbis(η^5 -cyclopentadienyl)titanium, and bis(η^5 -cyclopentadienyl)dimethylzirconium, respectively.

The bis(cyclooctatetraene) compound $[\text{U}(\eta^8\text{-C}_8\text{H}_8)_2]$ has sometimes been described as 'uranocene'. Related species are obtained from zirconium, $[\text{Zr}(\eta^8\text{-C}_8\text{H}_8)_2]$, and the lanthanoids, *e.g.* $[\text{Ce}(\eta^8\text{-C}_8\text{H}_8)_2]^-$. In such complexes, the carbocyclic rings are parallel and there are certain similarities to ferrocene in the molecular orbital descriptions of their bonding. However, some lanthanoids also form metal(II) cyclopentadienyl complexes, such as $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2]$. Extension of the 'ocene' nomenclature to $[\text{U}(\eta^8\text{-C}_8\text{H}_8)_2]$ and similar compounds can therefore lead to confusion and is strongly discouraged.

The cyclooctatetraene ring can also function as an η^4 -ligand, as in $[\text{Ti}(\eta^4\text{-C}_8\text{H}_8)(\eta^8\text{-C}_8\text{H}_8)]$. Compounds of cyclooctatetraene should therefore be named using standard organometallic nomenclature, *e.g.* bis(η^8 -cyclooctatetraene)uranium or [(1-4- η -cyclooctatetraene)](η^8 -cyclooctatetraene)titanium. The ligand $\text{C}_8\text{H}_8^{2-}$ is occasionally referred to as 'cyclooctatetraenyl'. This name is incorrect as it can only be used for the (as yet hypothetical) ligand C_8H_7 .

IR-10.3 NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS OF THE MAIN GROUP ELEMENTS

IR-10.3.1 Introduction

The nomenclature of organometallic compounds of the main group elements is an area of current and ongoing development. This section briefly describes key aspects of the naming of such compounds, leaving a full treatment of the subject to a future publication. Detailed information on the nomenclature of organic compounds containing the elements of groups 13-16 may be found in Sections P-68 and P-69 of Ref. 3.

In principle, all organometallic compounds, whether of the transition or main group elements, can be given names based on the additive system of nomenclature that is applied to coordination compounds. However, in addition to compounds of the metals and semi-metals, compounds of elements such as boron, silicon, arsenic and selenium are often considered to be organometallic, and compounds of these elements are commonly named by notionally substituting the hydrogen atoms of the parent hydride with the appropriate substituent groups. Thus, it is recommended that organometallic compounds derived from the elements of groups 13-16 be named by a substitutive process, while those derived from the elements of groups 1 and 2 be named using the additive system of nomenclature. Where an organometallic compound contains two or more central atoms (which may be associated with different nomenclature systems), a choice must be made to provide the basis of the name. A general rule is recommended in Section IR-10.3.4.

IR-10.3.2 Organometallic compounds of groups 1 and 2

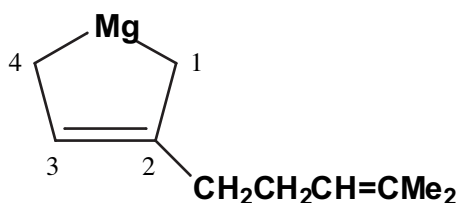
Organometallic compounds of the elements of groups 1 and 2 are named according to the additive system of nomenclature, the general definitions and rules of which are given in Sections IR-9.1 and IR-9.2. Thus, prefixes denoting the organic groups and any other ligands are placed in alphabetical order before the name of the metal. These prefixes may adopt either the additive 'ido', diido', *etc.* endings or the substitutive 'yl', 'diyl', *etc.* endings, the latter practice allowing names in common usage for organic groups to be

applied unchanged (see Section IR-10.2.2). In the examples below only one of these alternatives is illustrated, the other form, however, being equally acceptable. The presence of a hydrogen atom attached to the metal centre must always be indicated (by the prefix 'hydrido') and the name of a cyclic compound may be formed using appropriate locants of a divalent 'diido' or 'diyl' group to indicate chelate-type bonding to the metal.

Although many organometallic compounds of groups 1 and 2 exist in associated molecular form (as aggregates) or contain structural solvent, or both, their names are generally based on the stoichiometric compositions of the compounds. Any solvent is ignored unless it is specifically desired to draw attention to the extent of aggregation or the nature of any structural solvent, or both (see Example 3 below). Where an anionic ligand is involved and little or no structural information is available or is required to be conveyed, a compositional name (see Chapter IR-5) may be used (see Example 7 below). Note that metallocene terminology (Section IR-10.2.6) is not recommended for bis(cyclopentadienyl) compounds of the main group metals (see Examples 8 and 9 below).

Examples:

1. $(\text{LiMe})_n$
methyl lithium
2. BeEtH
ethanido hydrido beryllium
3. $[\{\text{Li}(\text{OEt})_2(\mu_3\text{-Ph})\}_4]$
tetrakis[(μ_3 -phenyl)(diethyl ether)lithium],
or tetrakis[(μ_3 -benzenido)(ethoxyethane)lithium]
4. $\text{Na-CH}_2=\text{CH}$
ethenidosodium,
or vinylsodium
5. $\text{Ph}_2\text{C}(\text{Na})-\text{C}(\text{Na})\text{Ph}_2$
1,1,2,2-tetraphenylethane-1,2-diyl disodium
- 6.



2-(4-methylpent-3-en-1-yl)but-2-ene-1,4-diylmagnesium

7. $[\{\text{MgI}(\text{Me})\}_n]$
iodido(methanido)magnesium,
or methylmagnesium iodide
8. $[\text{Mg}(\eta^5\text{-C}_5\text{H}_5)_2]$
bis(η^5 -cyclopentadienyl)magnesium
9. $[\text{PPh}_4][\text{Li}(\eta^5\text{-C}_5\text{H}_5)_2]$
tetraphenylphosphanium bis(η^5 -cyclopentadienyl)lithate

IR-10.3.3 Organometallic compounds of groups 13-16

Organometallic compounds of the elements of groups 13-16 are named according to the substitutive system of nomenclature, which is dealt with in Chapter IR-6. Thus, the name of the parent hydride (formed in accordance with the rules of Section IR-6.2) is modified by a prefix for each substituent, which is notionally considered to be substituting a hydrogen atom of the parent hydride. The prefix should be in appropriate substituent form (methyl, chloro, *etc.*) and not in ligand form (methanido, chlorido, *etc.*). Where there is more than one kind of substituent, the prefixes are cited in alphabetical order before the name of the parent hydride, parentheses being used to avoid ambiguity, and multiplicative prefixes being used as necessary. Non-standard bonding numbers are indicated using the λ -convention (see Section IR-6.2.2.2). An overview of the rules for naming substituted derivatives of parent hydrides is given in Section IR-6.3, while a detailed exposition may be found in Ref. 3.

Examples:

1. AlH_2Me methylalumane
2. AlEt_3 triethylalumane
3. $\text{Me}_2\text{CHCH}_2\text{CH}_2\text{-Al(H)-CH}_2\text{CH}_2\text{CHMe}_2$
bis(3-methylbutyl)alumane
4. $\text{Sb}(\text{CH}=\text{CH}_2)_3$ triethenylstibane (or trivinylstibane)
5. SbMe_5 pentamethyl- λ^5 -stibane
6. $\text{PhSb}=\text{SbPh}$ diphenyldistibene
7. GeCl_2Me_2 dichlorodimethylgermane
8. $\text{GeH}(\text{SMe})_3$ tris(methylsulfanyl)germane
9. BiI_2Ph diiodo(phenyl)bismuthane

10. $\text{Et}_3\text{Pb}-\text{PbEt}_3$ hexaethyldiplumbane
11. SnMe_2 dimethyl- λ^2 -stannane
12. $\text{SnBrH}_2-\text{SnCl}_2-\text{SnH}_2\text{Pr}$
1-bromo-2,2-dichloro-3-propyltristannane
13. $\text{Me}_3\text{SnCH}_2\text{CH}_2\text{C}\equiv\text{CSnMe}_3$
but-1-yne-1,4-diylbis(trimethylstannane)

In the presence of a characteristic group that may be expressed as a suffix (*e.g.* an amine, a carboxylic acid, an alcohol, *etc.*), the organometallic component is prefixed to the functionalized parent compound as a substituent group as described in Section IR-6.3.1, *i.e.* with the parent hydride name ending 'ane' changed to 'anyl' (or 'yl' for the group 14 elements), 'anediyl', *etc.*

Examples:

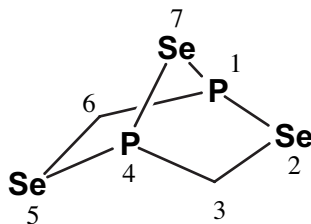
14. $(\text{EtO})_3\text{GeCH}_2\text{CH}_2\text{COOMe}$
methyl 3-(triethoxygermyl)propanoate
15. $\text{H}_2\text{As}(\text{CH}_2)_4\text{SO}_2\text{Cl}$
4-arsanylbutane-1-sulfonyl chloride
16. $\text{OCHCH}_2\text{CH}_2\text{GeMe}_2\text{GeMe}_2\text{CH}_2\text{CH}_2\text{CHO}$
3,3'-(1,1,2,2-tetramethyldigermane-1,2-diyl)dipropenal

Sometimes it may be necessary or preferable to consider a parent hydride in which several (four or more) skeletal carbon atoms of a hydrocarbon have been replaced by main group elements. In this method of skeletal replacement the heteroatoms are designated by the 'a' terms of replacement nomenclature (Table X) cited in the order given by Table VI and preceded by the appropriate locant(s). The rules for locant numbering are specified in Section IR-6.2.4.1 and this nomenclature is fully described in Section P-22.2.3.2 of Ref. 3.

Examples:

17. $\text{MeSiH}_2\text{CH}_2\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\text{SiH}_2\text{Me}$
2,5,8,11-tetrasiladodecane
18. $\text{MeSiH}_2-\text{OPH}-\text{OCH}_2\text{Me}$
3,5-dioxa-4-phospha-2-silaheptane
19. $\text{HSCH}=\text{NOCH}_2\text{SeCH}_2\text{ONHMe}$
3,7-dioxa-5-selena-2,8-diazanon-1-ene-1-thiol

20.



2,5,7-triselenium-1,4-diphosphabicyclo[2.2.1]heptane

Cyclic derivatives that have at least four elements from groups 13-16 replacing carbon atoms in their structures may be named using the 'a' terms of replacement nomenclature (to denote the heteroatoms) in conjunction with the extended Hantzsch-Widman procedures (to define the size of the ring). This nomenclature is fully described in Section IR-6.2.4.3 and in Section P-22.2.2 of Ref. 3 and will not be elaborated further here.

Section P-68 of Ref. 3 offers a more rigorous treatment of the nomenclature of organic compounds containing the elements of groups 13-16 than can be provided here, and is illustrated with many further examples.

IR-10.3.4 **Priority order for central atoms in organometallic compounds**

When an organometallic compound contains two or more different metal atoms, a choice must be made to provide the basis of the name. It is thus convenient to classify the possible central atoms as belonging to either (i) the elements of groups 1-12 (whose compounds are named according to the additive system of nomenclature) or (ii) the elements of groups 13-16 (whose compounds are named according to the substitutive system).

IR-10.3.4.1 *Central atoms from groups 1-12 only*

If both or all potential central atoms belong to class (i), then the compound is named additively using the methodology described in Section IR-9.2.5 and the element priority sequence given in Table VI (see Section IR-2.15.4). The metal atom last encountered in the direction of the arrow in Table VI is numbered '1' and listed in the name first; examples are given in Sections IR-10.2.3.4 and IR-10.2.3.5.

IR-10.3.4.2 *Central atoms from both groups 1-12 and groups 13-16*

If one possible central atom belongs to class (i) and another to class (ii), then the compound is named additively using the metal atom of class (i) as the central atom for the basis of the name. The other atom is named as a prefixed substituent group, *i.e.* with the parent hydride

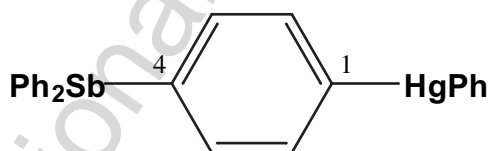
name ending 'ane' changed to 'anyl' (or 'yl' for the group 14 elements), 'anediyl', *etc.* More generally, no matter how many metal or semimetal atoms of both classes a compound contains, the compound is named additively using the metals of class (i), given in element priority sequence (Table VI), as the basis of the name.

Often the element of class (ii) will be a donor atom or otherwise a constituent atom of a ligand coordinating to a class (i) metal, in which case the class (i) element would in any case be selected as the central atom in the application of the additive nomenclature of coordination and organotransition metal compounds. Many such examples will be found in earlier parts of this Chapter.

Examples:

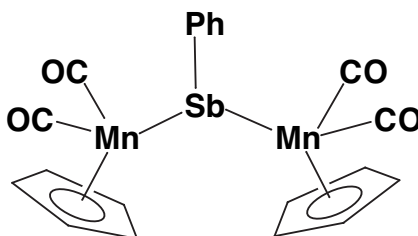
1. $\text{Li}(\text{GePh}_3)$
(triphenylgermyl)lithium
2. $(\text{Me}_3\text{Si})_3\text{CMgC}(\text{SiMe}_3)_3$
bis[tris(trimethylsilyl)methyl]magnesium
3. $[\text{Mo}(\text{CO})_5(\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2)]$
{bis[bis(trimethylsilyl)methyl]- λ^2 -stannyl}pentacarbonylmolybdenum

4.



[4-(diphenylstibanyl)phenyl](phenyl)mercury

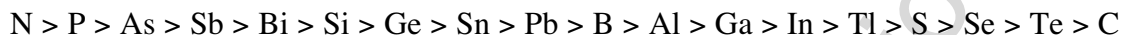
5.



(phenylstibanediyl)bis[dicarbonyl(η^5 -cyclopentadienyl)manganese]

IR-10.3.4.3 Central atoms from groups 13-16 only

If the possible central atoms are both or all from class (ii), then the compound is named substitutively as described in Section IR-10.3.3 (and in more detail in Section IR-6.3). The order of priority used to select the parent hydride is based on the seniority order of classes described in Section P-41 of Ref. 3:

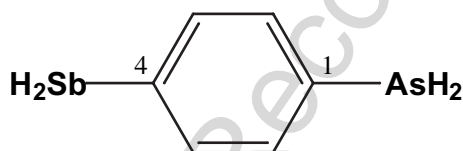


Thus, for a compound containing both arsenic and lead, the parent hydride would be selected as AsH_3 , which has priority over PbH_4 , the lead atom then appearing in the name as a prefixed substituent, often with its own substituent groups.

Examples:

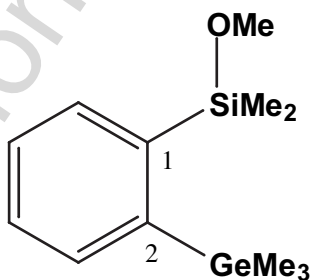
1. $\text{As}(\text{PbEt}_3)_3$
tris(triethylplumbyl)arsane

- 2.



4-(stibanylphenyl)arsane

- 3.



[2-(trimethylgermyl)phenyl]methoxydimethylsilane

4. $\text{Et}_3\text{PbCH}_2\text{CH}_2\text{CH}_2\text{BiPh}_2$
diphenyl[3-(triethylplumbyl)propyl]bismuthane
5. $\text{SiClH}_2\text{-Sn}(\text{Me})=\text{Sn}(\text{Me})\text{-SiClH}_2$
Si,Si'-(1,2-dimethyldistannene-1,2-diyl)bis(chlorosilane)

1. *Nomenclature of Inorganic Chemistry, Recommendations 1990*, Blackwell Scientific Publications, Oxford, 1990.
2. Nomenclature of Organometallic Compounds of the Transition Elements, *Pure Appl. Chem.*, **71**, 1557 (1999).
3. **New Blue Book**
4. Nomenclature of Fused and Bridged Fused Ring Systems, *Pure Appl. Chem.*, **70**, 143 (1998).
5. F.A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).
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IUPAC Provisional Recommendations