Hapticity

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1 Introduction

Organometallic compounds are traditionally defined as those complexes which contain a metal-carbon bond. However, as the field is rapidly expanding, the term is now loosely applied also to those compounds containing metals and organic fragments. Such compounds are more properly called metal-organics. In the Cambridge Structural Database (CSD), compounds are broadly classed as organic or metal-organic. The definitions are adapted slightly for practical purposes, so that metal-organic compounds must have a transition metal, lanthanoid or actinoid, or Al, Ga, Tl, Ge, Sn, Pb, Sb, Bi or Po.[1] There are over 190,000 true organometallic structures in the CSD and over 725,000 classified as metal-organic according to the CSD definition. Such large numbers of structures provides us with a wealth of information on the coordination geometry and other aspects of metal-ligand bonding in organometallic and related compounds.

In this module, we will explore the concept of hapticity using examples from the CSD. Hapticity is the term used in coordination chemistry to describe the number of atoms in an organic ligand which is directly bonded to a central metal atom. IUPAC guidelines indicate its occurrence by the Greek letter η (*eta*) followed by a superscript representing the number of bonded atoms. For example, η^2 means the ligand is bonded to the metal through two contiguous atoms.

1.1 Learning outcomes

At the end of this module, you will:

- understand the concept of hapticity as applied to acyclic and cyclic ligands
- know the nomenclature of hapticity
- have an appreciation of the structural perturbations of ligands as a function of their hapticity.

1.2 Materials

The structures needed to complete this module are available from the online Web service Access Structures.

https://www.ccdc.cam.ac.uk/structures/

This provides you with all the features required to complete this teaching module. Alternatively, you may prefer to use the structure visualization program Mercury, which you can download for free. Instructions for obtaining this software and links to resources to support you using it are given at the end of this document. This teaching module uses entries in the Teaching Subset; you can find out more about the Teaching Subset here: https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/.

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[1] Alkali/alkaline earth metals are excluded due to their common occurrence as counterions in organic salts. Nonetheless, it is worth remembering that true organometallic compounds of alkali/alkaline earth metals do exist.

1.3 Pre-required skills

No prior experience of crystallography is necessary; however, knowledge of coordination chemistry is required, including an understanding of coordination geometry, the orbital description of metal-ligand bonding and basic familiarity with electron counting rules.

2 Introduction to hapticity

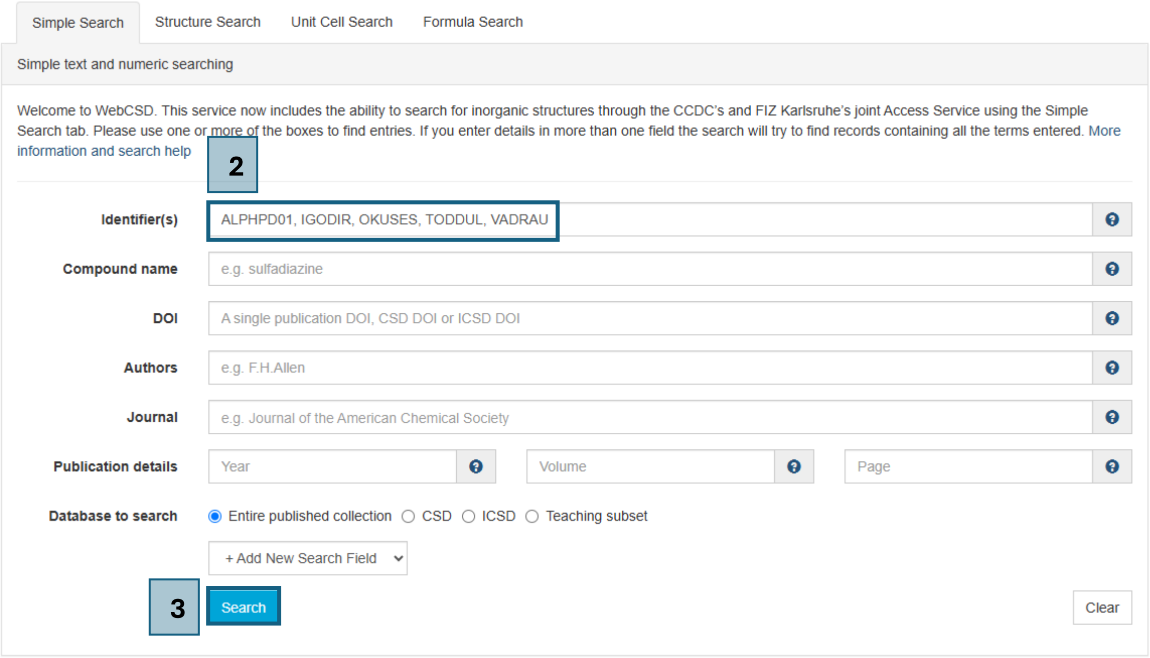
Ligands can bond to transition metals in several ways, including as terminal, bidentate/multidentate and bridging ligands. However, another category exists where a ligand bonds to a metal through contiguous atoms. Such a situation can arise where ligands are bonded in a side-on fashion; the exact nature of this bonding depends on the orbitals involved but often involves the π system of the ligand. To describe the coordination of such ligands, Cotton proposed in 1968 the *hapto* nomenclature, where the number of contiguous atoms of the ligand coordinated to the metal is referred to as the ligand's hapticity.[2] Though originally discussed in terms of π-coordinating ligands, the hapticity does not in itself specify whether σ or π electrons are used in bonding. Hapticity is indicated by the symbol η (eta) with a numerical superscript for the corresponding number of atoms; it's precise use is described by IUPAC.[3] We shall see how this nomenclature is applied with examples from the CSD.

2.1 Investigating metal-carbon bonding

1. In a Web browser, navigate to Access Structures at https://www.ccdc.cam.ac.uk/structures/

2. In the *Identifier(s)* field, type "ALPHPD01, IGODIR, OKUSES, TODDUL, VADRAU" (the commas are optional).

3. Press **Search**



Welcome to WebCSD. This service now includes the ability to search for inorganic structures through the CCDC's and FIZ Karlsruhe's joint Access Service using the Simple Search tab. Please use one or more of the boxes to find entries. If you enter details in more than one field the search will try to find records containing all the terms entered. More information and search help

Identifier(s) ALPHPD01, IGODIR, OKUSES, TODDUL, VADRAU

Database to search ● Entire published collection ○ CSD ○ ICSD ○ Teaching subset

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[2] F. A. Cotton, *J. Am. Chem. Soc.*, 1968, **90**, 6230–6232, DOI: 10.1021/ja01024a059.

[3] See, for example IUPAC, *Pure Appl. Chem.*, 2015, **87**, 1039–1049 DOI: 10.1515/pac-2014-0718

4. From the results page, make sure that all entries are selected (you may need to click **Select all** if they are not) and click **View Selected**.

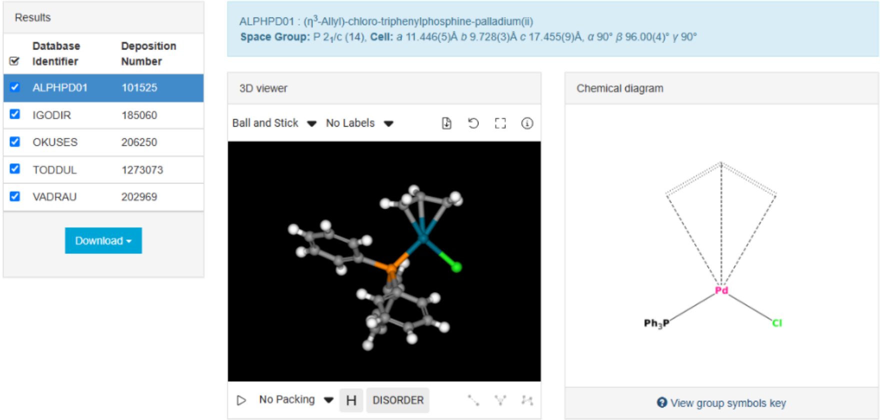
☑ ALPHPD01

Deposition Number(s): 101525
Teaching Structure
Space Group: P 2_1/c (14)
Cell: *a* 11.446(5)Å *b* 9.728(3)Å *c* 17.455(9)Å, *α* 90° *β* 96.00(4)° *γ* 90°

☑ IGODIR

Deposition Number(s): 185060
Teaching Structure
Space Group: P 2_1/n (14)

5. The results will be displayed in the detailed results page as a list of refcodes (a *refcode* is a 6–8-character CSD database identifier) on the left-hand side. You can move between results by clicking on the desired refcode. The structure is shown as a 2D chemical diagram in the right-hand side and in the 3D viewer.



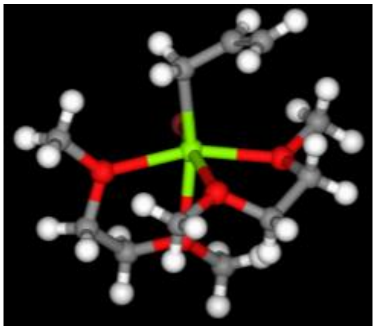
Results

☑ Database Identifier	Deposition Number
☑ ALPHPD01	101525
☑ IGODIR	185060
☑ OKUSES	206250
☑ TODDUL	1273073
☑ VADRAU	202969

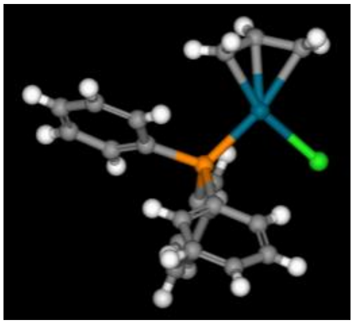
ALPHPD01 : (η^3-Allyl)-chloro-triphenylphosphine-palladium(ii)
Space Group: P 2_1/c (14), **Cell:** *a* 11.446(5)Å *b* 9.728(3)Å *c* 17.455(9)Å, *α* 90° *β* 96.00(4)° *γ* 90°

6. To manipulate the structure:
   - Left click and drag to rotate the structure.
   - Right click and drag to translate the structure.
   - Scroll up/down with the mouse wheel to zoom in/out.
   - At any time, hit ⟲ to reset the viewer.

We can now explore the nature of the metal-ligand bonding. Starting with OKUSES, notice how the allyl ligand bonds through only one carbon atom, despite their being three potential points of coordination. In contrast, looking at ALPHPD01, you will see that all three carbon atoms of the allyl ligand are bonded to the palladium centre.



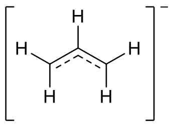
OKUSES



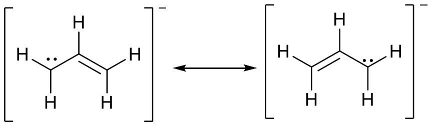
ALPHPD01

The allyl ligand is bonded in two different ways in these complexes, which we can distinguish by referring to their hapticity using the η (*hapto*) convention. In OKUSES, only a single atom of the allyl ligand is bonded to the metal, it therefore does not require a η prefix and we can simply refer to it as 'allyl'. On the other hand, in ALPHPD01, the allyl ligand bonds through the three contiguous atoms of its π system, therefore it should be labelled η^3-allyl and it can be described as *trihapto*. The full chemical names of ALPHPD01 and OKUSES are (η^3-allyl)chlorotriphenylphosphinepalladium and *cis*-allylbromobis(dimethoxyethane)magnesium, respectively.

To understand the difference in coordination modes, it is useful to consider the bonding in the allyl anion. If the anion is taken in isolation, we would consider all carbon atoms sp^2 hybridised and hence it to have a fully delocalised π system across all three carbons as in (a) below. This is an appropriate model for the symmetrically bonded η^3-ally ligand too, as in ALPHPD01. Alternatively, we can draw resonance structures as shown below in (b). Either of these extremes places a lone pair on the carbon adjacent to the double bond. You should notice that this actually *appears* to be a more appropriate model for the allyl ligand in OKUSES: the carbon bearing the lone pair is bonded directly to the metal centre, whilst the alkene does not.



(a)

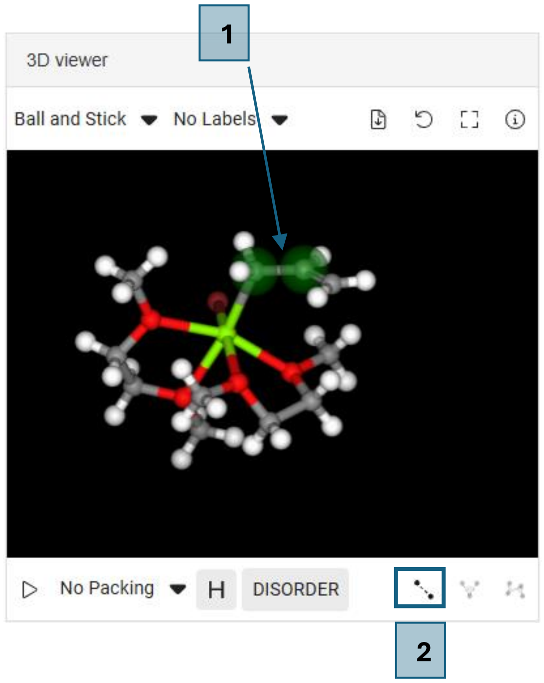


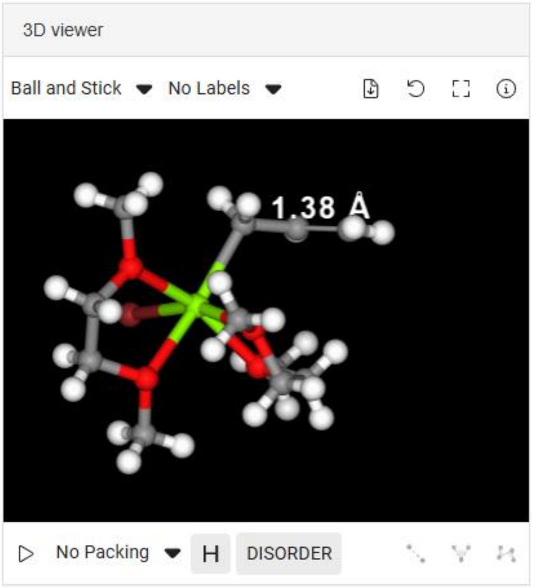
(b)

Exercise 1

Measure the C–C bond lengths in the allyl ligands of OKUSES and ALPHPD01 using the measurement tools in the 3D viewer, as follows:

1. Click on two consecutive atoms in the 3D viewer – they will be highlighted in green.
2. Click in the ⋱ symbol to measure the distance.





3. Repeat the measurements for the remaining allylic C–C bond in OKUSES, and for the allylic bonds in ALPHPD01. Record your measurement in a table.

CSD Refcode	1st C–C bond length / Å	2nd C–C bond length / Å
OKUSES		
ALPHPD01		

A typical C(sp^3) –C(sp^2) single bond length is 1.47 Å, whereas a typical C=C bond length is 1.34 Å. What do the measurements from the CSD structures tell you about the bonding in the allyl group in these complexes?

You should find that the allylic C–C bond lengths in OKUSES are quite similar, in contrast to ALPHPD01. However, in both cases, the C–C bond lengths are less than a typical single bond. This indicates a significant degree of π delocalisation in OKUSES, despite the geometry appearing to suggest σ bonding through a lone pair on one carbon atom. It's important to think about the context when interpreting hapticity. Mg^{2+} behaves very differently to Pd^{2+} because Pd^{2+} makes extensive use of its *d* orbitals in bonding, leading to greater covalency and stronger perturbation of the bonding within the allyl anion. On the other hand, Mg^{2+} is a much smaller cation, so steric crowding will be an important influence upon the hapticity.

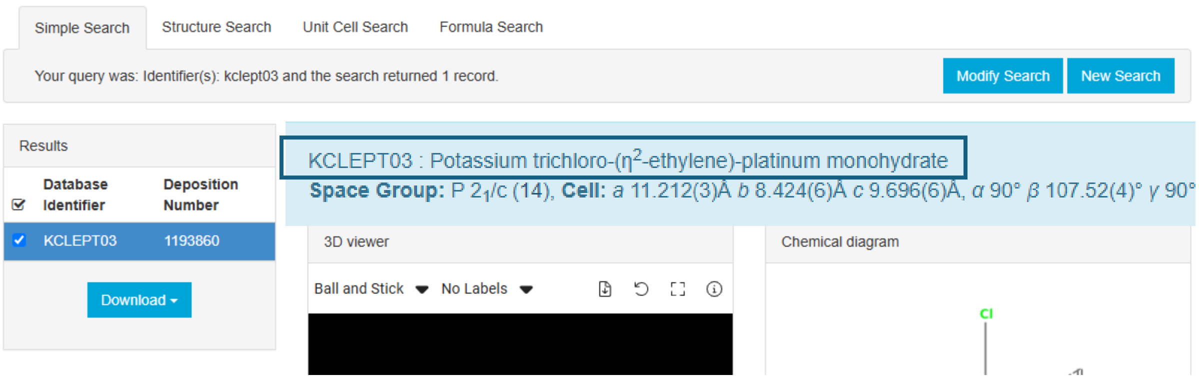
2.2 Acyclic and cyclic π-coordinating ligands

It is useful to consider acyclic and cyclic ligands separately as the latter includes (though is not limited to) aromatic ligands. We will start by looking at a selection of acyclic π-coordinating ligands found in complexes in the CSD.

2.2.1 Acyclic ligands

Exercise 2

Complete the table below by identifying the relevant π-bonded ligand and determine its hapticity from the 3D structure in Access Structures. Also find the chemical name from the top of the results page as shown below.

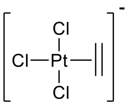
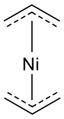
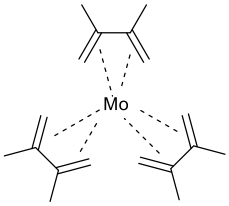
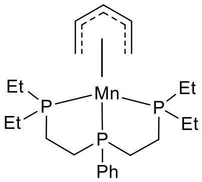


Your query was: Identifier(s): kclept03 and the search returned 1 record.

☑	Database Identifier	Deposition Number
☑	KCLEPT03	1193860

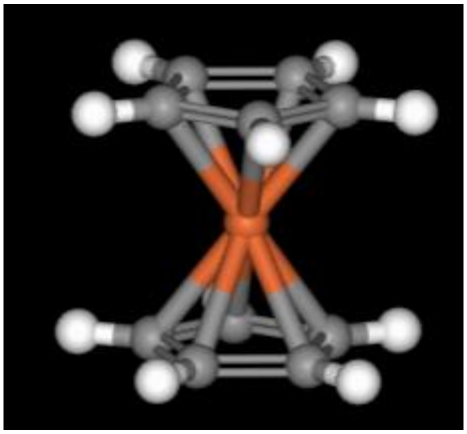
KCLEPT03 : Potassium trichloro-(η^2-ethylene)-platinum monohydrate

Space Group: P 2_1/c (14), **Cell:** *a* 11.212(3)Å *b* 8.424(6)Å *c* 9.696(6)Å, *α* 90° *β* 107.52(4)° *γ* 90°

CSD Refcode	**Complex**	**Uncoordinated ligand**	**Hapticity**	**Name**
KCLEPT03			η^2	Potassium trichloro-(η^2-ethylene)-platinum monohydrate
BIPJEP				
DIJHIN01				
DUMVEM				

2.2.2 Cyclic ligands

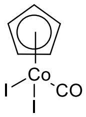
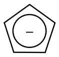
We will begin by examining a ubiquitous compound in organometallic chemistry: ferrocene. You can find ferrocene in Access Structures using refcode FEROCE78. You will see that it is composed of two *pentahapto*-cyclopentadienyl ligands coordinated to an iron(II) centre. The cyclopentadienyl ligand, $C_5H_5^-$, usually abbreviated as Cp^-, is exceptionally common, occurring in over 69000 transition metal compounds in the CSD. In ferrocene, the Cp ligand is planar and aromatic; this is overwhelmingly the case in complexes of Cp.



Ferrocene, CSD refcode FEROCE78.

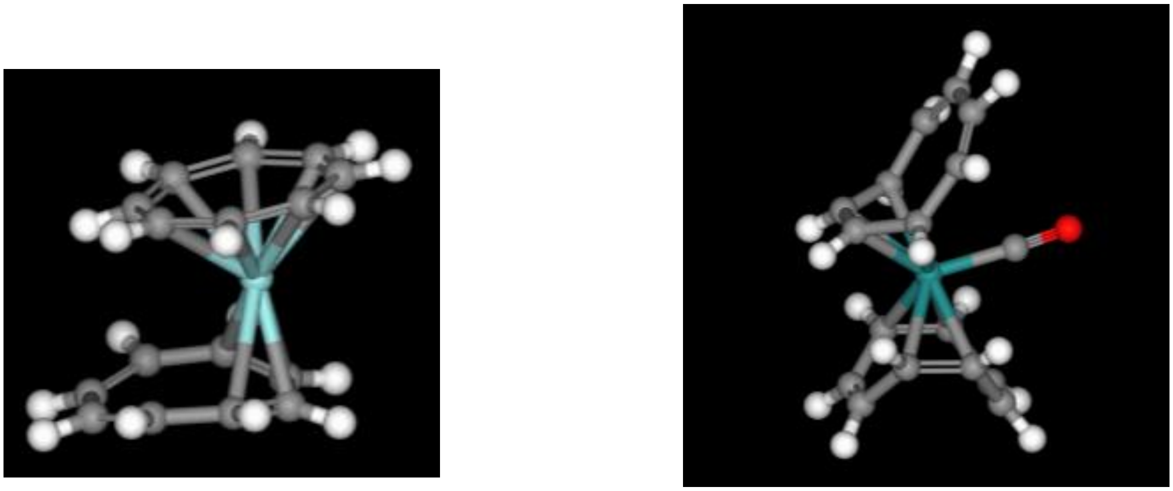
Exercise 3

In Access Structures examine the following structures: NOFPON, MULJIM, PEVHUT, FURROZ, ZOZLAB, and TPCPCQ. Based on the hapticity of the π-bonded ligands you observe, complete the table below. The fields have been filled in for MULJIM by way of example.

CSD Refcode	Complex	Uncoordinated ligand	Hapticity	Name
			η^3	
			η^4	
MULJIM			η^5	(η^5-cyclopentadienyl)-carbonyl-bis(iodo)-cobalt(iii)
			η^6	
			η^7	
			η^8	

You might notice that all the ligands in the complexes in table are drawn as aromatic. It is in general true that such ligands are aromatic when bound to a transition metal, even when the isolated (insofar as possible) ligand is not. This is pointedly the case with cyclobutadiene in tricarbonyl-(η^4-cyclobutenyl)-iron(0). Cyclobutadiene is not aromatic in its free state (and indeed is highly unstable in the absence of stabilising metal coordination). This is similarly the case for cyclooctatetraene; unlike cyclobutadiene, cyclooctatetraene is non-planar (look up refcode ZZZSAE01 in Access Structures to see its conformation) but becomes planar upon η^8 coordination to a metal, as you have seen in neptunocene (CSD refcode ZOZLAB)

Ligands such as cycloocatetraene (COT) need not necessarily use all unsaturated bonds in bonding to a metal centre. This is illustrated overleaf in CSD entry TALSEE, where you can see both η^4 and η^8 - coordination of COT and NEHLER – where each COT uses two double bonds – one COT is bound η^4, whereas the other is η^2, η^2.



Left: CSD entry TALSEE, showing one η^8-ring (top) and one η^4-ring (bottom). Right: CSD entry NEHLER, where separate alkene bonds in the lower ring coordinate η^2, compared with two adjacent alkene bonds in the top ring (η^4 coordination mode).

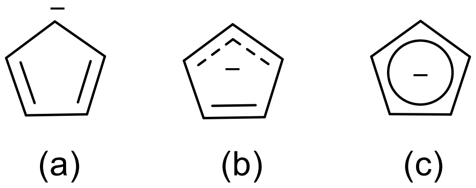
2.3 Conclusions

We have seen that ligands with conjugated π systems may sometimes bond through more than one atom to a metal centre and that when these atoms are contiguous, the ligand is said to have a certain hapticity, determined by the number of contiguous atoms of the ligand involved and indicated by an ‘η’ (eta) prefix. We have also seen that steric factors, as well as electronic ones can influence the hapticity shown by a particular ligand.

Cyclic unsaturated rings are exceptionally common organometallic ligands; there are over 85000 transition metal structures in the CSD with ligands bearing at least one η^2-coordinating unsaturated bond contained with 3-8 membered carbocyclic rings. The aromatic, 5-membered cyclic ligand cyclopentadienyl has a special place in organometallic chemistry, being one of the most common ligands and known for forming an extensive range of metallocene ‘sandwich’ complexes. It also has the ability to vary its hapticity which we will investigate this ligand further in the next section.

3 Variable hapticity

Many organometallic ligands are capable of variable hapticity. This can occur not only in 'static' solid state structures, where different hapticity of the same ligand can be observed in different crystal structures but also for a single complex during a reaction, when a change in hapticity can alter the electronic properties of the complex in such a way that it facilitates a reaction. For Cp, three hapticities are seen: η^1, η^3, and η^5. These can be understood by looking at (a)-(c) below; Cp may bond solely through a single carbon atom[4] bearing a lone pair, as in (a), through an allylic portion of the Cp ring, as in (b), or by using all carbon atoms in the ring, as in (c). Below are several exercises which demonstrate the variety of the Cp hapticities.



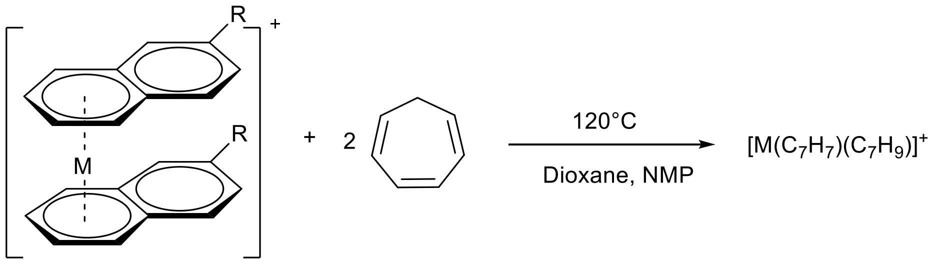
(a) (b) (c)

Exercise 4

Examine CSD entries CPICCP01 and SEHGUH. Determine the hapticity of each Cp (or Cp*, where Cp* = C_5Me_5) ligand in each structure. Are the features consistent with the different forms of Cp in (a)-(c) above?

Exercise 5

The reaction of certain technetium and rhenium sandwich complexes with cycloheptatriene (C_7H_8) leads to new complexes with formula $[M(C_7H_7)(C_7H_9)]^+$, where M is Tc or Re (see scheme below).[5]



M = Tc, R = Me; M = Re, R = H

Assuming that the number of electrons donated to the metal remains the same after the reaction, what hapticities would you predict for the new ligands? What would their formal charges be? Confirm your answer by looking at the technetium complex in CSD entry ZOJBEJ.

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[4] Technically, the η^1 notation should not be used here because the ligand is not bonded through contiguous atoms. Instead, κ (kappa) notation should be used, i.e. cyclopenta-2,4-dien-1-yl-κ*C*^{1}. 'η^1' is still often used informally, however.

[5] F. Battistin, R. Bollinger, M. L. Besmer, T. Fox, O. Blacque, H. Braband and R. Alberto, Inorg. Chem., 2024, **63**, 2701-2708 DOI: 10.1021/acs.inorgchem.3c04052.

The rhenium complex, $[Re(C_7H_7)(C_7H_9)]^+$ but not the technetium analogue, undergoes light-driven reactions with ligands such as nitriles, accompanied by a change in hapticity (known as 'ring slippage') as shown in the equation below.

$$[Re(C_7H_7)(C_7H_9)]^+ + 2\ MeCN \xrightarrow{\lambda = 629\ nm} [Re(C_7H_7)(C_7H_9)(NCMe)_2]^+$$

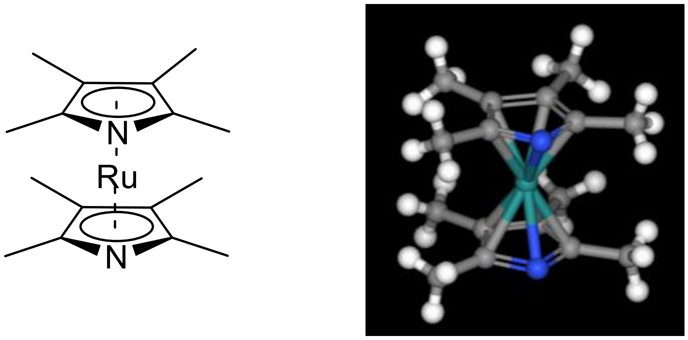
Assuming that the electron count of the product complex is the same as the starting complex, what hapticity do you expect for the tropylium cation (tropylium = $C_7H_7^+$)? Confirm you answer by examining CSD entry ZOHZOP.

3.1 Conclusions

In this section, we have seen that whilst ligands tend to have a preferred hapticity (e.g. *pentahapto* in the case of Cp) this is not always expressed because of steric crowding (think back to OKUSES in Exercise 1) or electronic effects. The latter is principally because organometallic complexes tend to obey the 18-electron rule[6] and a ligand may be forced to adopt an unusual hapticity to provide the right number of electrons to satisfy this. We have seen this in the context of a ligand association reaction of a cycloheptatrienyl complex.

4 Heterocyclic ligands

Up to this point, all the examples illustrated have used hapticity to describe metal to carbon bonding only; 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 and as seen in CSD entry EBEDUK.



Left: chemical diagram of bis(η^5-2,3,4,5-tetramethylpyrrolyl)-ruthenium(II). Right: CSD entry EBEDUK.

In the case of CSD entry EBEDUK above, all of the atoms in the ring, including the nitrogen atom, bond to the metal centre (hence the designation *pentahapto*) however this is not always so. For example, in CSD entry FECZFE, only certain carbon atoms of the azepine ring coordinate. A suitable

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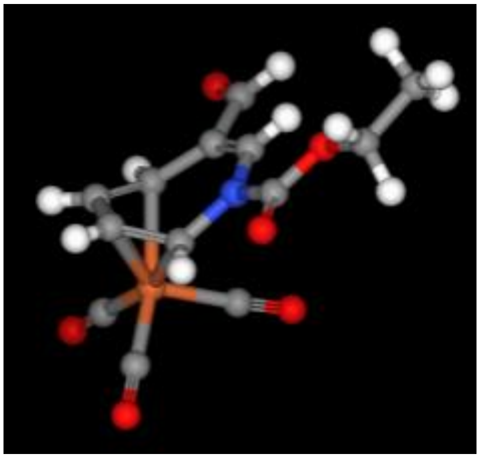
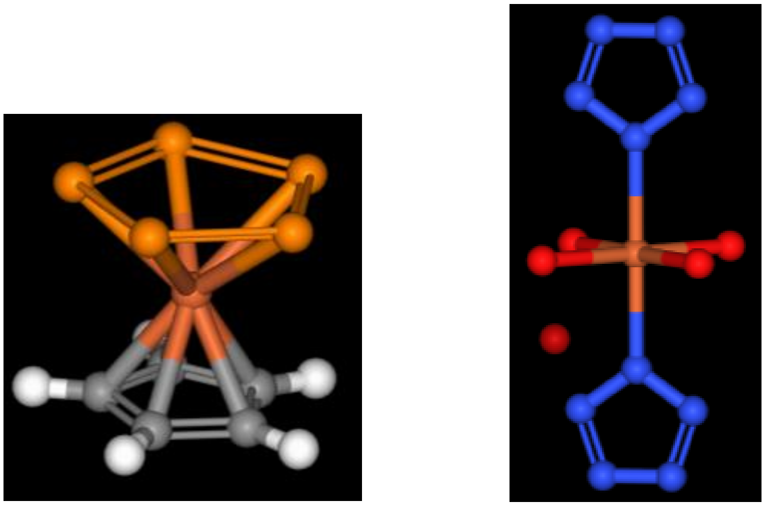
[6] Complexes which have 16 electrons with d^8 configurations and square planar geometry are exceptions to the rule.

name for 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.



CSD entry FECZFE showing only four carbon atoms of the azepine ring coordinate to iron.

π ligands do not necessarily need to have any carbon atoms to form complexes with metals. A simple but extremely important example is dioxygen, which can form η^2-O_2 complexes, such as seen in CSD entry QENYIS. Other, more exotic ligands such as cyclopentaphospholide ‘*cyclo*-P_5’ are known. Despite having no carbon atoms, *cyclo*-P_5 forms ferrocene like compounds, as might be expected based on the isolobal relationship between P and C–H – you can see this in CSD entry EMONAY. *Cyclo*-P_5 can also coordinate though its σ lone pairs in structures such as INEWUW. In contrast, isoelectronic pentazolate (N_5^-) only forms η^1 (κ*N* using kappa notation) complexes, as in CSD entry QECSAV.



Left: CSD entry EMONAY which contains the aromatic *cyclo*-P_5 ligand, coordinating in a π fashion. Right: CSD entry QECSAV, which forms a σ-complex with iron(II).

4.1 Conclusions

Although the majority of examples you will meet involve coordination of carbon-based π-systems, polyhapticity is not restricted to only them. In cases where a heteroatom is present and it possesses one or more σ-based lone pairs, coordination through these points will generally be preferred over π coordination. Sterically blocking these points of coordination, as in CSD entry EBEDUK can favour π coordination instead. For more complicated or unusual ligands, a more detailed understanding of electronic structure might be needed to make predications. Lastly, we have seen that whilst carbon-based systems dominate, hapticity is a general concept that may be easily extended to the interpretation of heteroatomic or completely inorganic ligands.

5 Summary

In this teaching module we have seen that π organometallic ligands can exhibit different modes of coordination to a metal centre. When the coordinating atoms are in a contiguous sequence, the η (eta) nomenclature is used to describe the ligand's hapticity. This allows for the possibility that not all atoms of a ligand with the potential to coordinate will do so. Indeed, we have seen that this is a fairly common occurrence, and variable hapticity is recognised as key to the reactivity of some organometallic species. Furthermore, whilst originally discussed in the context polyolefin complexes, the concept of hapticity is widely applicable and readily extended to ligands of various chemical classes. Lastly, we have gained an appreciation that the CSD, which contains an extremely large number of organometallic structures, provides unique insights into the typical hapticities of various ligands.

5.1 Next steps

If you would like to study the structures presented in this teaching sheet further, we suggest viewing them in Mercury, where you can customize the view of the molecules and make more advanced measurements. A free-for academic use version of Mercury is available for educational use. To learn more about Mercury, we recommend trying the online module "Visualization 101 – Visualizing Structural Chemistry Data with Mercury". You can find the structures used in this module in the Teaching Subset, which is pre-loaded into Mercury. See the links below for more information.

https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/
https://www.ccdc.cam.ac.uk/community/training-and-learning/csdu-modules/visualization-101/
https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/

If you wish to explore the CSD further and search for structures of interest to you, you can find a number of training resources, including self-guided workshops, online courses and videos to you get started from the CCDC's Training and Learning Web pages.

https://www.ccdc.cam.ac.uk/community/training-and-learning/

5.2 Acknowledgements

We would like to thank Professor Alice Brink (University of the Free State, South Africa) for providing helpful feedback on this teaching module.

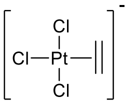
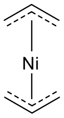
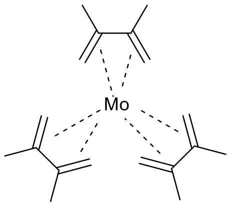
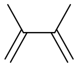
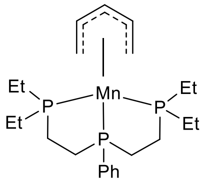
6 Answers to exercises

Exercise 1

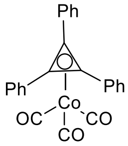
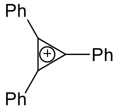
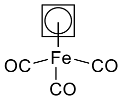
CSD Refcode	1st C–C bond length / Å	2nd C–C bond length / Å
OKUSES	1.38	1.35
ALPHPD01	1.40	1.33

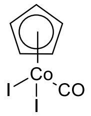
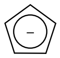
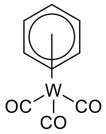
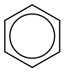
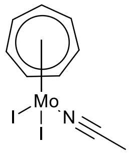
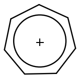
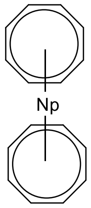
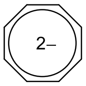
See main text for discussion.

Exercise 2

CSD Refcode	Complex	Uncoordinated ligand	Hapticity	Name
KCLEPT03			η^2	Potassium trichloro-(η^2-ethylene)-platinum monohydrate
BIPJEP			η^3	bis(η^3-Allyl)-nickel
DIJHIN01			η^4	tris(η^4-Dimethyl-1,3-butadiene)-molybdenum(0)
DUMVEM			η^5	bis((2-Diethylphosphino)ethyl)-phenylphosphine-(η^5-pentadienyl)-manganese

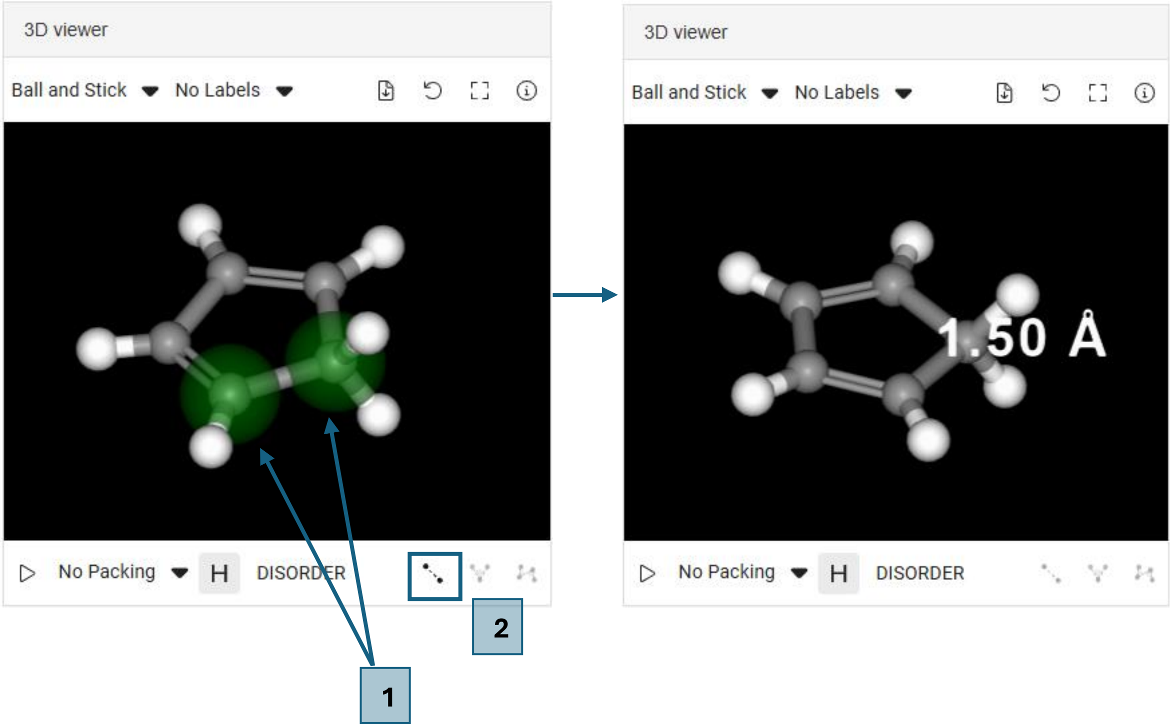
Exercise 3

CSD Refcode	Complex	Uncoordinated ligand	Hapticity	Name
TPCPCQ			η^3	(η^3-Triphenyl-cyclopropenyl)-tricarbonyl-cobalt
FURROZ			η^4	Tricarbonyl-(η^4-cyclobutenyl)-iron(0)

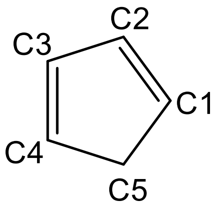
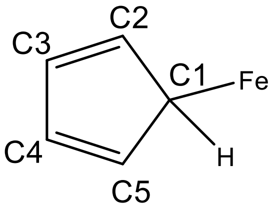
MULJIM			η⁵	(η⁵-cyclopentadienyl)-carbonyl-bis(iodo)-cobalt(iii)
NOFPON			η⁶	(η⁶-Benzene)-tricarbonyl-tungsten
PEVHUT			η⁷	(η⁷-Cycloheptatrienyl)-di-iodo-acetonitrilo-molybdenum
ZOZLAB			η⁸	bis(η⁸-Cyclo-octatetraenyl)-neptunium(iv)

Exercise 4

The two Cp rings in CPICCP01 have different hapticities – one ring is η⁵, like in ferrocene, whilst the other is η¹-coordinated (or more correctly κC coordinated). In SEHGUH there is also one η⁵-Cp ring, however the remaining one is η³. It is interesting to compare the η¹-coordinated Cp ring in CPICCP01 with cyclopentadiene itself, which has CSD refcode CPENAD01. You can measure the bond lengths in Access Structures as shown below.

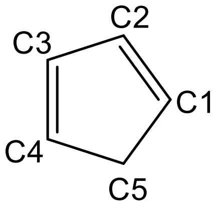
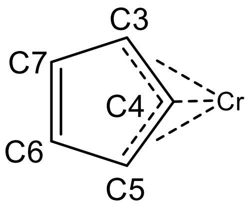


Left click atoms to select.

CSD Refcode	**Component**	**Bond length (Å)**	
CPENAD01	Cyclopentadiene 	C1–C2	1.34
		C2–C3	1.46
		C3–C4	1.34
		C4–C5	1.50
		C5–C1	1.50
CPICCP01	η^1-Cyclopentadienyl 	C2–C3	1.34
		C3–C4	1.45
		C4–C5	1.35
		C5–C1	1.47
		C1–C2	1.47

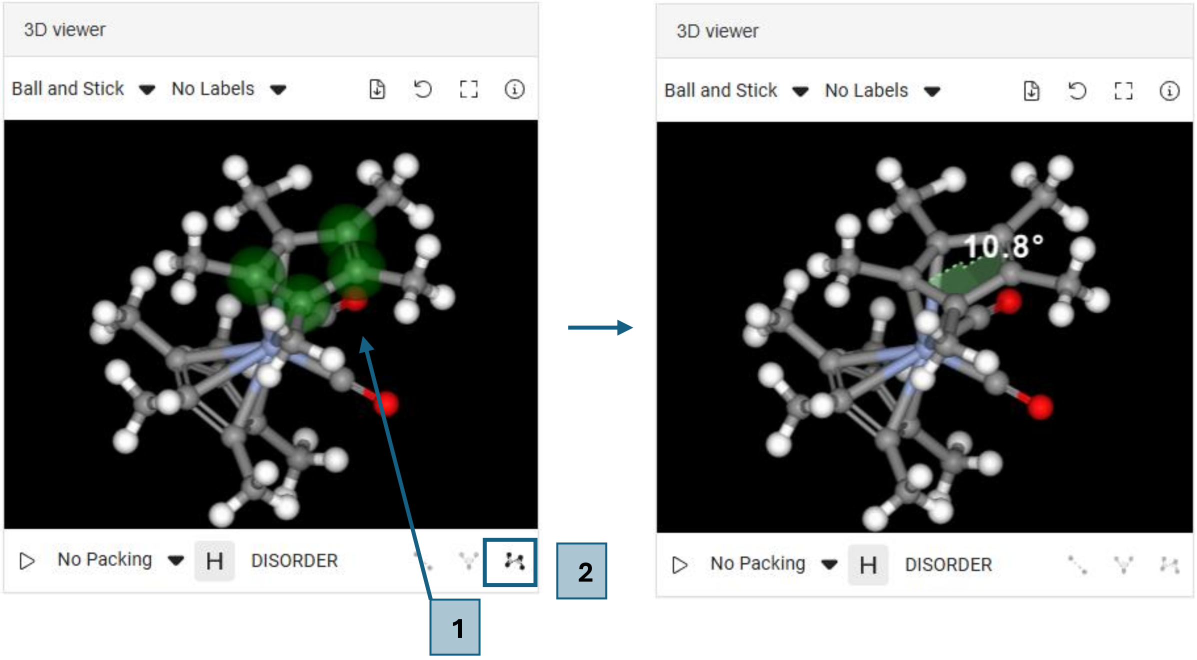
Aside from slight shortening of the *sp*^{3}-*sp*^{2} C–C bonds in the η^1-Cp ring in CPICCP01, the pattern of bond lengths is essentially the same, the ligand does appear to be σ-bonded through one carbon – imagine simply substituting one of hydrogens on C5 in CPENAD01 with Fe. In contrast, the mean value of the aromatic C–C bond length in the η^5-coordinated Cp in CPICCP01is 1.41 Å (with range 1.40–1.43 Å) which is intermediate between the double and single bond lengths in the η^1-coordinated Cp, as expected.

In the case of SEHGUH, the η^3-Cp* ring shows some interesting features. Let's have a look at the bond lengths.

CSD Refcode	**Component**	**Bond length (Å)**	
CPENAD01	Cyclopentadiene 	C1–C2	1.34
		C2–C3	1.46
		C3–C4	1.34
		C4–C5	1.50
		C5–C1	1.50
SEHGUH	η^1-Cyclopentadienyl 	C4–C5	1.42
		C5–C6	1.48
		C6–C7	1.34
		C7–C3	1.47
		C3–C4	1.43

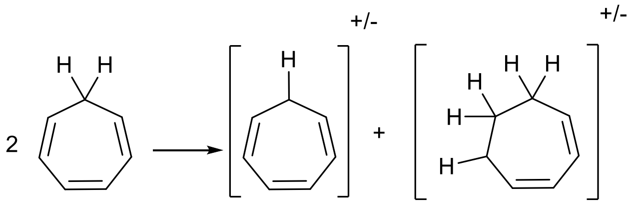
In this case, the nominally vinylic portion of the ring does indeed have a bond length typical of an alkene (as we can see from the reference cyclopentadiene), the allylic portion has C–C bond lengths intermediate between single and double bonds, whilst those between the allylic and vinylic portions are comparable with the 'middle' C–C bond of the diene. All of this is consistent with model (b) in Section 2.3. For reference, the average C–C bond length in the η^5-Cp* ring is 1.41 Å.

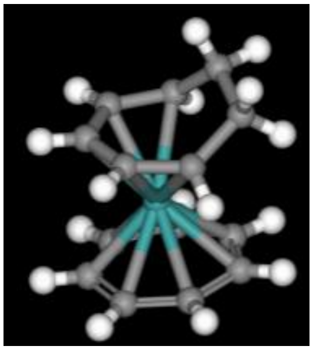
Another point of contrast is the non-planarity of the η^3-Cp* ring compared with the η^5- and η^1 Cp rings encountered previously. You can measure the relevant torsions in Access Structures as shown; you will see that they are ~11° (they would be 0° for a planar ring), such a change would be expected to reduce delocalisation around the ring based on p orbital alignment.



Exercise 5

The naphthalene ligands are each coordinated η^6 in the starting materials, providing a total of 12 electrons (six from each). According to the product formula, $[M(C_7H_7)(C_7H_9)]^+$, one hydrogen atom has been transferred from an equivalent of the reactant, C_7H_8, to a second equivalent of it. However, such a transfer would leave two radical ligands, which would be unfavourable. They might instead be expected notionally to form a pair of ions i.e. (a) $C_7H_7^+$-$C_7H_9^-$ or (b) $C_7H_7^-$-$C_7H_9^+$. In either of those cases, $C_7H_9^{+/-}$ would not be aromatic, however, in (a) $C_7H_7^+$ would be aromatic (6 π electrons), whilst in (b) $C_7H_7^-$ would not (it would have 8 π electrons). We would expect scenario (a) to prevail, giving two 6-electron donor ligands, implying η^7-$C_7H_7^+$ + η^5-$C_7H_9^-$. CSD entry ZOJBEJ confirms this hapticity.



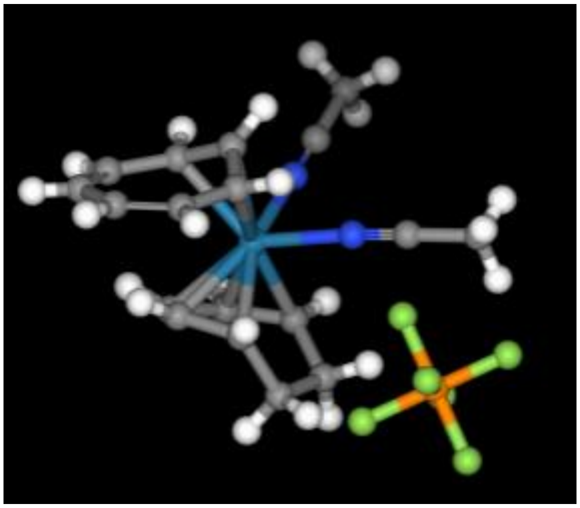


The cation of CSD entry ZOJBEJ, showing η^7-$C_7H_7^+$ and η^5-$C_7H_9^-$.

According to the equation below, two 2-electron donor ligands have been added to the complex during the reaction.

$$[Re(C_7H_7)(C_7H_9)]^+ + 2\ MeCN \xrightarrow{\lambda\ =\ 629\ nm} [Re(C_7H_7)(C_7H_9)(NCMe)_2]^+$$

To keep the electron count the same, either the $C_7H_7^+$ or $C_7H_9^-$ ligand, or both, would need to change hapticity ('slip') to provide only two electrons. Looking at CSD entry ZOHZOP, we can see that the $C_7H_7^+$ has slipped from *heptahapto* to *trihapto* – analogous to the allyl cation (which has only 2 π electrons). The planarity associated with the aromatic heptahapto tropylium has been lost too.



CSD entry ZOHZOP, showing an η^3-$C_7H_7^+$ ligand.