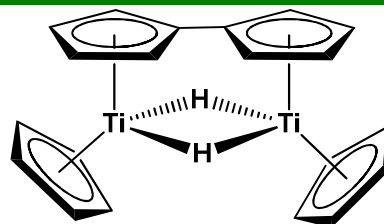
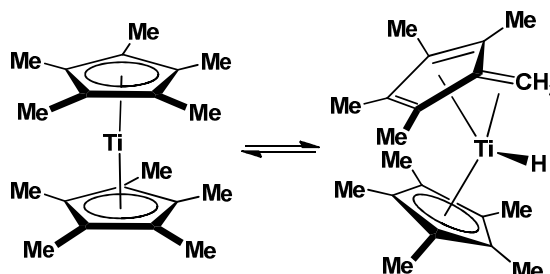


T6 T7 OMCh Problems

- 1 Electron-count the bimetallic Ti complex.
Should it have a Ti-Ti bond or not?



What advantage does the Cp^*_2Ti complex gain by doing a hydride abstraction to produce the hydride complex?



Stanley, Organometallic Chemistry, <http://chemistry.lsu.edu/stanley/Chem-4571-Notes.htm>, Cap. 9

- 2 Write electron configurations that account for the magnetic properties of the first transition metal cyclopentadienyl sandwich complexes.

- 3 Comment the data of the table

MCp_2	$\text{Ti}(\text{C}_5\text{H}_5)_2$	$\text{V}(\text{C}_5\text{H}_5)_2$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	$\text{Mn}(\text{C}_5\text{H}_5)_2$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	$\text{Co}(\text{C}_5\text{H}_5)_2$	$\text{Ni}(\text{C}_5\text{H}_5)_2$
mp (°C)	200 d	167	173	173	173	174	173

- 4 Comment the structural data for the following MCp_2 complexes.

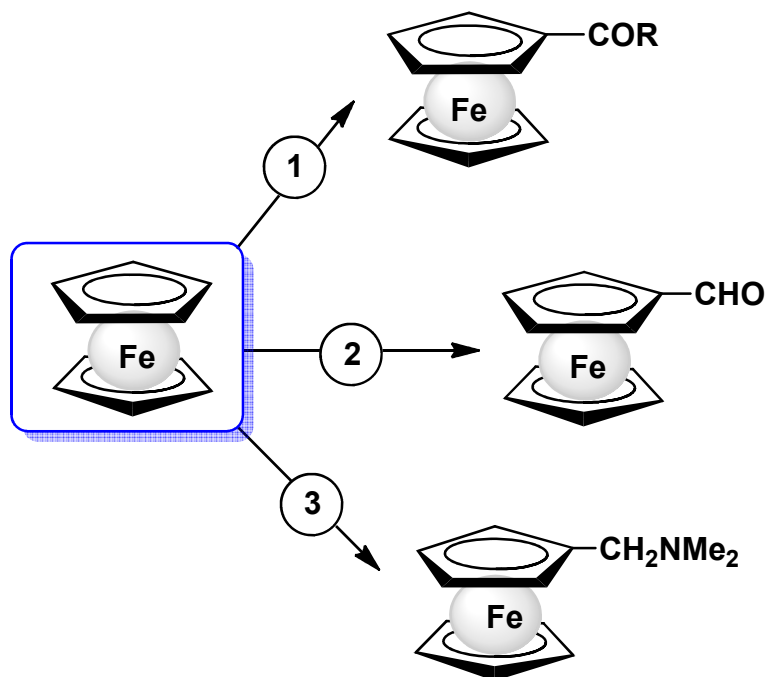
M	Refcode	Hits	T (K)	Symm	M-Cp (pm)	M-C (pm)	Cp...Cp (pm)	C-C (pm)
V	CPNDYV03	(3)	108	D_{5d}	192.3	226	384.6	141
Cr^+	VEBYEH	(3)	100	D_{5d}	184.6	220	369.3	140
Cr	CYXOCR01	(1)	173	D_{5d}	179.0	215	358.1	140
Fe^+	AFALID	(140)	173	D_{5d}	171.1	209	342.2	142
Fe^+	HIGHUA		RT	D_{5h}	170.2	208	340.4	141
Fe	NAHMEP		120	D_{5d}	164.6	204	329.2	141
Fe	FEROCE24		98	D_{5h}	165.5	206	331.6	142
Co^+	LEIXIJ	(84)	223	D_{5d}	163.6	203	327.3	142
Co^+	HENNUJ		150	D_{5h}	161.7	201	323.5	141
Co	DCYOCO04	(1)	100	D_{5d}	172.2	210	344.5	142
Ni^+	MEKKUI	(1)	150	D_{5d}	170.0	207	339.9	141
Ni	NCKLCN01	(4)	101	D_{5d}	181.7	218	363.3	142
Re^+	DAXJIV	(2)	RT	D_{5h}	190.2	228	367.4	148
Ru	CYCPRU08	(5)	100	D_{5h}	181.3	218	362.7	143
Os	SINWER	(1)	RT	D_{5h}	180.3	219	360.8	145

Explain why the Fe-C distance lengthens for $[\text{FeCp}_2]^+$, while the Co-C distance shortens for $[\text{CoCp}_2]^+$.

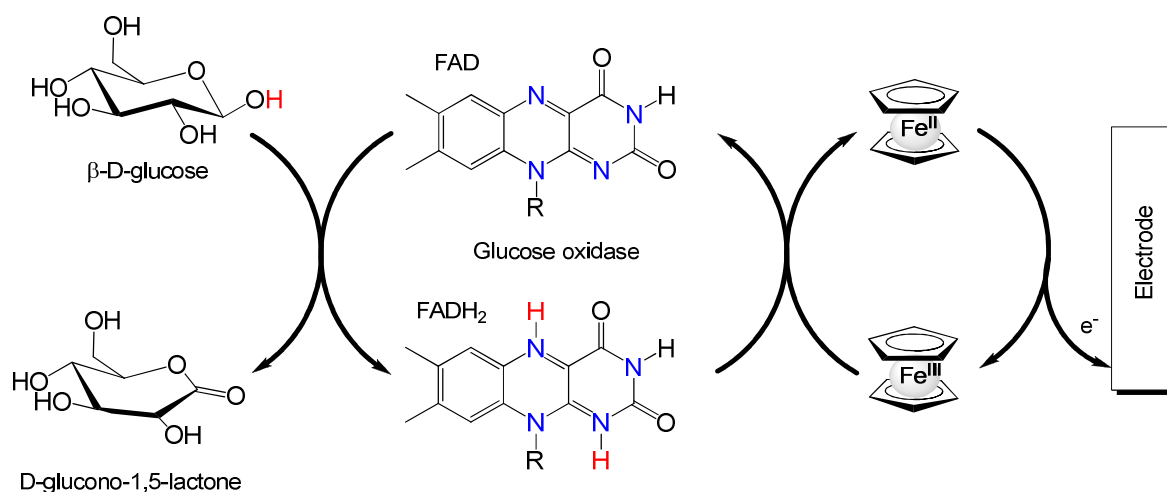
- 5 Accounts for the observation that reduction of the 18-electron cation $[(\eta^5\text{-Indenyl})_2\text{V}(\text{CO})_2]^+$ gives the $[(\eta^5\text{-Indenyl})(\eta^3\text{-Indenyl})\text{V}(\text{CO})_2]$ radical after slippage of one five-membered ring, whereas the same treatment of the corresponding cyclopentadienyl complex $[\text{Cp}_2\text{V}(\text{CO})_2]$ leads to the cleavage of a molecule of CO.

Miller et al, *J. Organomet. Chem.*, **1990**, 383, 271

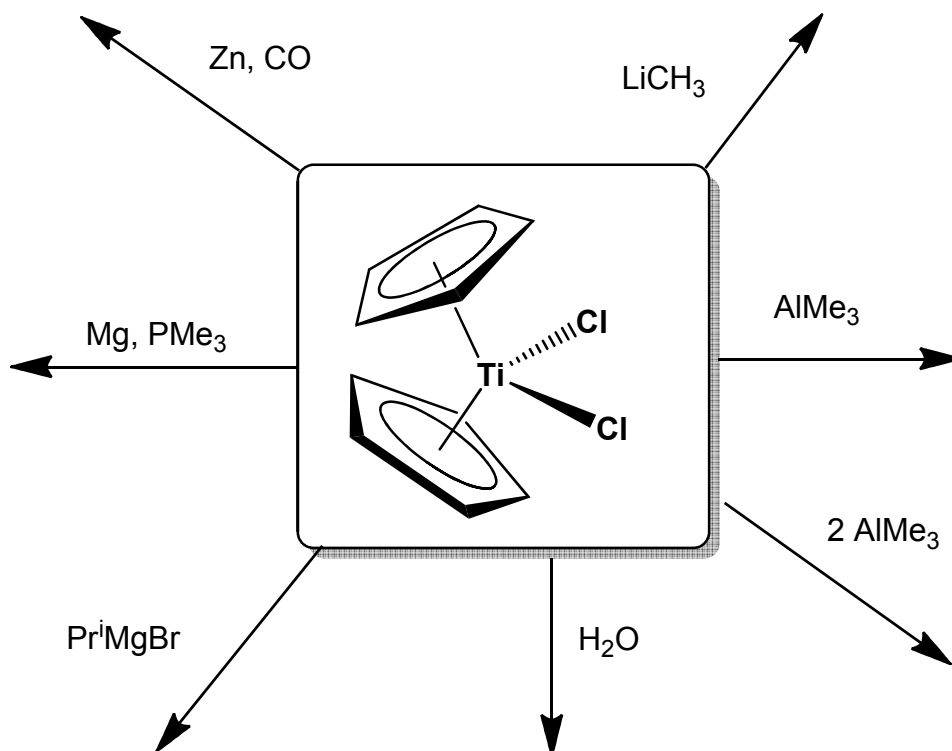
- 6 Propose plausible mechanisms for the following ferrocene reactions:



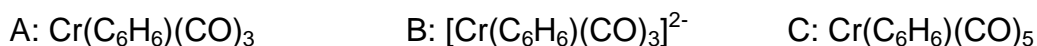
- 7 The ferrocenes represent a commonly used family of mediators. Comment the following scheme:



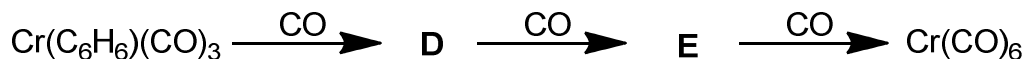
8 Predict the reaction products of the bent titanocene dihalide:



9 Draw the structure of the following 18-e chromium arene carbonyl complexes:



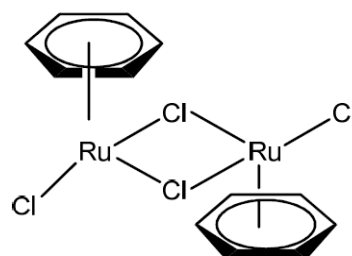
Compound A reacts with CO to give the $\text{Cr}(\text{CO})_6$ complex according to the scheme:



Describe the structure of D and E knowing that both compounds meet the 18-e rule.

VOE & OP, 2010

10 Propose a synthetic route to obtain the ruthenium dimer knowing that one of the reactants is cyclohexadiene.



Additional problems

Atkins, Overton, Rourke, Weller, Armstrong, *Inorganic Chemistry*, 4 ed, OUP, Oxford, 2006. 21.9; 21.18; 21.19; 21.21.
 Butler, Harrod, *Inorganic Chemistry. Principles and applications*, Benjamin Cummings, Redwood City, 1989. 22.19.
 Crabtree, *The Organometallic Chemistry of Transition Metals*, 4 ed, Wiley, Hoboken, 2005. Chap. 5: 4, 8, 10.
 Douglas, McDaniel, Alexander, *Concepts and Models of Inorganic Chemistry*, Wiley, New York, 1994. 12.21; 13.7.
 Spessard, Miessler, *Organometallic Chemistry*, Prentice Hall, Saddle River, 1997. Ex. 5.3; Ex. 5.4; 5.3, 5.5; 5.6; 5.7.