

INTRODUCTION

- The naming of organometallic compounds is similar to the naming of coordination compounds, but certain ligands can exhibit multiple modes of bonding, referred to as the hapticity.
- Over half of the compounds in the Cambridge Structural Database are organometallic in nature, making the database an ideal resource for examining the bonding of such compounds.

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This module is divided into the following sections:

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SUMMARY OF KEY CONCEPTS (see page 12)

OBJECTIVES

- To investigate the concept of hapticity by analysing experimental crystal structure data.
- To learn the nomenclature of hapticity by analysing experimental crystal structure data.
- To examine the structural perturbations of ligands as a function of their hapticity.

GETTING STARTED

- If you do not subscribe to the Cambridge Structural Database (CSD) System:
 - Open *free* Mercury (the free version of Mercury can be downloaded from http://www.ccdc.cam.ac.uk/free_services/mercury/)
 - Open the free teaching subset of the CSD (downloadable from http://www.ccdc.cam.ac.uk/free_services/teaching/downloads) by selecting **File** from the top-level menu, followed by **Open** in the resulting menu, and then selecting the database file `teaching_subset.ind`
 - Database reference codes (*refcodes*) of the structures in the teaching database will appear in a list on the right hand side of the main Mercury window. To view a structure select the corresponding *refcode* in the list.
- If you subscribe to the Cambridge Structural Database (CSD) System:
 - Open MercuryCSD.
 - The full database should be detected and opened within the *Structure Navigator* on the right hand side of the main Mercury window. To view a structure select, or type in, the corresponding *refcode*.

1 STEPS REQUIRED

1.1 Investigating metal-carbon bonding

- Examine the structures of the first 4 entries in the file (these include csd refcodes: *VADRAU*, *IGODIR*, *TODDUL*, *OKUSES*).
- You will notice that each of these structures contains at least one metal-carbon bonding interaction. Each may be selected by clicking on the identifier (such as *VADRAU*) from the *Structure Navigator* on the right hand side of the main Mercury window. Bonds between metal and carbon atoms are referred to as organometallic bonds. A ligand that contains a carbon atom which bonds to a metal is an organometallic ligand.

To manipulate structures in Mercury

- 1. Structures can be rotated by moving the cursor in the display area while keeping the left-hand mouse button pressed down.*
- 2. To zoom in and out move the cursor up and down in the display area while keeping the right-hand mouse button pressed down.*
- 3. To translate structures hold down the middle mouse button while moving the cursor in the display area (three-button mouse only). Alternatively, move the cursor in the display area while keeping both the left-hand mouse button and the keyboard Ctrl key pressed down.*
- 4. At any stage the display area can be returned to the default view by hitting the **Reset** button at the bottom of the window.*
 - Change the display style from wireframe to spacefill. In spacefill, atoms are displayed as standard van der Waals radii. Generally when these radii overlap significantly, a bond between the two atoms is present. Mercury will automatically connect bonding atoms, based on a predetermined set of maximum bonding distances. Notice that in these five examples, each carbon atom bonded to a metal is from a separate ligand.

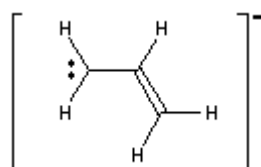
To change the display style:

Set the required style in the tool-bar Style box, located near the top of the main Mercury window. Alternatively, right-click in the display-area background, pick Styles from the pull-down menu, and select the required style (Wireframe, Capped sticks, Ball and stick, Spacefill, Ellipsoid).

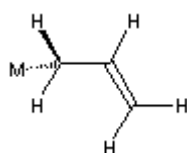
- Inspect the structure of *OKUSES* closely. Which atoms are in van der Waals contact with the magnesium ion? Notice that the allyl ligand bonds to the magnesium ion with only one carbon

atom.

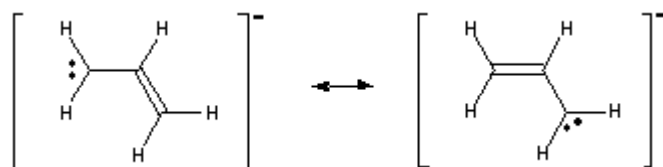
- Next, inspect the structure of *ALPHPD01* closely. Again, identify which atoms are in van der Waals contact with the palladium ion. Notice that the allyl ligand has all three carbon atoms sufficiently close to the palladium ion to consider them all to be bonding to the palladium ion.
- Clearly there is a difference in the way the allyl ligand is bonding to the different ions in the *OKUSES* and *ALPHPD01* complexes. The nature of the bonding is not important to this exercise. All examples in this exercise utilize structural data from molecules which have been synthesized, crystallized and characterized by single crystal X-ray crystallography.
- Now let's focus upon nomenclature. The number of contiguous ligand atoms bonding to a singular metal atom is defined as hapticity and is denoted using the Greek symbol η , eta, followed by a superscript indicating the number. The allyl ligand in *OKUSES* is attached to the metal by one carbon atom, so it is designated η^1 -allyl. The allyl ligand in *ALPHPD01* is attached to the metal by three contiguous carbon atoms, so it is designated η^3 -allyl.
- The allyl ligand may be described with the following Lewis structure.



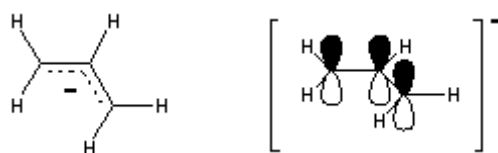
- When the allyl ligand bonds to a metal with only one of its carbon atoms, the bonding is η^1 -allyl:



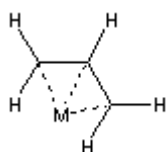
- The allyl anion may be represented by two resonance structures:



- The allyl anion has a delocalized pi system and may also be represented as follows:



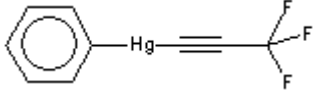
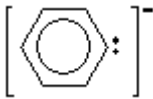
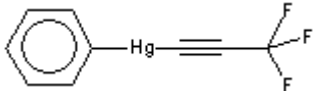
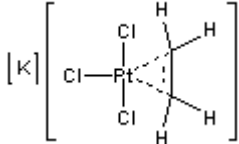
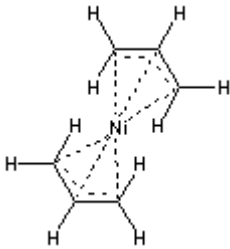
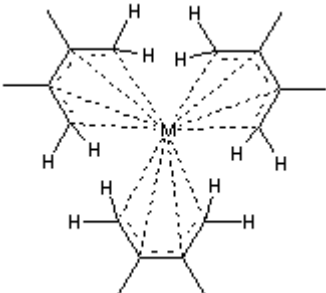
- A metal may interact with this delocalized pi system so as to have bonding interactions with all three allyl carbon atoms, that is the bonding is η^3 -allyl

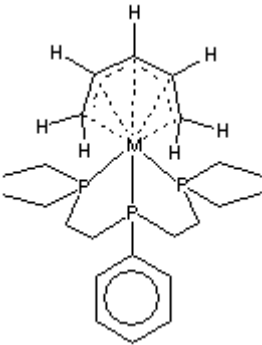


- Closely examine the orientation of the η^3 -allyl ligand with respect to the metal in structure *ALPHPD01*. Notice that the allyl carbon and hydrogen atoms are essentially coplanar; however, the metal does not reside in this plane.
- With refcode *ALPHPD01* selected in the *Structure Navigator*, click the **More Info** button followed by **Structure Information** from the resulting menu. Notice that the compound name is (η^3 -allyl)chlorotriphenylphosphinepalladium. The hapticity of the allyl ligand has been clearly denoted. While keeping the information window opened, select *OKUSES* in the *Structure Navigator*. Notice the compound name is cis-allylbromobis(dimethoxyethane)magnesium. In cases where the ligand binds η^1 to the metal, the η^1 binding mode is assumed and need not be noted. This is particularly true in cases where there is only one atom likely to bond to the metal. See for example the names for *VADRAU* and *IGODIR*.
- **WARNING:** Although formally the lack of a hapticity notation implies the ligand bonds η^1 , very often chemists neglect to indicate hapticity, even when it is other than η^1 . Such omission often occurs when a ligand is bonding with its most commonly observed hapticity. Be sure to consider the chemistry when assigning hapticity to ambiguously named compounds.

1.2 Acyclic ligands

- Examine the structures of the next 5 entries in the file (these include refcodes: *KCEYPT*, *DUMVEM*, *BIPJEP*, *LAXLAY*, *DIJHIN01*).
- Identify the hapticity of the organometallic ligands and complete the table below. For diagrams, provide standard organic stick diagrams (Note: *LAXLAY* has two different organometallic ligands).

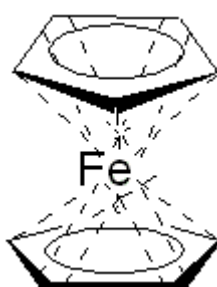
CSD Refcode	Compound	Uncoordinated Ligand	Hapticity	Name
LAXLAY			h^1 (eta-1)	(3,3,3-trifluoroethynyl phenylmercury(II))
LAXLAY				
KCEYPT				
BIPJEP				
DIJHIN01				

CSD Refcode	Compound	Uncoordinated Ligand	Hapticity	Name
DUMVEM				

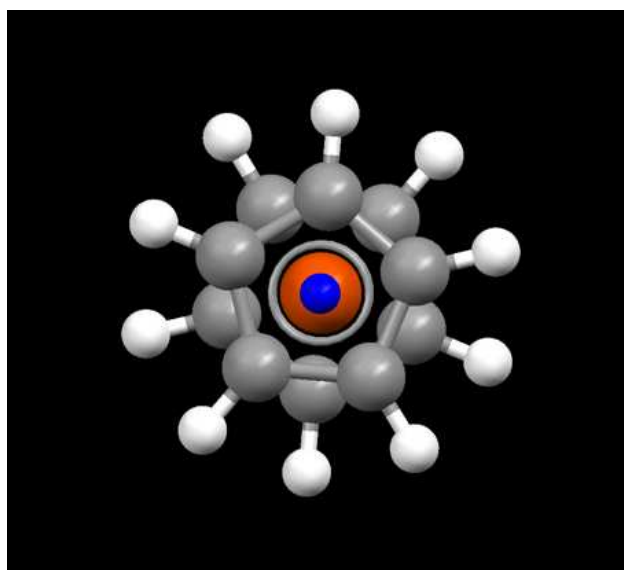
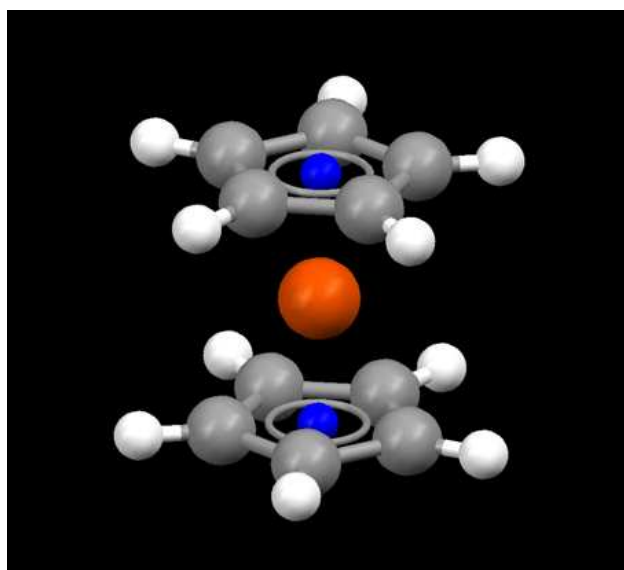
- Notice that metal bonding fragment of all of the organometallic ligands in the above table are acyclic ligands.

1.3 Cyclic ligands

- Examine the structure of Refcode entry *FEROCE27*.
- The metal bonding fragments of organometallic ligands are not restricted to being acyclic. In fact there are many (tens of thousands of examples in the Cambridge Structural Database alone†). The classic example is that of ferrocene which is comprised of two pentahapto cyclopentadienyl ligands bound to an iron(II) ion. That is, two $C_5H_5^-$ ligands are bonding h^5 to an iron ion, as depicted in the following diagram:



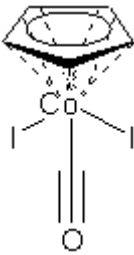
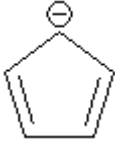
- Like some of the above acyclic organometallic ligands, the atoms of the $C_5H_5^-$ ligand are essentially planar. The ferrocene iron ion is situated between two parallel $C_5H_5^-$ ligands, halfway between the two rings and along the perpendicular connecting the ring centroids. These features are highlighted below, and are more clearly illustrated when you manipulate *FEROCE27* in Mercury.



Ferrocene (refcode FEROC27) ring centroids are shown in blue

- Ferrocene is properly named bis(h^5 -cyclopentadienyl)iron(II) and may be represented by the formula: $(h^5-C_5H_5)_2Fe$. The cyclopentadienyl fragment is often abbreviated Cp, i.e. $(h^5-Cp)_2Fe$. The h^5 coordination mode is so common for Cp that when hapticity is not noted, i.e. Cp_2Fe , the h^5 is assumed.‡
- Examine the structures of the next 6 entries in the file. (These include refcodes: *NOFPON*, *MULJIM*, *PEVHUT*, *FURROZ*, *ZOZLAB*, *TPCPCQ*.)
- Excluding any h^1 - ligands, identify the hapticity of the organometallic ligands and complete the table below. For diagrams, provide standard organic stick diagrams.

CSD Refcode	Compound	Uncoordinated Ligand	Hapticity	Name
			h^3 (eta-3)	
			h^4 (eta-4)	

CSD Refcode	Compound	Uncoordinated Ligand	Hapticity	Name
MULJIM			h^5 (eta-5)	carbonyl (h^5 -cyclopentadienyl) diiodocobalt (III)
			h^6 (eta-6)	
			h^7 (eta-7)	
			h^8 (eta-8)	

† Over 40,000 structures containing h^2 - or greater hapticity carbon atom rings ranging in size from three to eight carbon atoms were in the CSD (database version 5.28, 2007 release).

‡ Over 15,000 h^5 --Cp containing structures were in the CSD (database version 5.28, 2007 release).

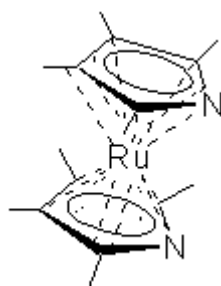
1.4 Variable hapticity

- Many organometallic ligands are capable of variable hapticity. Earlier we saw that the allyl ligand can bond either h^1 or h^3 to a metal. In cis-allylbromobis(dimethoxyethane)magnesium, sterics dictate that the allyl ligand bonds h^1 to the magnesium ion (see *OKUSES*). In contrast, there is sufficient space in h^3 -allylchloro(triphenylphosphine)palladium(II) for the allyl ligand to bond h^3 to the palladium ion (see *ALPHPD01*). It is even possible to isolate compounds where the same type of ligand bonds with variable hapticity to the same metal. A fine example is the compound (h^3 -allyl)bis(h^1 -allyl)(1,2-bis(diphenylphosphino)benzene)iridium(III) (see *WIZKEV*).
- The cyclopentadienyl ligand, $C_5H_5^-$, or Cp^- is also versatile in its bonding modes, examples include CSD refcodes *CACWOS*, *PEJGAM*, and *MULJIM*. For each of these structures identify

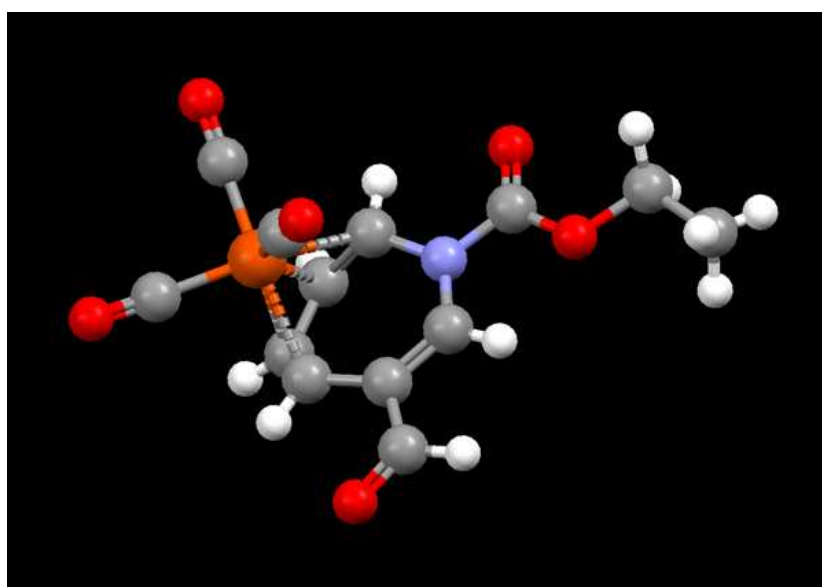
the mode of bonding of the Cp^- ligand.

1.5 Heteroatoms in rings

- Examine the structure of Refcode entry *EBEDUK*.
- To this point, all the examples illustrated have only used hapticity to describe metal to carbon bonding; however, the use of hapticity terminology may be used to describe the bonding of any organic moiety to a metal. For example, bis(h^5 -2,3,4,5-tetramethylpyrrolyl)ruthenium(II). That is, two $\text{C}_4\text{Me}_4\text{N}$ - ligands are bonding h^5 to a ruthenium ion, as depicted in the following diagram:



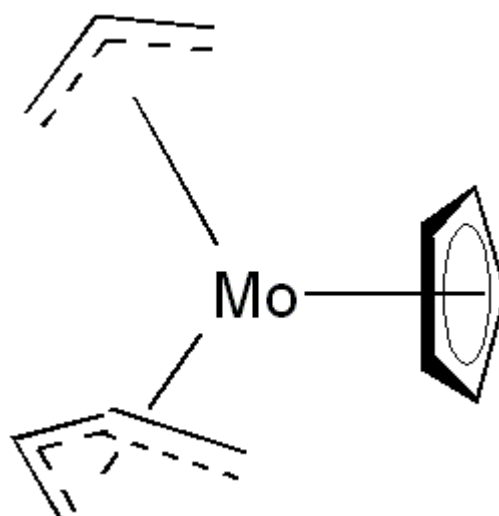
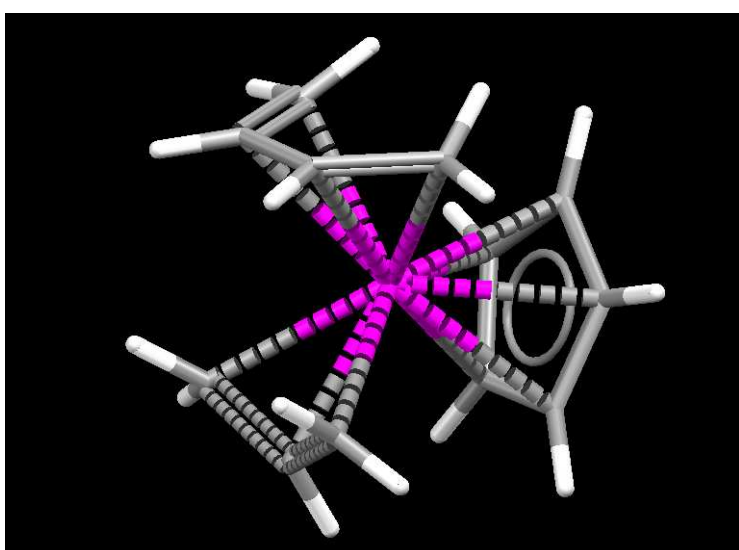
- In the case of $(\text{C}_4\text{Me}_4\text{N})_2\text{Ru}$, all ring carbon atoms AND the nitrogen heteroatoms are bonding to the metal, so the h^5 designation is appropriate. A heteroatom in a ring need not necessarily bond to the metal, in which case it would not be included in the hapticity count. For example, the compound $\text{C}_{13}\text{H}_{11}\text{FeNO}_6$ below has tetrahapto coordination to four carbon atoms; however, the nitrogen in the ring does not bond to the metal.



- A good name for the this compound is 4,5,6,7- η^4 -(3-formyl-N-ethoxycarbonylazepine)tricarbonyl iron(0). The "4,5,6,7" preceding the " η^4 " is necessary to explicitly distinguish between this compound and other isomers such as the 2,3,4,5- η^4 isomer. Sketch the 2,3,4,5- η^4 isomer.

SUMMARY OF KEY CONCEPTS

- Often a ligand with carbon donor atoms can exhibit multiple bonding modes. For example, we have seen that the cyclopentadienyl ligand can bond to *d*-metal atoms in three different ways. Thus we need additional nomenclature to describe these different modes of bonding.
- Use of the Greek prefix h (eta) accompanied by a superscript number (e.g. η^4) describes the number of atoms in a ligand that are considered formally to be bonded to the metal atom. This is the hapticity of the ligand.
- For example, (η^3 -Allyl)-(η^4 -butadiene)-(η^5 -cyclopentadienyl)-molybdenum(ii) (CSD refocde *RATQUY*), shown below.



- In 1968, F. A. Cotton proposed the hapticity nomenclature in a letter to the Journal of the American Chemical Society. (Cotton, F. A. *J. Am. Chem. Soc.* **1968**, 90(22), 6230-6232: <http://dx.doi.org/10.1021/ja01024a059>.) The notation he proposed remains the standard today.
- Cotton illustrates the notation using 16 examples. If you have full access to the Cambridge Structural Database (CSD) then, as an additional exercise, use ConQuest to find structure entries which match the 16 examples. Which of the 16 have CSD entries which exactly match the structures as depicted by Cotton? Which, if any have matching formulas, but are structurally different than depicted by Cotton? For those examples that lack exact formula matches, find the CSD entries which are most similar. In each case, give the name, according to Cotton's nomenclature, that correctly describes each molecule.