1 HAPTICITY

1.1 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.

1.2 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.

1.3 GETTING STARTED

- Open the interactive WebCSD teaching database by going to the following URL:

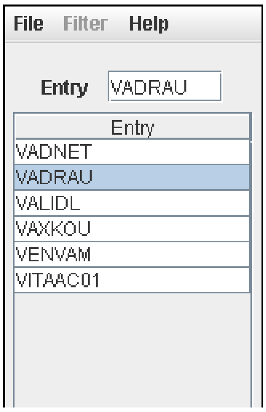
  http://webcsd.ccdc.cam.ac.uk/teaching_database_demo.php

- This demo version of WebCSD allows you to browse all 500 entries in the teaching subset of the Cambrdige Structrual Database.
- Reference codes (refcodes) of the structures in the teaching set will appear in a list on the left hand side of the WebCSD page. Only those refocde beginning with "A" are displayed intially. To show those refcodes starting with "B" click on the > button.
- To view a structure select the corresponding refcode in the list by left-clicking on it. Alternatively, you can type a refocde in the **Entry** box above the structure list.

1.4 STEPS REQUIRED

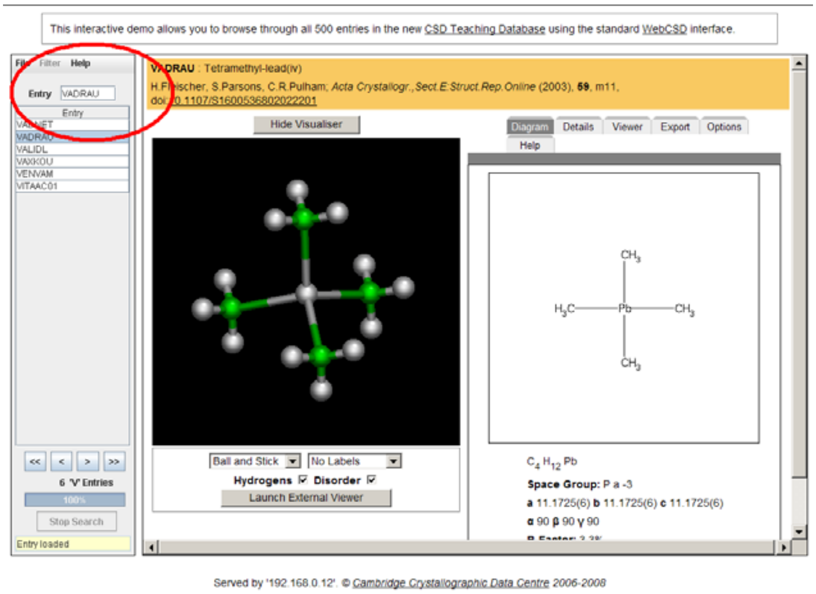
1.4.1 Investigating metal-carbon bonding

- Examine the following structures: structure reference codes (refcodes): *VADRAU*, *IGODIR*, *TODDUL*, and *OKUSES*. To display a structure type it's reference code (refcode) in the **Entry** box above the structure list on the left hand side of the WebCSD page:



Entry VADRAU

Entry
VADNET
VADRAU
VALIDL
VAXKOU
VENVAM
VITAAC01



This interactive demo allows you to browse through all 500 entries in the new CSD Teaching Database using the standard WebCSD interface.

Entry VADRAU

VADRAU : Tetramethyl-lead(iv)

H.Fleischer, S.Parsons, C.R.Pulham; *Acta Crystallogr.,Sect.E:Struct.Rep.Online* (2003), **59**, m11, doi:10.1107/S1600536802022201

Ball and Stick | No Labels

Hydrogens ☑ **Disorder** ☑

6 'V' Entries

100%

Entry loaded

$C_4H_{12}Pb$

Space Group: P a -3

a 11.1725(6) **b** 11.1725(6) **c** 11.1725(6)

α 90 **β** 90 **γ** 90

Served by '192.168.0.12'. © *Cambridge Crystallographic Data Centre 2006-2008*

- You will notice that each of these structures contains at least one metal-carbon bonding interaction. 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 the 3D viewer:

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 both the shift key and the left-hand mouse button pressed down.

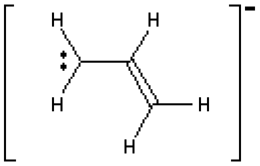
3. To translate structures move the cursor in the display area while keeping both the left-hand mouse button and the keyboard Ctrl key pressed down.

4. At any stage the display area can be returned to the default view by hitting the r button on the keyboard.

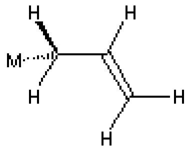
- Change the display style to spacefill using the drop down menu located under the 3D viewer. In spacefill, atoms are displayed as standard van der Waals radii. Generally when these radii overlap significantly, a bond between the two atoms is present. In the viewer bonding atoms are automatically connected, based on a predetermined set of maximum bonding distances. Notice that in these four examples, each carbon atom bonded to a metal is from a separate ligand.
- 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.

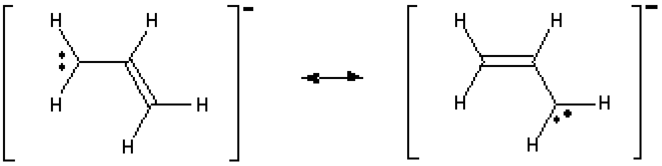
- Next, inspect the structure of *ALPHPD01* closely. Again, identify which atoms are in van der Waals contact with the palladium ion. Notice that the allyl ligand has all three carbon atoms sufficiently close to the palladium ion to consider them all to be bonding to the palladium ion.
- Clearly there 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.



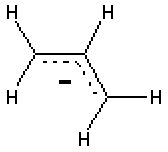
- When the allyl ligand bonds to a metal with only one of its carbon atoms, the bonding is η^1-allyl:

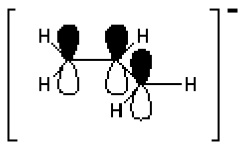


- The allyl anion may be represented by two resonance structures:

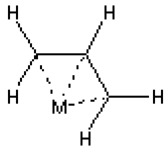


- The allyl anion has a delocalized pi system and may also be represented as follows:





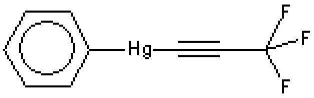
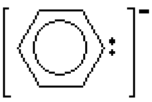
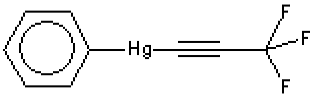
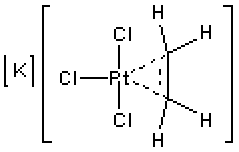
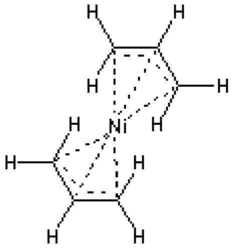
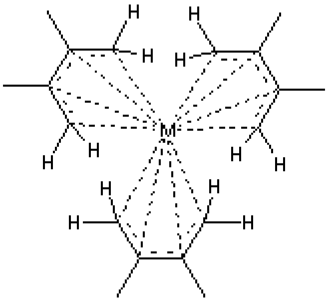
- A metal may interact with this delocatized pi system so as to have bonding interactions with all three allyl carbon atoms, that is the bonding is η^3-allyl

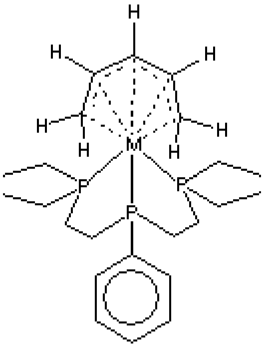


- Closely examine the orientation of the η^3-allyl ligand with respect to the metal in structure *ALPHPD01*. Notice that the allyl carbon and hydrogen atoms are essentially coplanar; however, the metal does not reside in this plane.
- Look at structure refcode *ALPHPD01*, click the **Details** tab to view further information about this structure. Notice that the compound name is (η^3-allyl)chlorotriphenylphosphinepalladium. The hapticity of the allyl ligand has been clearly denoted. Next, view structure refcode *OKUSES*. 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 compound 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.

1.4.2 Acyclic ligands

- Examine the structures of the following 5 refcodes: *KCEYPT*, *DUMVEM*, *BIPJEP*, *LAXLAY*, and *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).

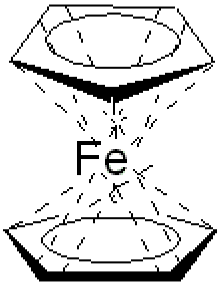
CSD Refcode	**Compound**	**Uncoordinated Ligand**	**Hapticity**	**Name**
LAXLAY			η^1 (eta-1)	(3,3,3-trifluoroethynyl phenylmercury(II)
LAXLAY				
KCEYPT				
BIPJEP				
DIJHIN01				

CSD Refcode	**Compound**	**Uncoordinated Ligand**	**Hapticity**	**Name**
DUMVEM				

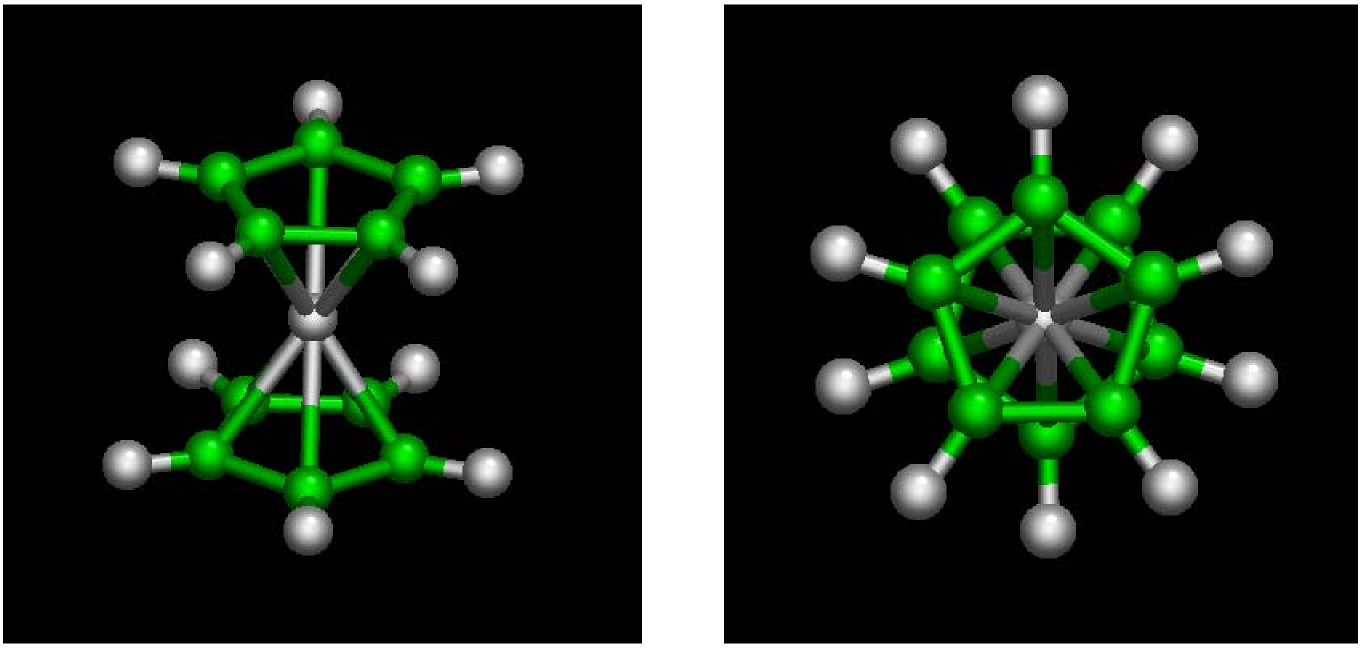
- Notice that metal bonding fragment of all of the organometallic ligands in the above table are acyclic ligands.

1.4.3 Cyclic ligands

- Examine the structure of refcode *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 $\eta^5$to an iron ion, as depicted in the following diagram:



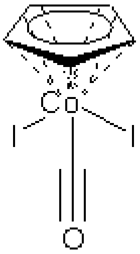
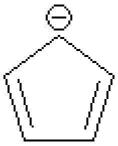
- Like some of the above acyclic organometallic ligands, the atoms of the $C_5H_5^-$ ligand are essentially planar. The ferrocene iron ion is situated between two parallel $C_5H_5^-$ ligands, halfway between the two rings and along the perpendicular connecting the ring centroids. These features are highlighted below, and are more clearly illustrated when you manipulate *FEROCE27* in the 3D viewer.



Ferrocene (refcode FEROCE27)

- Ferrocene is properly named bis(η^5-cyclopentadienyl)iron(II) and may be represented by the formula: (η^5-C_5H_5)$_2$Fe. The cyclopentadienyl fragment is often abbreviated Cp, i.e. (η^5-Cp)$_2$Fe. The η^5 coordination mode is so common for Cp that when hapticity is not noted, i.e. Cp$_2$Fe, the η^5 is assumed.‡
- Examine the structures of the following 6 refcodes: *NOFPON*, *MULJIM*, *PEVHUT*, *FURROZ*, *ZOZLAB*, and *TPCPCQ*.
- Excluding any η^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**
			η^3 (eta-3)	
			η^4 (eta-4)	

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

† Over 40,000 structures containing η^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 η^5*--Cp containing structures were in the CSD (database version 5.28, 2007 release).*

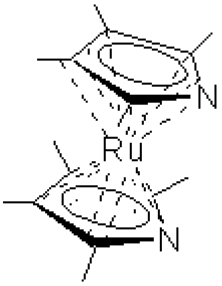
1.4.4 Variable hapticity

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

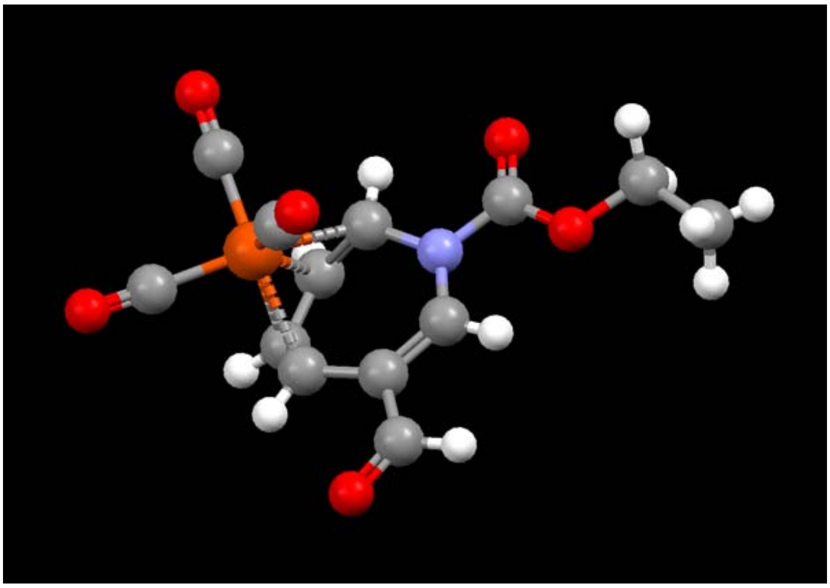
the mode of bonding of the Cp^- ligand.

1.4.5 Heteroatoms in rings

- Examine the structure of refcode *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(η^5-2,3,4,5-tetramethylpyrrolyl)ruthenium(II). That is, two C_4Me_4N- ligands are bonding η^5 to a ruthenium ion, as depicted in the following diagram:



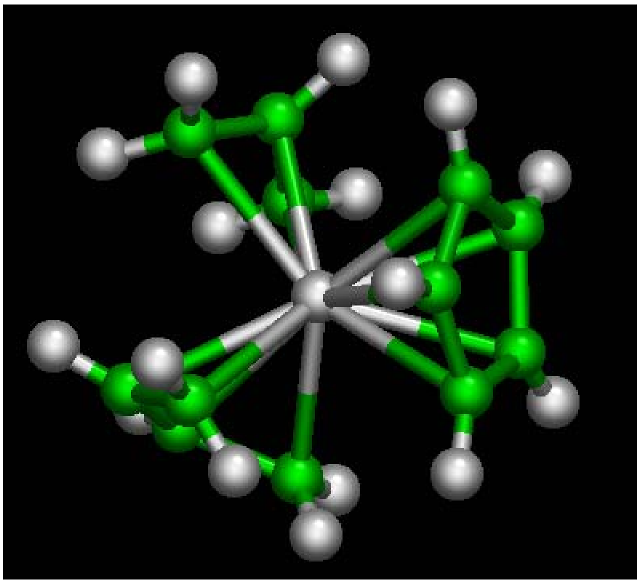
- In the case of $(C_4Me_4N)_2Ru$, all ring carbon atoms AND the nitrogen heteroatoms are bonding to the metal, so the η^5 designation is appropriate. A heteroatom in a ring need not necessarily bond to the metal, in which case it would not be included in the hapticity count. For example, the compound $C_{13}H_{11}FeNO_6$ below (available in the full Cambridge Structural database) has tetrahapto coordination to four carbon atoms; however, the nitrogen in the ring does not bond to the metal.

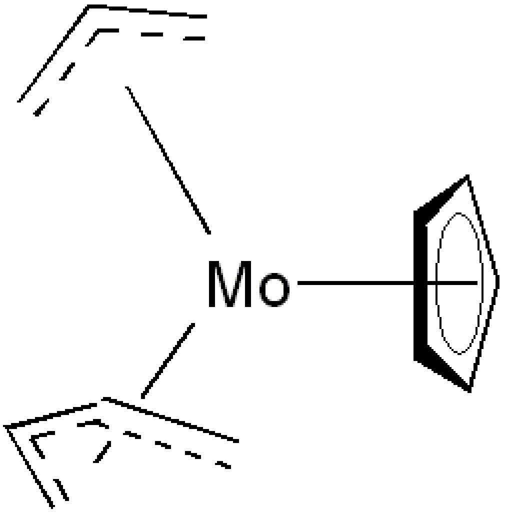


- A good name for the this compound is 4,5,6,7-η^4-(3-formyl-N-ethoxycarbonylazepine)tricarbonyl iron(0). The "4,5,6,7"preceding the "η^4" is necessary to explicitly distinguish between this compound and other isomers such as the 2,3,4,5-η^4 isomer. Sketch the 2,3,4,5-η^4 isomer.

1.5 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 η (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) (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 access to the full Cambridge Structural Database System then, as an additional exercise, use WebCSD, or 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.