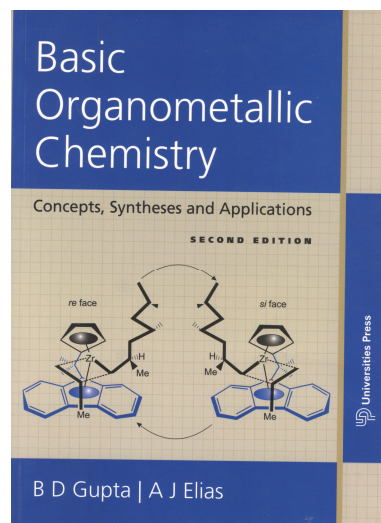


100 Problems and Exercises in Organometallic Chemistry

Anil J. Elias

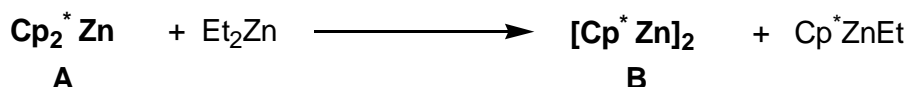
This is a supplement to exercises and problems of the textbook “Basic Organometallic Chemistry: Concepts Syntheses and Applications of Transition metals” by B. D. Gupta and A. J. Elias (Universities Press (Second Edition 2013) & CRC Press, 2010). This provides a collection of new class tested problems in organometallic chemistry which will be updated (current update: April 30, 2015).

Unlike the problems given in the textbook, solutions to these new problems are not provided and one can either check the original research article references provided for the same or contact the author at eliasanil@gmail.com



Chapter 2: 18 electron rule

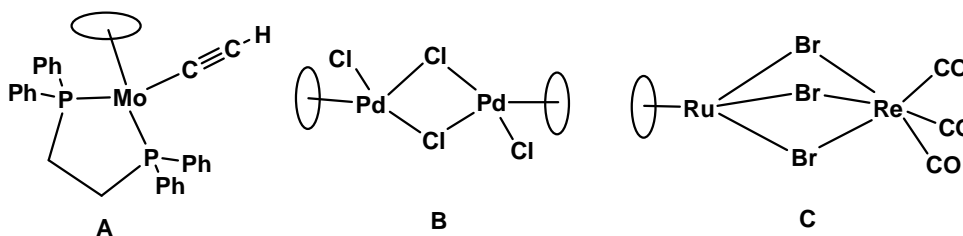
1. Compounds A and B in the given equation obey the 18 electron rule.



Draw structures of compounds A and B clearly indicating hapticity of Cp*. Also indicate oxidation state of Zn in both A and B [The η^3 hapticity can be ruled out as it is extremely rare].

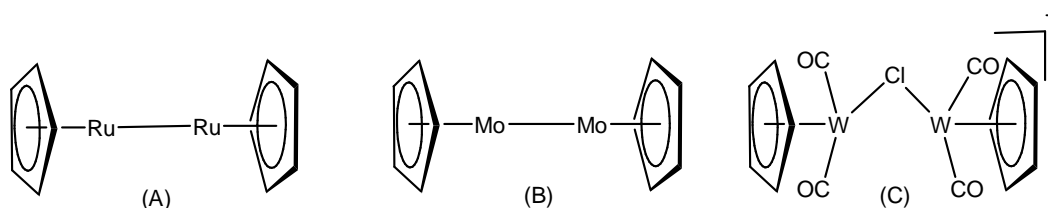
(Carmona E, Science, 2004, 305, 1136)

2. Given that it shows the highest hapticity possible, find out the missing planar, unsaturated and conjugated carbocyclic haptic ligands in the following compounds, all of which obey the 18 electron rule.



(Severin K, Dalton Trans, 2000, 2960)

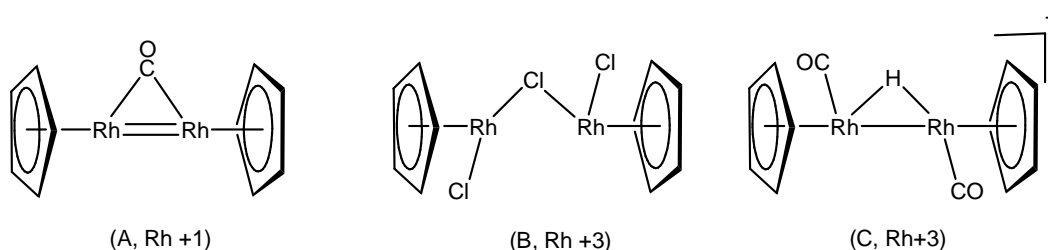
3. $[\text{Cp}^*\text{RuCl}]_4$ adopts a symmetrical structure having no metal–metal bonds where all the Ru centres have 18 electrons. Predict its structure
(Fagan, *Organometallics*, 1990,9, 1843) Hint. The bridging of chlorine units are slightly unusual
4. Four chlorine ligands are missing in each of the given skeletons of dimeric compounds A, B and C. Given that all of them obey the 18 electron rule and no additional metal-metal bonds are present, attach the missing Cl ligands on the complexes in the most appropriate manner.
(Lorenz I. P. et al. *Z. Anorg. Allg. Chem.*, 2000, 626, 1958; Green M.L.H et al, *Dalton Trans.*, 1990, 3793; Pregosin P.S. et al., *Organometallics*, 2006, 25, 4520.)



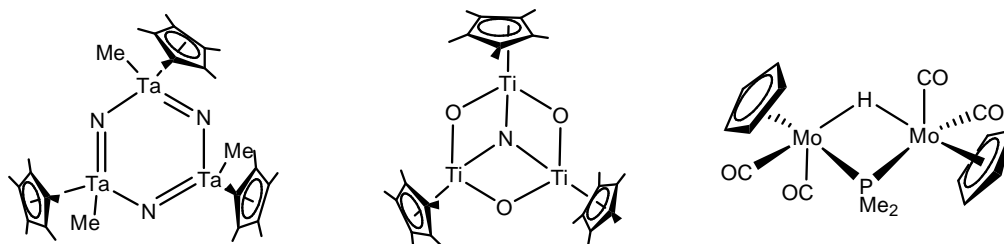
5. Reduction by sodium amalgam (Na/Hg), of $\eta^5\text{-(CH}_3\text{C}_5\text{H}_4\text{)MCl}_4$ compounds (M = Mo, W) were found to give dimeric molecules as products which are at the same time neutral, symmetrical, and tetrachlorinated in nature. Given that the new tungsten complex is a 16 electron species and the molybdenum complex is of 18 electrons, propose structures for these compounds.
(Green M.L.H et al, *Dalton Trans.*, 1990, 3793)

6. One μ_2 -bridging ligand is missing in each of the given dimeric rhodium cyclopentadienyl complexes and all of them obey the 18 electron rule. Find out and insert the most suitable from the list of ligands provided.
 $[\text{Cl}^-$, H^- , CO , CH_2^{2-}]

(Kurbanov, T Kh et al, *Zh. Obsch. Khim.*, 1989, 52, 1803; Herrman W A, *J. Am. Chem. Soc.*, 1981, 103, 63)

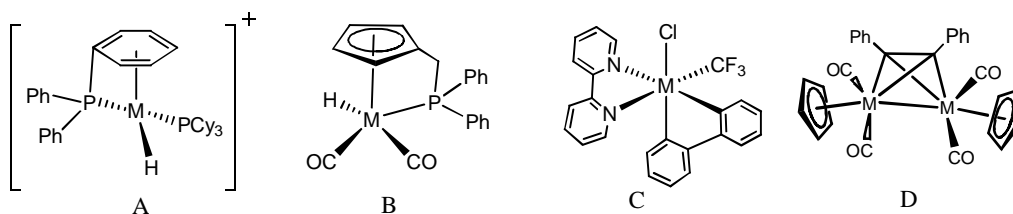


7. Count the electrons in the following compounds and indicate the electron count per metal unit



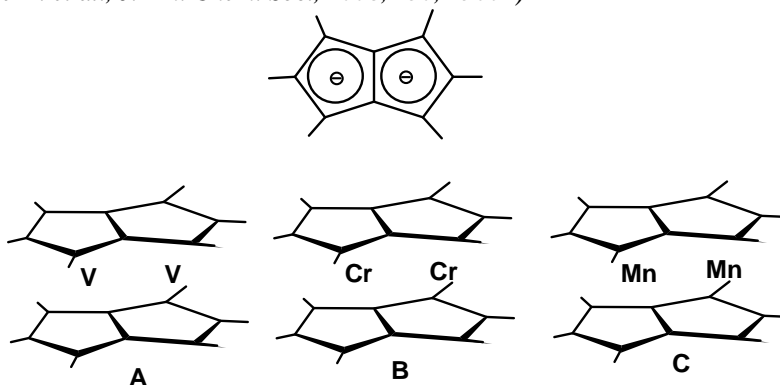
(Roesky, H.W. *Angew Chem.* 1988, 100, 1377; Santamaria C, *Inorg Chem.*, 2011, 50, 6269)

8. The following organometallic compounds are stable and have a second row transition metal at their centre. Find out the metal and its formal oxidation state.



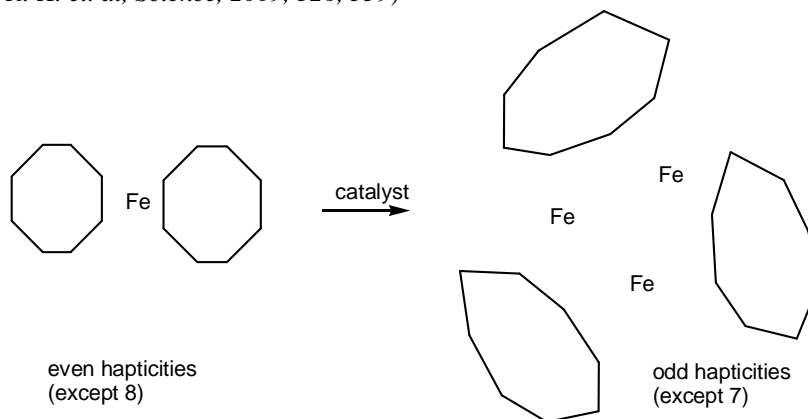
9. Permethylpentalene whose structure is given below is a dianionic ligand which forms bimetallic complexes with transition metals (also known as double metallocenes). Each of the five membered rings of this ligand can show η^5 or η^3 hapticity (a) Determine the number of metal–metal bonds in compounds A-C given that the ligand utilizes its maximum hapticity and all compounds obey 18 electron rule. (b) The ligand also forms a dinickel complex with no metal – metal bonds which has 18 or 16 valence electrons. Draw its possible structures clearly indicating hapticity

(O'Hare D. et al., *J. Am. Chem. Soc.*, 2008, 130, 15662)



10. $\text{Fe}(\text{COT})_2$ in the presence of catalytic amounts of a carbene catalyst was found to undergo a rearrangement to give $[\text{Fe}(\text{COT})]_3$. In $\text{Fe}(\text{COT})_2$, each COT binds the metal in different hapticities which are even numbers (except η^8). In $[\text{Fe}(\text{COT})]_3$ all COT units bind in the same fashion and each COT shows two odd number hapticities (except η^7) and are found to bridge two iron units. Given that both compounds obey the 18 electron rule draw their structures using the outline provided (COT = cyclooctatetraene).

(Grubbs R. H. et. al, Science, 2009, 326, 559)



11. $[\text{NiCl}_4]^{2-}$ and $\text{Ni}(\text{CO})_4$ are both tetrahedral. But only one of them obeys 18 electron rule. Identify the compound and give a reason based on ligand features why the other does not obey the rule.
12. Reaction of $\text{IrCl}_3(\text{tht})_3$ (tht=tetrahydrothiophene) with allyllithium (LiC_3H_5) in 1:3 molar ratio gave a neutral organometallic compound A which does not have Cl or tht as ligands. Compound A was found to undergo addition reactions further with (a) 1 mole of PPh_3 and (b) 2 moles of PMe_3 to give compounds B and C respectively. Compounds A, B and C obey the 18 electron rule. Draw the structures of compounds A-C clearly indicating mode of bonding of ligands involved.
- Sattelberger A P, Baker R T, Chem. Commun, 2000, 581.*

Chapter 3: Metal Carbonyls

13. The 16 electron dirhodium complex, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ can in principle have five structural isomers possible, all having 16 electrons per rhodium centre. Draw these isomeric structures. Given that the IR spectra of this compound gives bands for ν_{CO} in the range of $2012\text{--}2086\text{ cm}^{-1}$ only, and that μ_2 bridging is favoured over metal-metal bond formation in this complex, predict the most probable structure among the five structural isomers possible.
- Bettahar, M.M.; Delcourt, M. O., Radiat. Phys. Hem., 32, 779, 1988*
14. Infra red spectral analysis of the following three complexes showed a set of two IR bands for the ν_{CO} stretching frequencies. Match the correct set of IR bands to the given compounds and justify your reason for the assignment.
- (a) $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$
 (b) $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{CO})_2$
 (c) $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CO})_2$
- [$1956 \text{ \& } 1875\text{ cm}^{-1}$; $1930 \text{ \& } 1850\text{ cm}^{-1}$; $1979 \text{ \& } 1897\text{ cm}^{-1}$]
(Desmersman, B. Mahe R, Dixneuf, P.H., Chem. Commun., 1984, 1394)

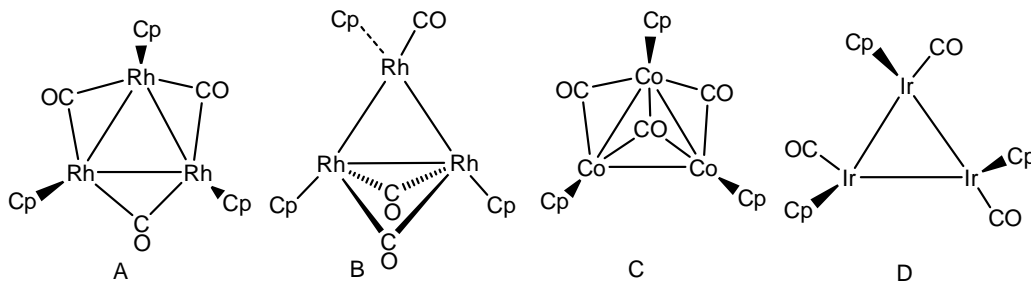
15. Although the 17 electron species $V(CO)_6$ has not been found to dimerize to give $V_2(CO)_{12}$, the latter has been found to form along with $V(CO)_6$ and remain stable at extremely low temperatures when a V/CO mixture in the ratio 1:10² was condensed into a pure CO matrix at 6-12 K. Infrared spectral analysis of $V_2(CO)_{12}$ showed three bands at 2014, 2050 and 1850 cm^{-1} . Given that this dimer obeys the 18 electron rule and vanadium has a coordination number of eight, propose a structure for the same.

(Ozin G A, *Inorg. Chem.*, 1976, 15, 1666)

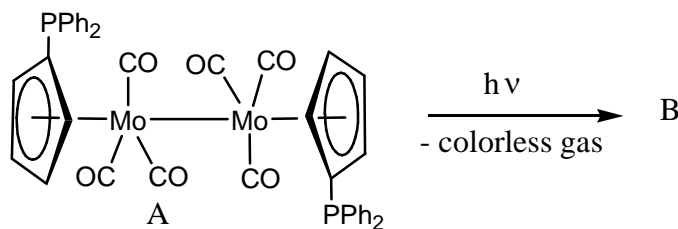
16. Select the appropriate set of ν_{CO} stretching infrared spectral bands from (1) to (5) and match with the correct trimetallic tricarbonyl complexes A-D.

(Cotton F A., *J. Am. Chem. Soc.*, 1976, 98, 1273, Shapley J. R. *Inorg. Chem.* 1982, 21, 1701, Shapely J.R., *J. Am. Chem. Soc.*, 1976, 98, 7435, Fischer, E. O, *J. Organomet. Chem.*, 1967, 10, P3).

- (1) 1833, 1775, 1673 cm^{-1}
 (2) 1827, 1783, 1766 cm^{-1}
 (3) 1960, 1918 cm^{-1}
 (4) 1935, 1975, 1653 cm^{-1}
 (5) 1973, 1827, 1794, 1744 cm^{-1}



17. The molybdenum compound A under UV irradiation liberates two moles of a gas giving a new compound B. The phosphorus NMR spectra of compound A gave a singlet at -17.0 ppm while for B a singlet was observed at $+68.2$ ppm. The ν_{CO} stretching bands of both A and B were found to be in the range of 1896 to 1959 cm^{-1} . Given that both A and B obey the 18 electron rule and B has a symmetrical structure, provide the structure of compound B.



(Poilblanc R., *Organometallics*, 1993, 12, 1503)

18. Reaction of OsO_4 with CO at 125 $^{\circ}C$ and 75 atm was found to result in a stable compound A with the empirical formula OsC_4O_4 . Compound A was found to contain 3 metal-metal bonds. Reaction of A with excess of sodium metal followed

by treatment with H_3PO_4 was found to result in compound B with the molecular formula $\text{OsH}_2\text{C}_4\text{O}_4$. Heating of B was found to result in the release of a colourless gas and formation of a compound C with empirical formula OsHC_4O_4 . C on treatment with MeI was found to get converted to D with release of a hydrocarbon gas. D on further treatment with Na/Hg followed by MeI gave E with the empirical formula $\text{OsC}_5\text{H}_3\text{O}_4$. Compounds A-E obey 18 electron rule and all of them show infrared absorptions in the vicinity of 2000 cm^{-1} . No bridging ligands were also observed. Suggest structures for compounds A-E.

(Norton J. R, Anderson O. P, J. Am. Chem. Soc, 1982, 104, 7325)

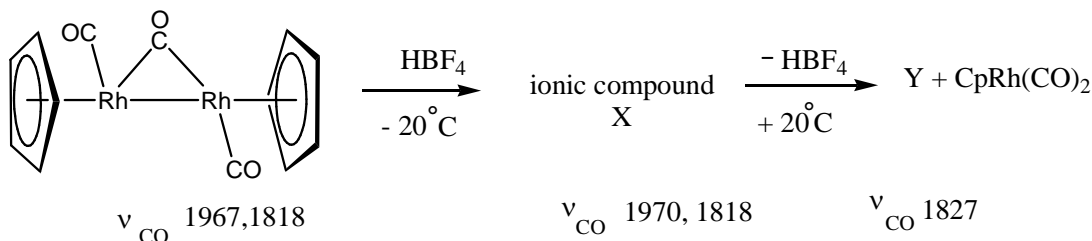
19. Starting from CrCl_3 suggest steps and reagents to make *fac* $[\text{Cr}(\text{CO})_3(\text{PPh}_3)_3]$ (*fac* = facial isomer)
20. The dimeric compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{Cr}(\text{CO})_2]_2$ (A) obeys 18 electron rule and shows IR absorptions around 1870 cm^{-1} . A on treatment with excess CO at 1200-450 psi and $175\text{ }^\circ\text{C}$ for 10 hrs gave another dimeric chromium compound B which also obeys 18 electron rule and also showed absorptions around 1876 cm^{-1} . Photolysis of A with UV radiation was found to result in a 17 electron dimeric compound C along with the release of CO gas. IR spectrum of C showed a single band at 1788 cm^{-1} and analysis showed it to have the same bond order as compound A between the chromium atoms. Draw the structures of A, B and C clearly indicating Cr-Cr bond order and nature of CO bonding.
(Wrighton, M.S et al., Inorg Chem., 1981, 20, 1133; Turner J.J. Organometallics, 1997, 16, 5879)
21. Two moles of $\text{Ni}(\text{CO})_4$ reacted with two moles of allyl chloride ($\text{CH}_2=\text{CH}-\text{CH}_2\text{-Cl}$) with copious evolution of a colorless gas to give a new compound which gave 16 electron count. Infrared spectra of the new compound did not show any bands in the range of $1650\text{-}2200\text{ cm}^{-1}$ while chemical analysis after decomposition indicated presence of chlorine. Metal-metal bonds are also not present in the new molecule. Draw the structure of the new compound.
(Semmelhack, M. F., Org. Synth., Coll. Vol. 1988, 6, 722)
22. $[\text{CpRh}(\text{CO})_3]$ has been found to exist as two isomers; (a) with three symmetrically bridging carbonyls and (b) with two carbonyls bridging the same edge and a terminal carbonyl. In contrast, the solid state structures of $[\text{CpCo}(\text{CO})_3]$ and $[\text{CpIr}(\text{CO})_3]$ were found to be different from these. Both of them, like the Rh clusters obey the 18 e rule and have a triangle of metal atoms. Propose structures for these compounds based on the IR data given for ν_{CO} bands. Provide a possible reason why Co and Ir forms such clusters.
- $[\text{CpCo}(\text{CO})_3]$ ν_{CO} 1833, 1775, 1673
 $[\text{CpIr}(\text{CO})_3]$ ν_{CO} 1960, 1918
 Cotton F A., J. Am. Chem. Soc., 1976, 98, 1273, Shapley J. R Inorg. Chem. 1982, 21, 1701
23. A reaction of $\text{Ru}_3(\text{CO})_{12}$ with C_{60} in refluxing hexane for 2 days was found to yield a novel organometallic fullerene derivative with the molecular formula $\text{C}_{60}\text{Ru}_3(\text{CO})_9$ in 4 % yield. Given that only one face of the C_{60} has been used for the three ruthenium atoms to bind, draw the structure of the cluster which obeys

18 electron rule, contains metal-metal bonds and shows ν_{CO} IR bands in the range of 1985-2078 cm^{-1} .

(Shapely J. R. *J. Am. Chem. Soc.*, 1996, 118, 9192)

24. The given dimeric rhodium cyclopentadienyl carbonyl compound on reaction with one mole of HBF_4 at -20°C gave a new symmetrical ionic complex X. The solution of X on warming to $+20^\circ\text{C}$ underwent a rearrangement (similar to disproportionation) displacing HBF_4 and forming two rhodium based complexes one of them being $\text{CpRh}(\text{CO})_2$. The other compound Y is trimeric and like X, obeys the 18 e rule. Given that X shows ν_{CO} bands at 1970 and 1818 cm^{-1} and Y shows ν_{CO} bands only at 1827 cm^{-1} propose structures for X and Y.

(Herrman W. A. *J. Am. Chem. Soc.*, 1981, 103, 63)



25. From the given list of ν_{CO} bands, match the correct values to the third row (5d) transition metal carbonyls. Justify in one word



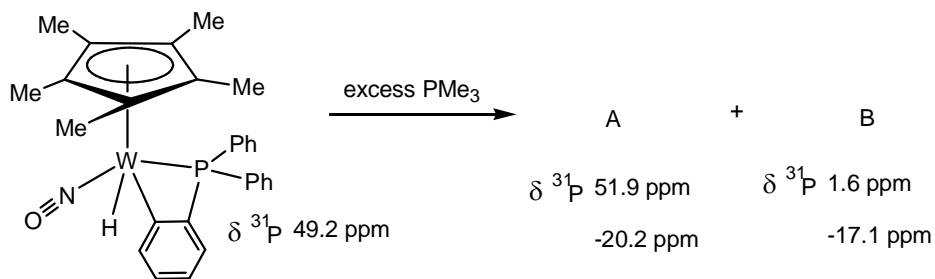
1977, 2085, 2254, 2190, 1850, 1757

(Frenking, G. *Organometallics*, 1997, 16, 4807)

Chapter 4: Neutral spectator ligands: Phosphines and N- heterocyclic carbenes

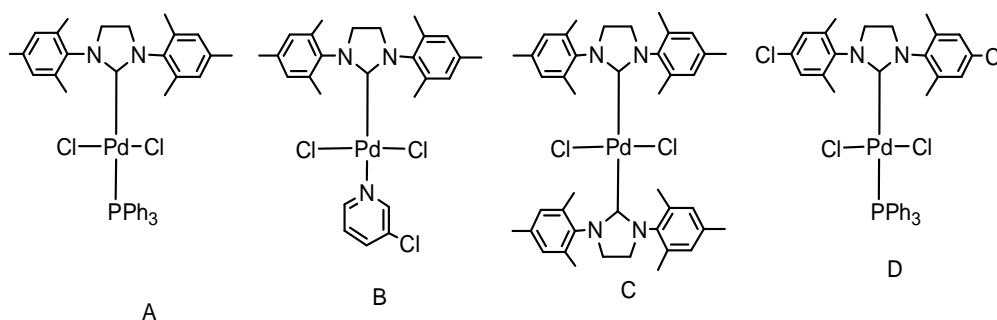
26. The reaction of the given 18 electron compound with excess of PMe_3 gave two new complexes A and B in the ratio 1:3, both obeying 18 electrons rule and both having PMe_3 as one of the ligands. NO acts as a linear ligand in both A and B. The ^{31}P NMR chemical shifts of the compound are provided. Draw the structures of compounds A and B (Note: chemical shift variations of a few ppm in ^{31}P NMR may not indicate significant changes in the chemical environment of the species involved)

(Legzdins, *J. Am. Chem. Soc.*, 1997, 119, 1139)



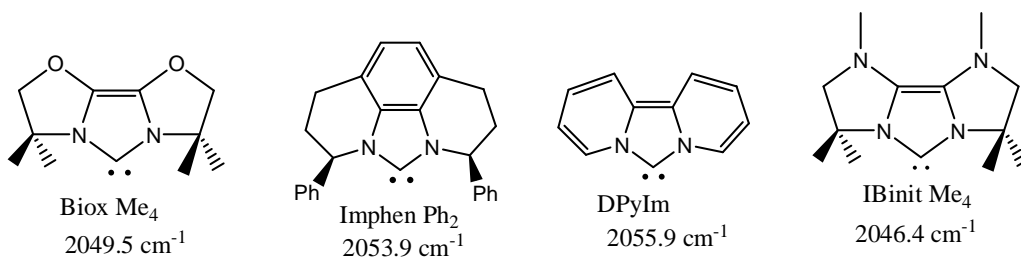
27. The following Pd-NHC complexes have been found to be useful in Suzuki coupling reactions of aryl chlorides. Arrange them in the order of increasing reactivity providing justification.

(Cetinkaya, B, *J. Organomet.Chem.*, 2006, 691, 3749)

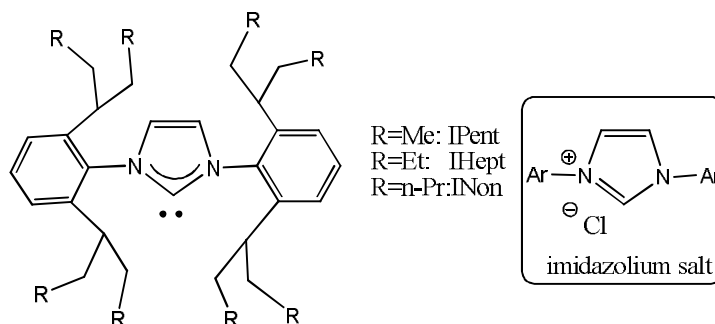


28. Stretching frequencies [ν_{CO}] for $\text{Ni}(\text{CO})_3\text{NHC}$ complexes having the given fused NHC's were predicated using theoretical calculations and are provided below. Arrange these ligands in the increasing order of σ donor strength and calculate Tolman's electronic parameters [χ] for them [given χ for PCy_3 (ν_{CO} 2056.4) is 0.3].

(Gusev, D.G., *Organometallics*, 2009, 28, 6458)



29. ITent (tent= tentacular) are a new class of NHC ligands which have 'flexible steric bulk' (See Fig.) The ν_{CO} bands obtained for the $\text{Ni}(\text{CO})_3$ complexes of IPent, IHept and INon are 2049.3, 2048.6 and 2048.5 cm^{-1} respectively.



- (a) Calculate the χ values for IPent, IHept and INon ligands and also comment on their donor capability compared to IMes (2050.7 cm^{-1} $\chi = -5.4$)
- (b) Reaction of one mole of the imidazolium chloride salt of ITent ligands was carried out with one mole of $Pd(acac)_2$ to give new set of complexes with the elimination of one mole of acetylacetonone. Propose a structure for this square planar complex.
- (Nolan S P et al. *Chem. Eur. J.*, 2013, 19, 17358)

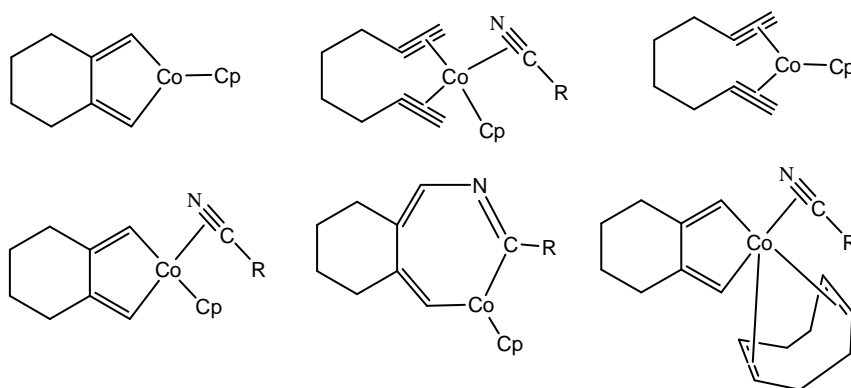
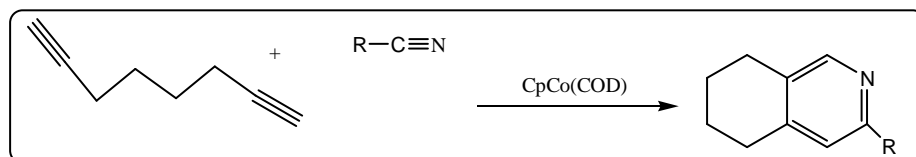
Chapter 5: Alkenes and alkynes as ligands

30. The reaction of $Mo(CO)_6$ with dicyclopentadiene ($C_{10}H_{12}$) under microwave conditions yields a stable compound A with the empirical formula $C_8H_5O_3Mo$ along with evolution of CO and H_2 gas. The infrared spectrum of this compound gives peaks in the range of $1859-1960 \text{ cm}^{-1}$. Compound A on refluxing in toluene releases CO gas and on cooling and further bubbling acetylene gas for 12 hours converts to a new compound B with the empirical formula $C_8H_6O_2Mo$. The infrared spectrum of this compound shows ν_{CO} stretching bands in the range of 1852 to 1997 cm^{-1} . While proton NMR of A shows a single peak, that of B shows two peaks in the ratio 5:1. Suggest (a) structures for compounds A and B both of which obeys the 18 electron rule. (b) the Mo-Mo bond order of the intermediate obtained when A is refluxed.
- (Song, L.C. et al., *Inorg. Chim. Acta*, 1996, 249,175)
31. Ethynylferrocene, $CpFe[C_5H_4(C\equiv CH)]$ (molecular weight 210) on reaction with catalytic amounts of $TaCl_5$ was found to result in a mixture of two ferrocene based compounds which are structural isomers with molecular weight 630. While ethynyl ferrocene showed in its IR spectrum an alkyne band at 2112 cm^{-1} , no such bands were found in the new compounds in the range of 1900 to 2300 cm^{-1} . Provide the structures of the new compounds.
- (Stepnika, P, *Coll. Czech. Chem. Commun.*, 1997, 62, 1577)
32. A reaction of Cp_2Ni and $Ni(CO)_4$ resulted in a dark red crystalline compound A which showed a very strong ν_{CO} stretching band at 1834 cm^{-1} only. Reaction of one mole of A with one mole of $PhC\equiv CPh$ resulted in the release of a gas and formation of a new compound B which did not show any IR bands in the normal range for carbonyl groups. Both A and B obey 18 electron rule and showed a

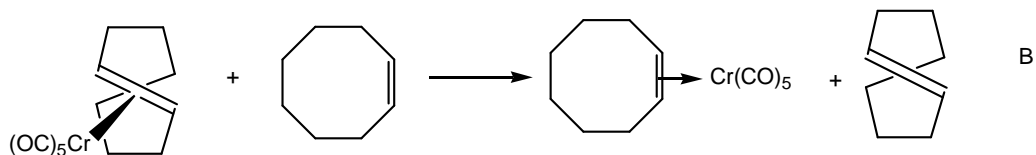
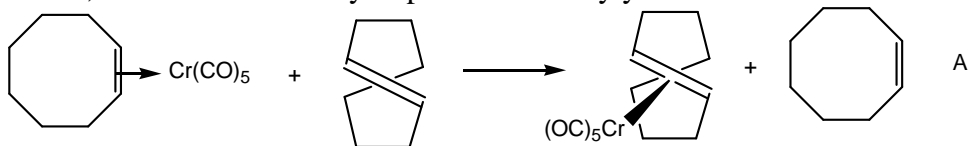
single peak in ^1H NMR for the Cp ring and B showed additional ^1H NMR peaks for phenyl groups. Draw structures of both A and B

(J. F. Tillney Basset, *J. Chem. Soc.*, 1961, 577)

33. Among the given structures some are possible intermediates for the cyclotrimerization reaction given in the box. Select the right structures and arrange them in the correct sequence in which the reaction mechanism is most likely to proceed (Cp = $\eta^5\text{-C}_5\text{H}_5$).



34. Between the two reactions A and B given below involving cis and trans cyclooctenes, which is more likely to proceed? Justify your answer.



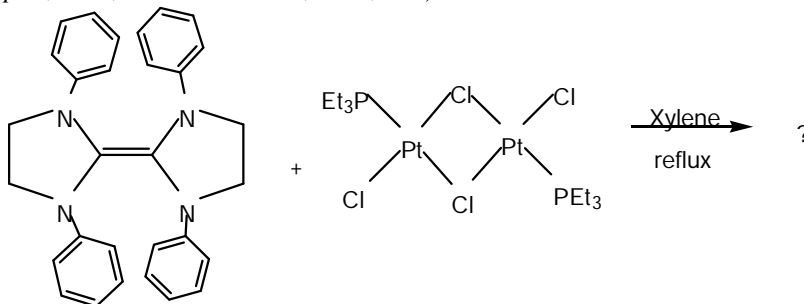
(Skibbe V, *Chem. Commun.*, 1984, 262)

Chapter 6: Carbenes and Carbynes: complexes with metal-carbon double and triple bonds

35. The following equimolar reaction involving a square planar 16 electron dimeric platinum complex was found to result in the formation of two moles of another

square planar 16 electron monomeric platinum complex with no other side products. Predict the structure of this new compound.

(Lappert, M.F., *Chem. Commun.*, 1971, 400)

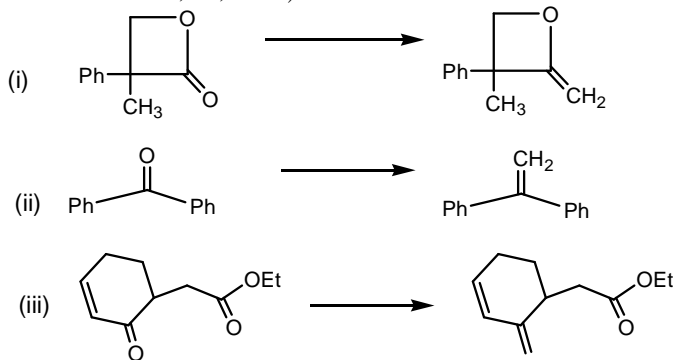


36. Reaction of lithiated phenylacetylene ($\text{PhC}\equiv\text{CLi}$) with $\text{W}(\text{CO})_6$ followed by Meerwein's salt ($\text{Et}_3\text{O}^+\text{BF}_4^-$) resulted in a stable compound A. The IR spectrum of this compound (emp. formula: $\text{WC}_{16}\text{H}_{10}\text{O}_6$) showed ν_{CO} stretching bands in the range of $1957\text{-}2070\text{ cm}^{-1}$ and an additional band at 2154 cm^{-1} . Compound A on further reaction with BCl_3 resulted in the formation of new stable compound B along with evolution of a gas and BCl_2OEt . The IR spectrum of compound B showed ν_{CO} stretching bands in the range of $2047\text{-}2109\text{ cm}^{-1}$ and an additional band at 2130 cm^{-1} . Draw the structures of compounds A and B

(Fischer E. O. et al., *J. Organomet. Chem.*, 1972, 35, 647 & 1974, 81, C23)

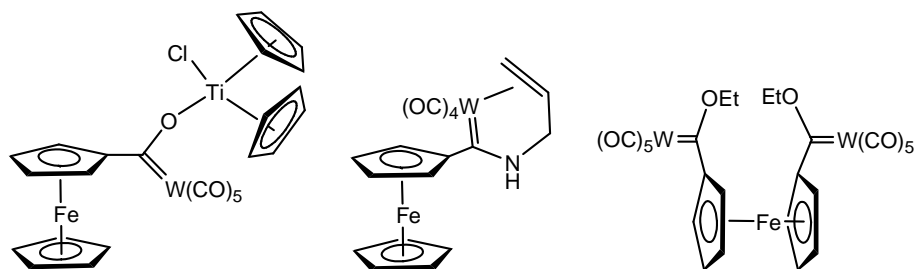
37. Write the structure of the most appropriate reagent and conditions for carrying out the following reactions resulting in the highest possible yields. Indicate additional reagents if required.

(Hartley R C et al. *Tetrahedron*, 63, 4825)



38. Provide synthetic routes for the preparation of the following Fischer carbene complexes starting from ferrocene and $\text{W}(\text{CO})_6$ and using reagents such as Cp_2TiCl_2 , Meerwien's salt and allyl amine.

(Bezuidenhout D I et al. *Coord. Chem. Rev.*, 2012, 256, 479)

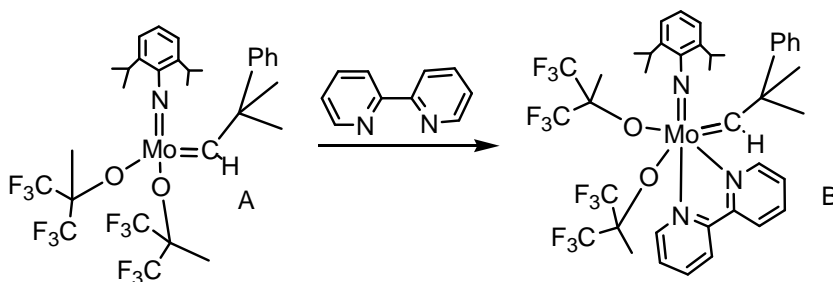


39. The Fischer carbene $(\text{CO})_5\text{W}=\text{CMe}(\text{OMe})$ upon UV irradiation was found to lose a gas and form an unstable intermediate. This intermediate immediately underwent isomerization involving a shift of the OMe group to give a new 18 electron compound which was no more a carbene. Propose a structure for the new 18 electron compound.

(Hartwig J. *F Organotransition metal chemistry*, 2010, University Science Books, pp494)

40. Imido ($\text{R}-\text{N}=\text{}$) and nitrosyl (NO) ligands share a unique similarity with respect to their geometry and electrons donated in forming stable organometallic complexes. Schrock's olefin metathesis catalyst (A) which is highly reactive and air sensitive, on reaction with bipyridine becomes B which has no catalytic activity in olefin metathesis and is highly air stable. (a) Indicate the reason for this change in properties (invoking electron count and geometry of the imido ligand) (b) The catalytic activity of B is regained when it is reacted with ZnCl_2 . Why?

(Furstner, A., *Angew. Chem. Int. Ed.* 2011, 50, 7829)



Chapter 7: Alkyl aryl and ligands with higher hapticity

41. Reaction of ferrocene with AlCl_3 and aluminium powder in toluene for 6 hours followed by treatment with H^+PF_6^- was found to result in an ionic compound X with the molecular formula $[\text{C}_{12}\text{H}_{13}\text{Fe}]\text{PF}_6$. X on reaction with sodium salt of the substituted cyclopentadiene, $\text{Na}^+[\text{C}_5\text{H}_4(\text{COOEt})]^-$ gave a new compound Y with the molecular formula $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Fe}$. Compounds X and Y both obey 18 electron rule. Propose structures for them.

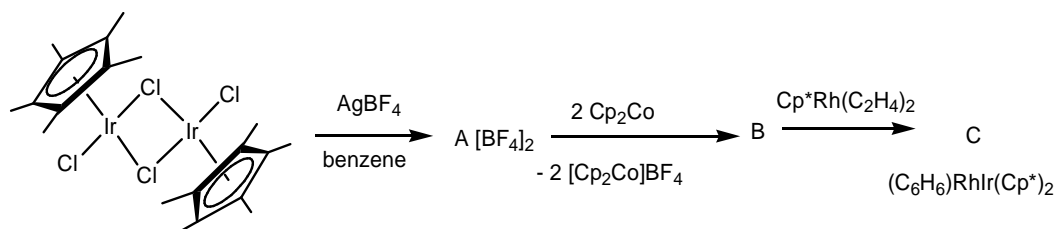
(Astruc, D; *Inorg. Chem.*, 2010, 49, 1913)

42. Given a mixture of 1-octene and 4-octene, suggest a reaction which will convert this mixture into pure 1-bromooctane.

(Hart D.W et al., *J. Am. Chem. Soc.*, 1974, 96, 8115)

43. Reaction of $(Cp^*IrCl_2)_2$ with $AgBF_4$ followed by benzene resulted in the formation of compound A which was found to be a monomeric iridium dication. Compound A on reduction with 2 moles of cobaltocene (Cp_2Co) gave a neutral monomeric iridium compound B. Both A and B had the same molecular formula $C_{16}H_{21}Ir$. Reaction of B with $Cp^*Rh(C_2H_4)_2$ gave a bimetallic complex C having the general formula $(C_6H_6)RhIr(\eta^5-Cp^*)_2$. Compounds A, B and C obey 18 electron rule and has η^5-Cp^* as one of its ligands. Draw their structures clearly showing ligand binding and hapticities.

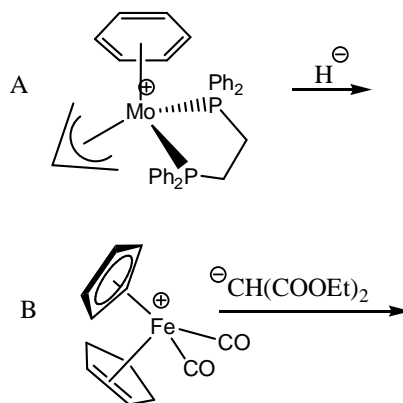
(Maitlis P.M. *J. Organomet. Chem.*, 1984, 272, 265; Mueller J. J. *J. Organomet. Chem.*, 1994, 480, 213; Gladysz J.A., *Chem. Commun.*, 2012, 48, 7925)



44. $Ni(CO)_4$ on reaction with 1,2,3 triphenyl cyclopropenium bromide, $(Ph_3C_3)Br$ was found to result in a dimeric compound having two nickel units along with release of some gaseous CO. The new compounds showed strong ν_{CO} stretching band only at 2039 cm^{-1} and its elemental analysis indicated presence of bromine as well. Draw the structure of this dimeric compound which obeys 18 electron rule.

(E. W. Gowling and S F A Kettle, *Inorg. Chem.*, 1964, 3, 604)

45. Predict the product in the following reactions



46. A reaction of freshly prepared cyclopentadiene (2 moles) with $EtONa$ (2 moles), diethyl carbonate $[(EtO)_2C(O)]$ (2 moles), followed by $FeCl_2$ (1 mole) resulted in a stable symmetrical sandwich compound A. The reaction resulted in the formation of $EtOH$ and $NaCl$ as side products. Compound A on hydrolysis was found to result in B, another stable sandwich compound which was found to dimerize immediately, assisted by two intermolecular hydrogen bonds. B was also found to test positive for sodium bicarbonate test. Propose the actual structures of A and B.

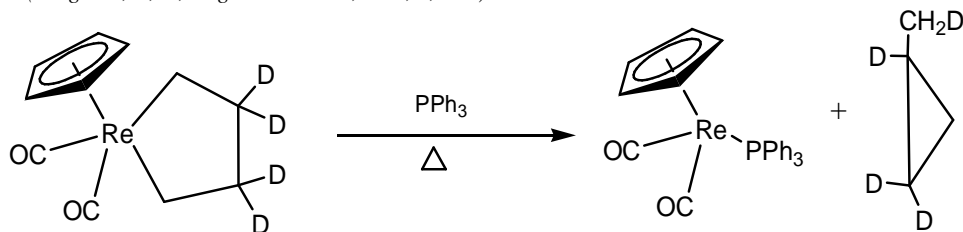
(Mathias Tamm, *Organometallics*, 2013, 32, 5946)

Chapter 8: Unique reactions in organometallic chemistry

47. Catalytic oligomerization of ethylene gas in the presence of CrCl_3 and $\text{R}_2\text{PN}(\text{R}')\text{PR}_2$ (R= para-methoxybenzene, R'= isopropyl) (with an alumoxane activator) has been found to result in 1-octene (70%). The same reaction but in the presence of $\text{R}_2\text{PN}(\text{R}')\text{PR}_2$ (R = ortho-methoxybenzene, R' = methyl) was found to result in 1-hexene (90%). [6]
- (a) Propose a catalytic cycle for both products showing major steps and which involves metallacyclic intermediates. Mark the reactions happening at each step
- (b) What is the limiting reaction which differentiates between 1-octene and 1-hexene formation?
- (c) Why is that 1-butane is not obtained as a product of this catalysis reaction?
Overett M. J. J. Am. Chem. Soc., 2005, 127, 10723 Overett M. J. Chem. Commun., 2005, 622

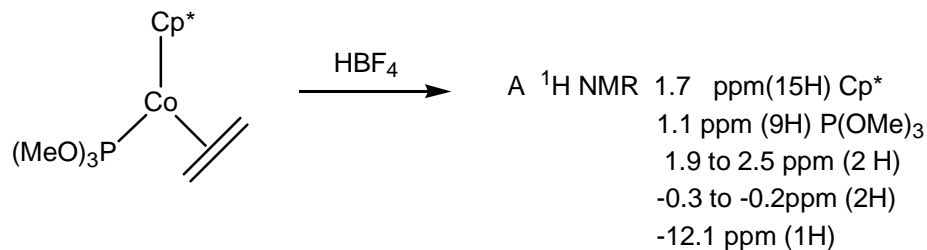
48. Reaction of $\text{Ir}(\text{acac})_3$ with 3 moles of 2-phenylpyridine was found to result in a new octahedral complex with the removal of 3 moles of acetylacetonone [$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$]. Given that the new compound has three Ir-C bonds and that the reaction involves orthometallation, draw the structure of the new compound. Does the compound show any structural isomerism? Explain.
K. Hori, Bull. Chem. Soc., Jpn, 2012, 85, 209

49. For the following reaction, kinetics indicated that dissociation of CO does not occur. The proposed mechanism has a hapticity change involving Cp ring which is not normally observed. Write the mechanism for the reaction indicating type of reaction happening at each step.
(Bergman, R, G, Organometallics, 1985, 4, 129)



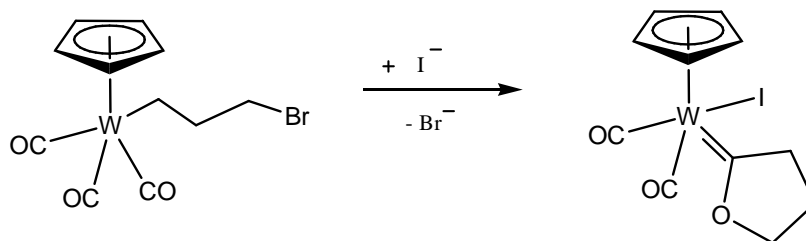
50. The given cobalt ethylene complex on protonation leads to a new stable cationic complex A whose proton NMR data at -70°C is given. On warming up to warmer temperatures the peak at -12.1 ppm disappears and only two types of hydrogen's in the ratio 2:3 are observed instead of the 2:2:1 spectra (for the unassigned hydrogen's). Draw the structure of A at -70°C . Will compound A form directly from the given complex or will there be an intermediate, if so what? Give reason for the unusual -12.1 ppm proton chemical shift.

(Brookhart M, Organometallics, 1989, 8, 1212)



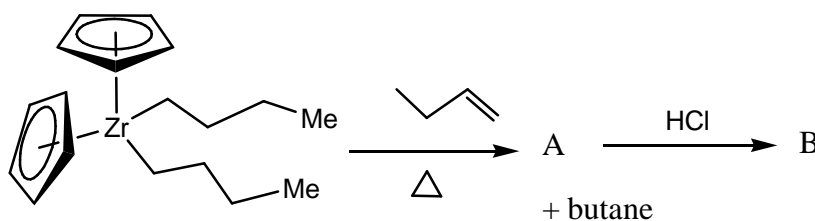
51. Suggest a mechanism for the following reaction. The proposed mechanism indicates the first step to be a migratory insertion.

(Winter M. J. Dalton Trans, 1984, 2, 273; 1983, 2397)



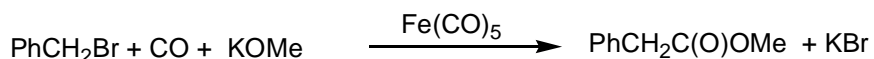
52. Thermal decomposition studies on $\text{Cp}_2\text{Zr}(\text{n-Bu})_2$ indicated formation of one mole each of 1-butene and butane but formation of octane was not observed. Heating of $\text{Cp}_2\text{Zr}(\text{n-Bu})_2$ with 1 mole of 1-butene was found to result in a metallacyclic compound A along with butane. (a) Write the mechanism of the reaction and structure of compound A (b) Predict the products formed when A is reacted with 2 moles of HCl?

(Negishi, E I., J. Org.Chem., 1989, 54, 3521, Tetrahedron Lett., 1986, 27, 2829)



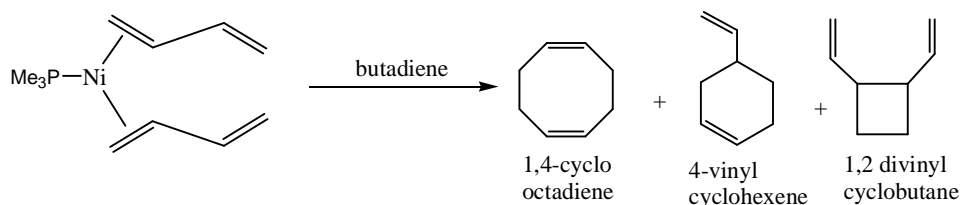
53. For the following reaction, the original mechanism proposed by the authors centres around a potassium analogue of Collman's reagent. However, one can propose an equally feasible mechanism using oxidative addition, migratory insertion of CO, ligand cleavage, ligand exchange, ligand association and reductive elimination (not in this order). Write this mechanism.

(Weinberger B, Tetrahedron Lett., 1983, 24, 4005)



54. Butadiene in the presence of nickel- PMe_3 catalyst gives three cyclic products as shown below. Given that the mechanism involves hapticity changes between η^1 ,

η^2 and η^3 as well as oxidative coupling and reductive elimination steps, propose mechanism/intermediates for the formation of the given three products
(Tobisch, S., *J. Am. Chem. Soc.*, 2002, 124, 4881)

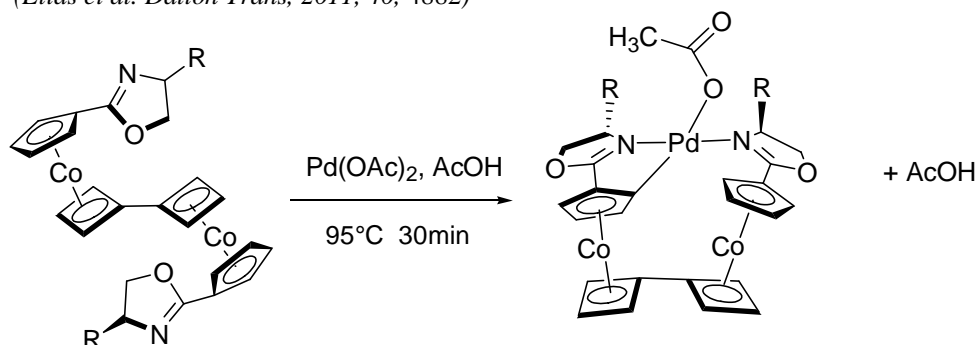


55. How does one differentiate between agostic and anagostic interactions? Give an example of a compound having agostic interaction

(Green M.L.H, Brookhart, M, *Proc. Natl. Acad. Sci. USA*, 2007, 104, 6908)

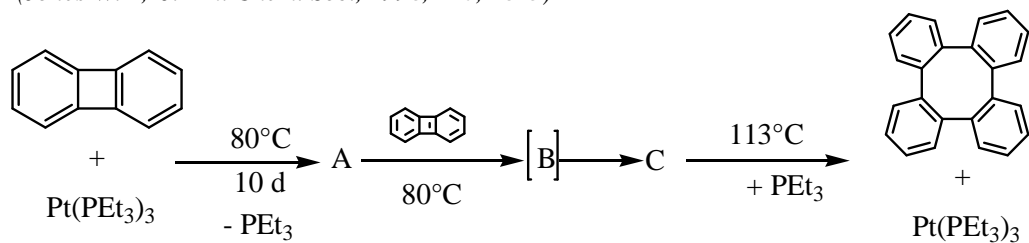
56. Reaction of the given organometallic bidentate ligand with $\text{Pd}(\text{OAc})_2$ results in the evolution of acetic acid and formation of a palladacycle with a Pd-C bond between one of the Cp's and palladium. Propose a mechanism for this reaction.

(Elias et al. *Dalton Trans*, 2011, 40, 4882)

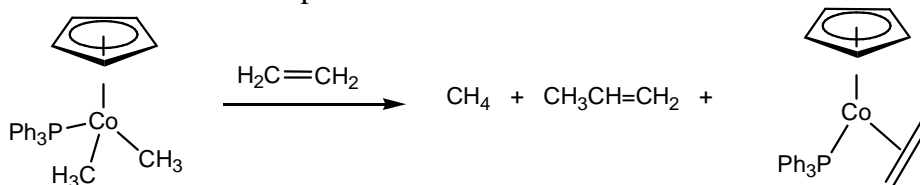


57. The reaction of $\text{Pt}(\text{PEt}_3)_3$ with 1 mole of biphenylene over a period of 10 days at 80°C was found to result in a 16e compound A along with the release of PEt_3 . Compound A on further reaction at 80°C with one more mole of biphenylene was found to give a 16e compound C through an 18e intermediate B. Reaction of C with PEt_3 at 113°C was found to give tetraphenylene along with $\text{Pt}(\text{PEt}_3)_3$. Write the structures of A, B and C. Indicate type of reactions happening at all stages.

(Jones W.D, *J. Am. Chem. Soc.*, 1998, 120, 2843)



58. For the following reaction (a) choose the possible sequence of steps which will be followed in the reaction mechanism. (b) Although as per the mechanism another hydrocarbon product is also possible, it does not form in the actual reaction. What is this compound?



- A) PPh₃ cleavage B) ethylene coordination C) 1,2- migratory insertion of methyl group D) β-H elimination E) PPh₃ coordination F) Reductive elimination of CH₄ G) propene displacement with ethylene

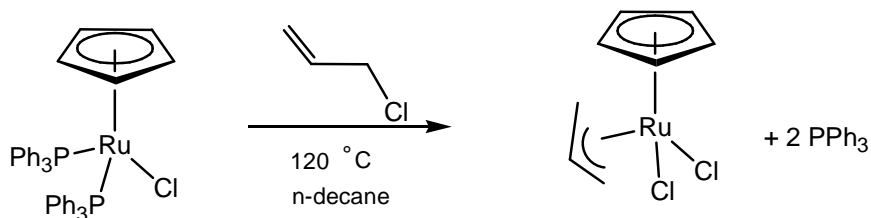
- A) PPh₃ cleavage B) ethylene coordination C) 1,2- migratory insertion of methyl group D) β-H elimination E) Reductive elimination of CH₄ F) PPh₃ coordination G) propene displacement with ethylene

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- A) PPh₃ cleavage B) ethylene coordination C) ethylene coordination D) 1,2- migratory insertion of methyl group E) β-H elimination F) Reductive elimination of CH₄ F) PPh₃ coordination G) propene cleavage

(Bergman, R.G. *J. Am. Chem. Soc.*, 1980, 102, 7003)

59. Select the correct sequence of mechanistic steps for the reaction provided



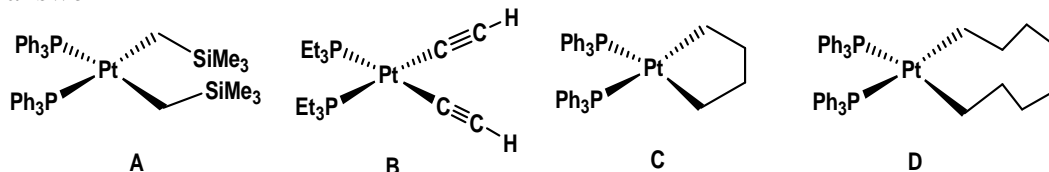
McElwee White et al., *Organometallics*, 2011, 30, 5568

- (a) PPh₃ dissociation (b) oxidative addition of allyl chloride (c) hapticity change of allyl from η¹ to η³ (d) PPh₃ dissociation
- (a) PPh₃ dissociation (b) oxidative addition of allyl chloride (c) PPh₃ dissociation (d) hapticity change of allyl from η¹ to η³
- (a) oxidative addition of allyl chloride (b) PPh₃ dissociation (c) hapticity change of allyl from η¹ to η³ (d) PPh₃ dissociation
- (a) oxidative addition of allyl chloride (b) PPh₃ dissociation (c) PPh₃ dissociation (d) hapticity change of allyl from η¹ to η³

60. Bubbling of CO through $\text{IrCl}(\text{PPh}_3)_3$ resulted in a new compound A. The same compound A was also obtained when $\text{Ir}(\text{PPh}_3)_2\text{Cl}(\text{N}_2)$ was stirred under a CO atmosphere. A on keeping in a non polar solvent for weeks converted to the well known square planar Vaska's complex. ^1H NMR of A, in addition to peaks in 6-8 ppm gave an extra peak around -18 ppm and the ^{31}P NMR of A showed two peaks at +24 and -69 ppm (Unlike Vaska complex which showed ^{31}P NMR peak only at +24.8 ppm). Crystal structure of A indicated an octahedral geometry around iridium. Suggest the structure of A.

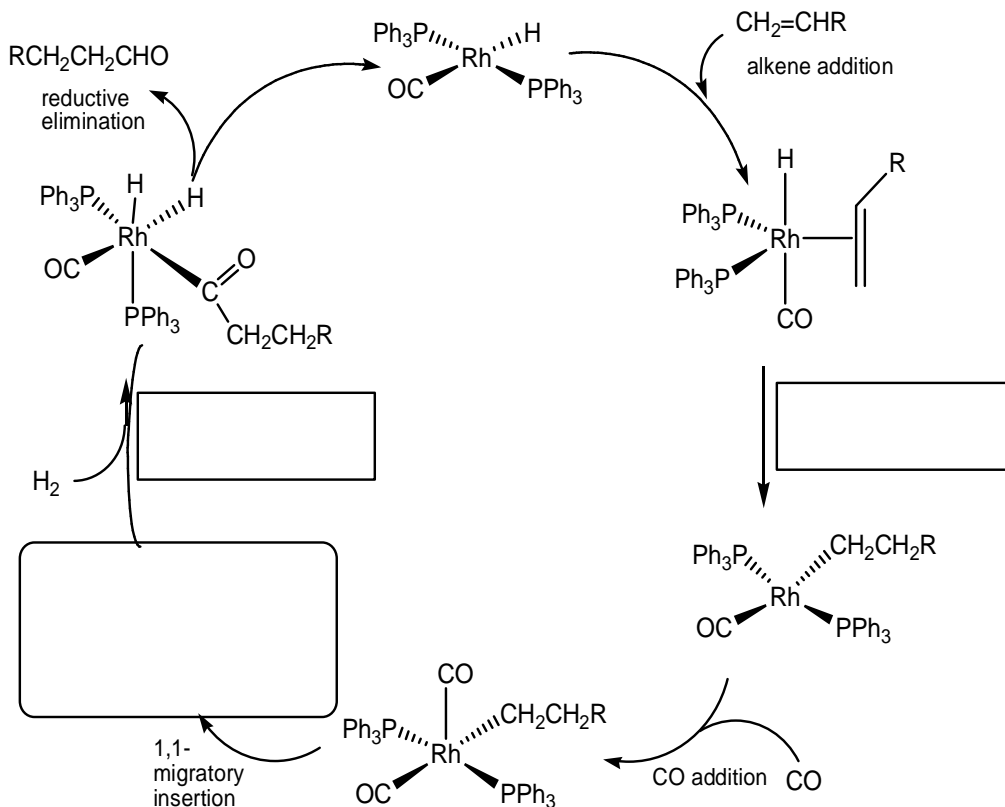
Valentine J.S *Chem Comm*, 1973, 857., Cameron Jones *Trans. Metal. Chem.*, 2003, 28, 595,

61. Select the most **unstable** platinum σ complex from the given list. Justify your answer

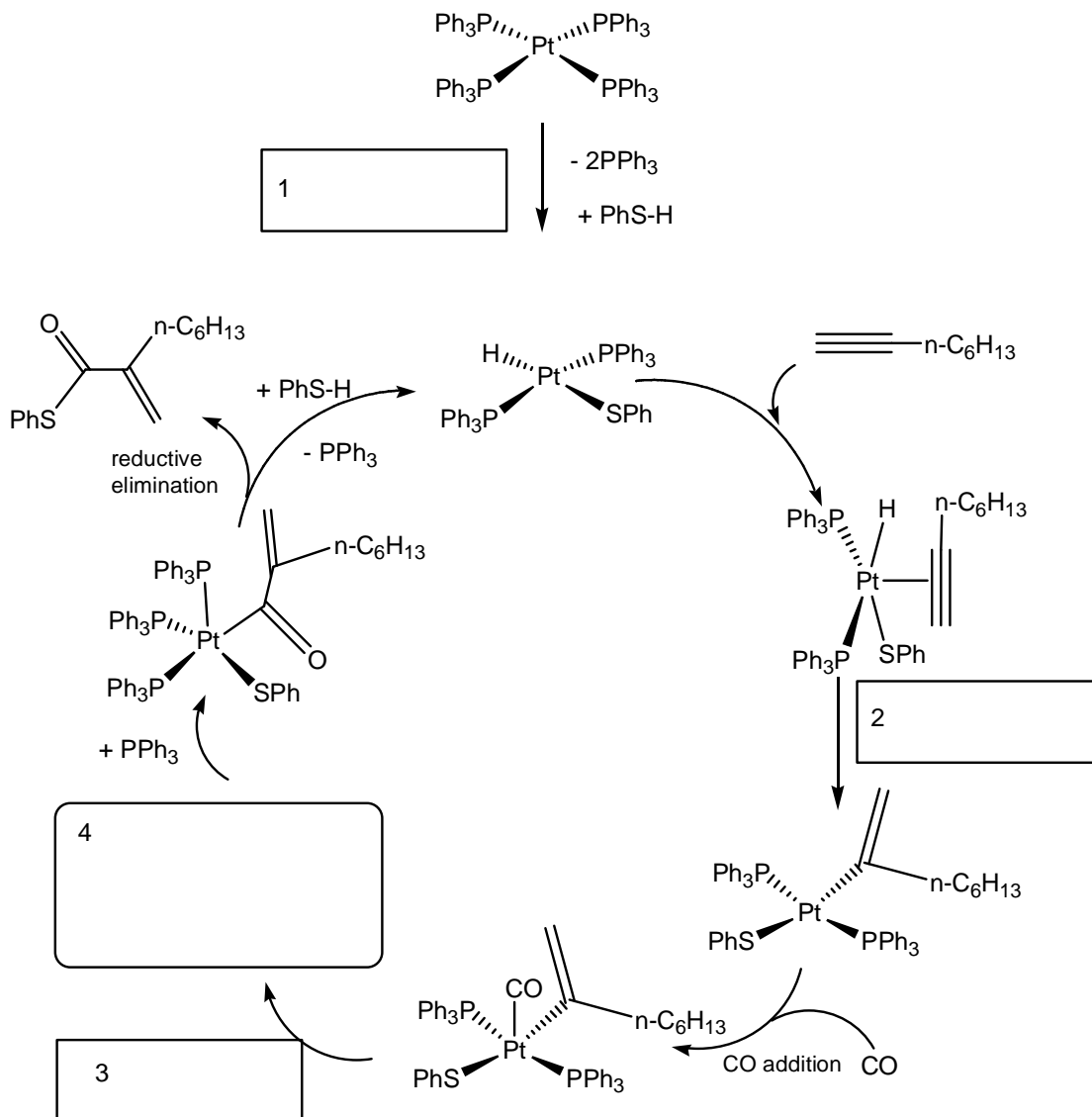
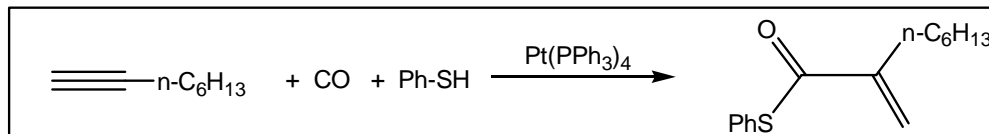


(Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, 98, 6521)

62. In the given catalytic cycle of hydroformylation, fill in the blanks with the name of the reactions (boxes adjacent to the arrows) and the structure of the specific intermediate with the correct geometry at the given step.

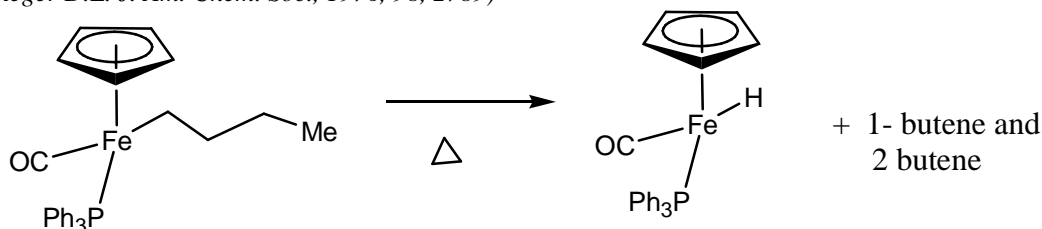


63. Hydrothiocarbonylation of 1-octyne with CO and PhSH gives an α,β -unsaturated thioester using $\text{Pt}(\text{PPh}_3)_4$ as catalyst. Identify the type of reactions (1-3) and draw the missing intermediate in the catalytic cycle (4).
(Ogawa A., Tetrahedron, 2003, 59, 3521)

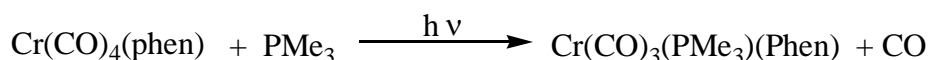


Chapter 9: Ligand substitution reactions, metal-metal bonding and fluxionality in organometallic compounds

64. Indicate how 1-butene and 2-butene are formed in the following reaction by writing a suitable mechanism. No alkanes are produced in this reaction. Kinetic studies indicated that $\Delta S^\ddagger = 20 \pm 3$ eu.
(Reger D.L. *J. Am. Chem. Soc.*, 1976, 98, 2789)



65. The activation volume [ΔV^\ddagger] for the pressure dependant substitution reaction



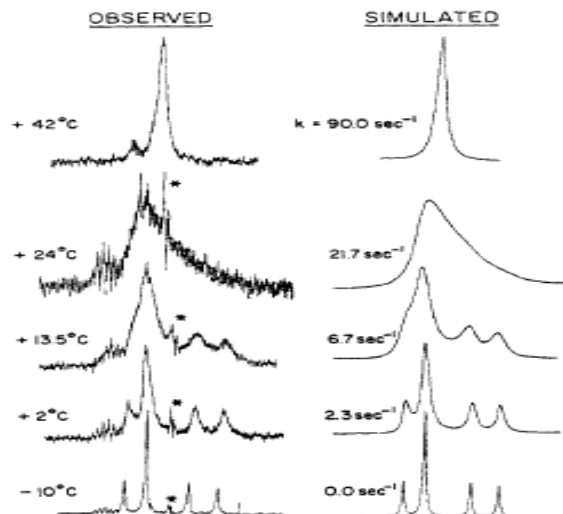
was determined in the ligand field (LF) excited state and at the MLCT excited state. The values obtained are as follows. Indicate the type of substitution reaction mechanism operating at each of the excited states

LF	(at 366 nm)	$\Delta V^\ddagger = 9.9 \pm 1.8 \text{ cm}^3 \text{ mol}^{-1}$
MLCT	(at 546 nm)	$\Delta V^\ddagger = 2.1 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$

(Rudi van Eldik, *Inorg. Chim. Acta*, 1996, 251, 341).

66. COT forms an 18 e complex with Fe(CO)_3 fragment. The ^1H NMR spectra of this compound shows a single peak at -60°C and four peaks at -113°C . Draw the structure of the complex clearly indicating bonds. Give reason for the differences in the spectra at the two temperatures.
(Cotton F.A., *J. Am. Chem. Soc.*, 1975, 98, 1443)
67. Two electron electrochemical reduction of the 18-electron cation $[(\eta^5\text{-indenyl})_2\text{V(CO)}_2]^+$ is reversible while the same reduction of the complex $[\text{Cp}_2\text{V(CO)}_2]^+$ leads to the cleavage of a molecule of CO. Give reasons.
(Miller et al, *J. Organomet. Chem.*, 1990, 383, 271)
68. Which among the following compounds are most likely to undergo *ring whizzing*? Give a one sentence justification for your answer
(a) Cp_2TiCl_2 (b) $\text{Cp}_2\text{Fe(CO)}_2$ (c) $\text{Cp}_2\text{W(CO)}_2$ (d) Cp_4Ti (e) CpCo(CO)_2

69. Given on the right is the variable temperature $^1\text{H-NMR}$ spectrum of $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_6\text{Me}_6)$ from -10°C to $+42^\circ\text{C}$. At -10°C four peaks at 1.92, 1.77, 1.47 and 1.27 ppm are observed while at 42°C they coalesce to a single peak.



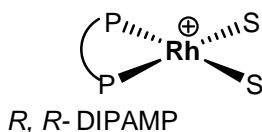
- Account for the 4 peaks at low temperature with a diagram
- Given that a 20e species is unstable and unlikely to form predict a possible intermediate species which will account for the single peak at 42°C .

(E.L. Muetterties, M.Y. Darensburg, *J. Am. Chem. Soc.*, 1978, 100, 7425.)

Chapter 12: Hydrogenation of alkenes and asymmetric hydrogenation of prochiral alkenes

70. The active form of the catalyst used for asymmetric hydrogenation of methyl acetamido cinnamate (L-Dopa synthesis) is given below which has two solvent molecules on the metal centre. Propose a suitable precursor complex and indicate by steps how the given active di-solvated form of catalyst is generated *in situ* from that precursor complex.

(Knowles W.S., *J. Am. Chem. Soc.*, 1977, 99, 5946)



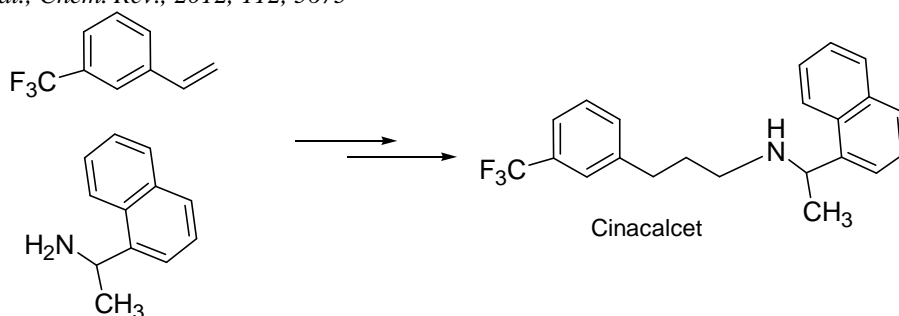
- Among the well known transition metal based hydrogenation catalysts which is the most efficient and based on what data? Compare this catalyst with Wilkinson's catalyst and give three reasons why its efficiency is much better than Wilkinson's catalyst.
- In the hydrogenation of alkenes by Wilkinson's catalyst, the first step of the mechanism was conventionally given as a PPh_3 falling off from $\text{RhCl}(\text{PPh}_3)_3$. However detailed mechanistic evidence obtained later has shown this not to be exactly true.
 - What is the first step proposed in the revised mechanism?
 - Give one experimental evidence to support the revised mechanism.
 - What is the reason for PPh_3 falling off according to the revised mechanism?

Chapter 13: Hydroformylation

73. In the catalytic cycle of hydroformylation starting with active catalysts $\text{HCo}(\text{CO})_3$ or $\text{trans Rh}(\text{PPh}_3)_2(\text{CO})(\text{H})$, the first step is the coordination of the alkene on the metal. If instead, one proposes oxidative addition of H_2 as the first step (followed by removal of a spectator ligand and then alkene coordination) will it make any difference in the product composition of the reaction? If yes, give reasons.

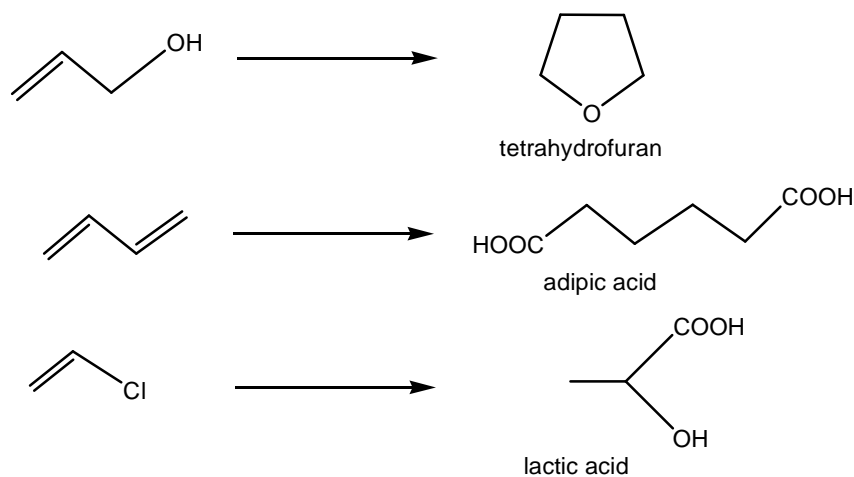
74. Cinacalcet is a calcimimetic drug that mimics the action of calcium on tissues and is sold by the trade names Sensipar or Mimpara to treat secondary hyperparathyroidism as well as hypercalcemia. Given that use of Rh-Xanthphos catalyst is involved in its industrial synthesis, suggest appropriate steps for the synthesis using the given starting materials.

Boerner A et al., Chem. Rev., 2012, 112, 5675



75. Given that hydroformylation is the first and key step in the following conversions steps for the same indicating probable reagents and catalysts at every step

Boerner A et al., Chem. Rev., 2012, 112, 5675



Chapter 14: Methanol carbonylation and olefin oxidation

76. High concentrations of chloride and copper (II) chloride favour formation of a new product, chlorohydrin ($\text{ClCH}_2\text{CH}_2\text{OH}$) in the Wacker process. Using part of the catalytic cycle of Wacker process explain how and at which step this product is likely to form.

Chapter 15: Olefin metathesis

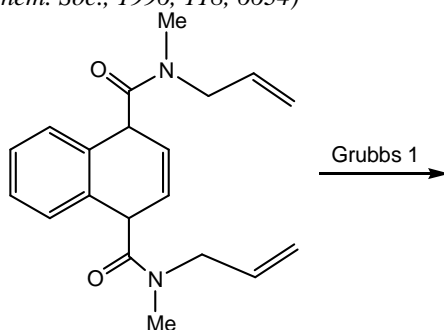
77. For the following statements on olefin metathesis catalysts assign the most suitable catalyst(s) (among Schrock's molybdenum, Grubbs I, Grubbs II and Grubbs-Hoveyda II) which will be in agreement with the statement.

- (i) This catalyst can be recycled many times without losing activity
- (ii) This catalyst is most suitable for olefins having primary amino groups
- (iii) For reactions leading to hindered alkenes, this catalyst is not suitable
- (iv) This catalyst cannot be handled without very good inert atmosphere techniques
- (v) For ROMP of cyclic substrates with OH functional groups and low ring strain this(these) catalyst(s) work(s) best.

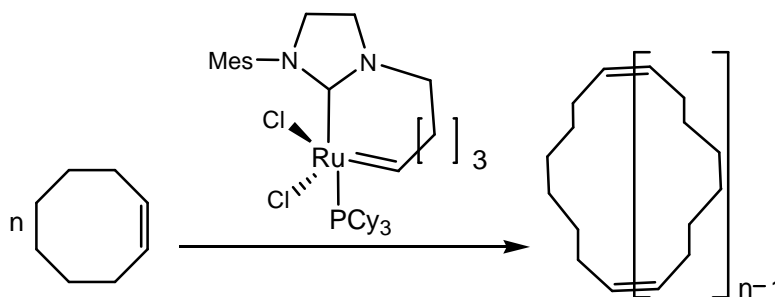
(Gupta B D Elias A J. Basic Organometallic Chemistry 2010 CRC press pp262)

78. The reaction of the given compound proceeds readily with Grubbs 1 catalyst. Write the structure of the product formed indicating all mechanistic steps.

(Grubbs R.H., J. Am. Chem. Soc., 1996, 118, 6634)



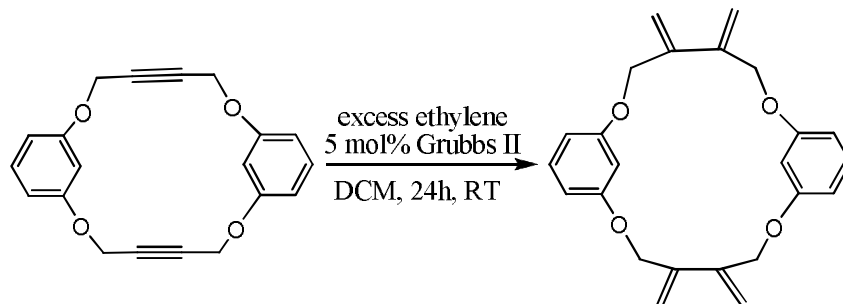
79. Ring expansion metathesis polymerization (REMP), a variation of olefin metathesis reported in 2008 is carried out using a modified Grubbs catalyst shown below resulting in large cyclic poly olefins. (a) Draw the structures of the major intermediates formed during the ring expansion of the given cyclooctene.



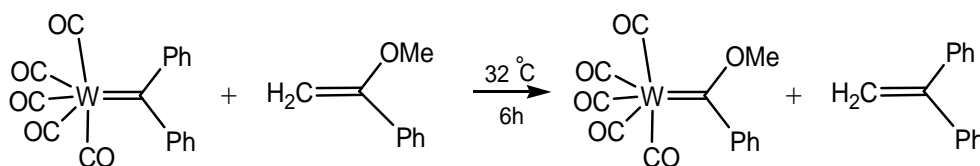
(b) Suggest ways by which termination of the reaction can be brought about.

(Grubbs, R, H., J. Am. Chem. Soc., 2008, 130, 12775)

80. Write a mechanism for the following olefin metathesis reaction using Grubbs second generation catalyst clearly indicating steps involved
(Kotha, S.; Waghule, G. T., *J. Org. Chem.*, 2012, 77, 6314)



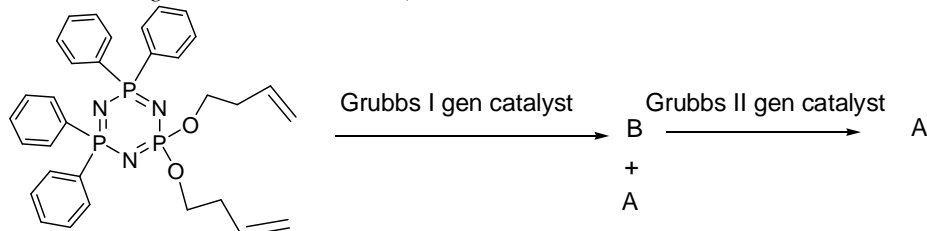
81. For the given reaction (a) show how the products are formed by drawing the intermediate/transition state of the reaction
(Casey C P., *J. Am. Chem. Soc.*, 1974, 96, 7808)



The reaction also yielded traces of another product formed possibly by reductive elimination of the intermediate. What is this product and why it is obtained in poor yield?

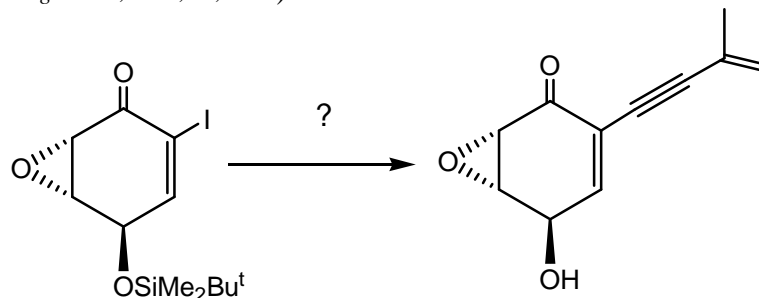
82. 1, 1, 3, 3- tetraphenyl 5,5- dihomooallyloxy cyclotriphosphazene (figure given) has been found give two compounds A and B on treatment with Grubbs 1 gen catalyst with B as the major product. Compound B on reaction with Grubbs 2nd Gen catalyst was found to give compound A. Compound A has one cyclophosphazene unit while compound B has two cyclophosphazene units. Draw the structures of A and B which are both cyclic alkoxy derivatives of cyclophosphazene. What metathesis reactions happen at each stage of the reaction?

(Elias, A. J., *Inorg. Chem.*, 2011, 50, 250)

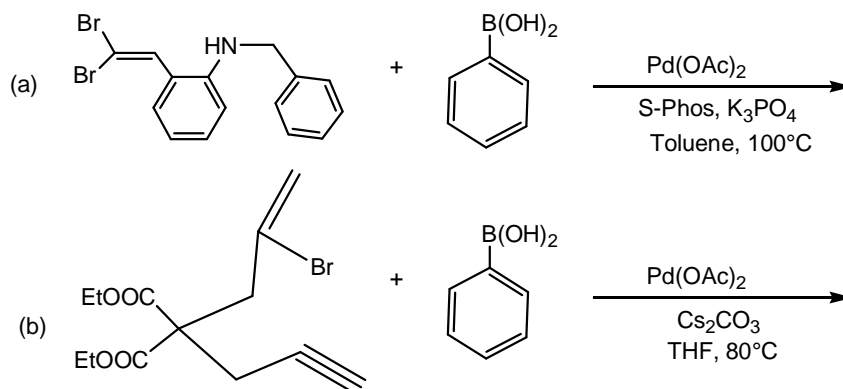


83. The natural product harveynone isolated from the fungus *Pestalotiposis theae* has anticancer properties. The laboratory synthesis of this compound involves the final step shown below. Suggest reactants and reagents to carry out the step and name the reaction

(Johnson, *J. Org. Chem.*, 1997, 62, 1582)



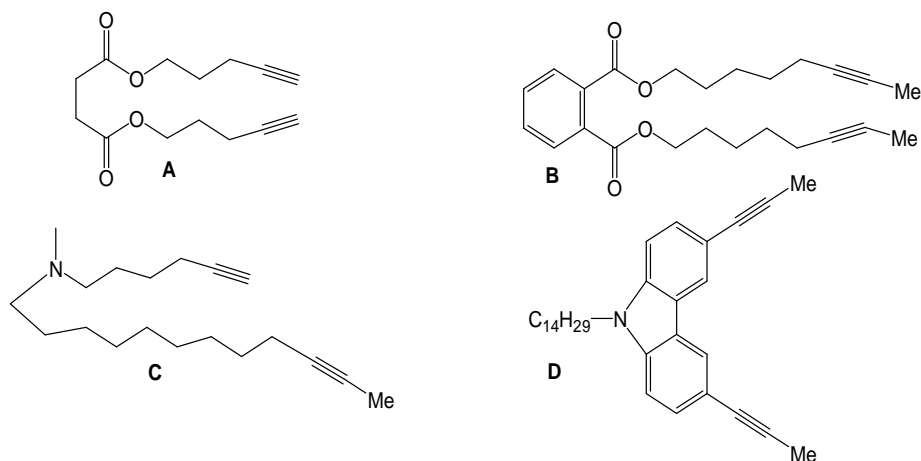
84. Write the name of the cross coupling reaction/reactions against each statement
- (i) This reaction requires CuI as a cocatalyst
 - (ii) This reaction is not suitable as a step for preparing medicines and drug molecules
 - (iii) Activation of one of the coupling partners is required in this/these reaction(s)
 - (iv) The product releasing final step of this reaction is a beta hydrogen elimination.
 - (v) This reaction involves Grignard reagents as one of the coupling partners
85. How can one make aryl/alkyl chlorides also undergo Suzuki coupling reaction. What steps in the catalytic cycle are involved and how?
86. Select the most suitable phosphine to use along with palladium catalyst for the following cross coupling reactions
BINAP, S-PHOS, DPPF, TPPTS.
- a Suzuki coupling of sterically hindered aryl chlorides
 - b Suzuki coupling in water medium
 - c α - Arylation of carbonyl compounds
 - d Kumada coupling as well as Suzuki coupling of alkyl group bound 9-BBN and vinyl bromides
87. Draw the structure of the final product formed in the following reactions and indicate the named reactions happening
(Lautens, *J. Org. Chem.*, 2008, 73, 538; Mook, *Tetrahedron. Lett.*, 2003, 44, 267)



88. What is a “throw away” ligand? What is the advantage of having such a ligand on a catalyst? Give an example and the names of two catalysts, one in olefin metathesis and one in cross coupling reaction where it is found.

Chapter 17: Olefin polymerization and oligomerisation reactions

89. Similar to SHOP process but mechanistically different, a chromium catalyst $[\text{Cr}(\text{PNP})]^+$ [$\text{PNP} = \text{HN}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$] has been found to trimerize ethylene selectively to 1-hexene. Draw the catalytic cycle for the same. The cycle involves oxidative coupling, ligand additions, reductive elimination, β -hydride elimination and migratory insertion (not in this order !)
90. 1, 4- Butanediol is the chosen solvent in the ethylene growth reaction of SHOP process. Give reasons
91. A palladium catalyst with bulky neutral alpha diimine ligands named *Versipol* has been developed by DuPont in collaboration with Prof. Maurice Brookhart of University of North Carolina for ethylene polymerization with polar comonomers. The catalyst however was found to give hyperbranched polymer microstructure, the extent of branching dependant on ethylene pressure. Illustrate by drawing a mechanism how hyperbranching takes place while polymerizing ethylene with this catalyst
92. Which among the following compounds are likely to undergo intramolecular alkyne metathesis reaction? Justify your answer
(Furstner A, *J. Am. Chem. Soc.*, 2009, 131, 9468)

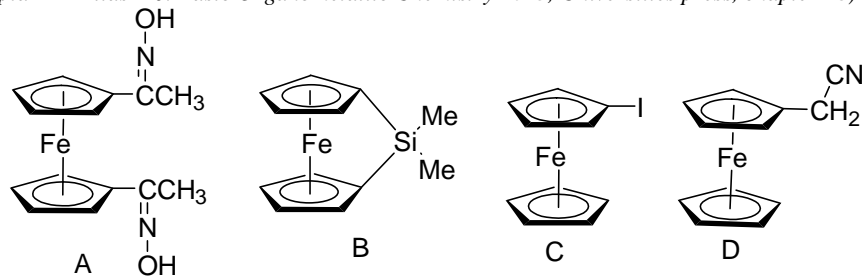


Chapter 18: Ferrocene: Structure bonding and reactions

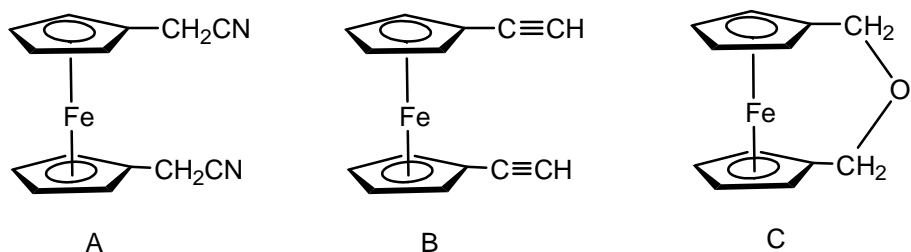
93. Each of the compounds A-D have been prepared using different well known ferrocene derivatives as starting materials. Identify these ferrocene derivatives and select from the given sets of reagents, the most suitable reaction conditions to convert ferrocene to these ferrocene derivatives from which compounds A-D can be prepared using the minimum number of steps.

1. Ferrocene, n-BuLi, TMEDA
2. Ferrocene, AlCl₃, Mg, CO₂
3. ferrocene, acetylchloride, AlCl₃, (1:2:2 ratio)
4. Ferrocene, acetic anhydride, H₃PO₄
5. Ferrocene, Me₂NCH₂NMe₂, H₃PO₄
6. Ferrocene, t-BuLi

(Gupta B D Elias A J. *Basic Organometallic Chemistry* 2013, Universities press, chapter 18)

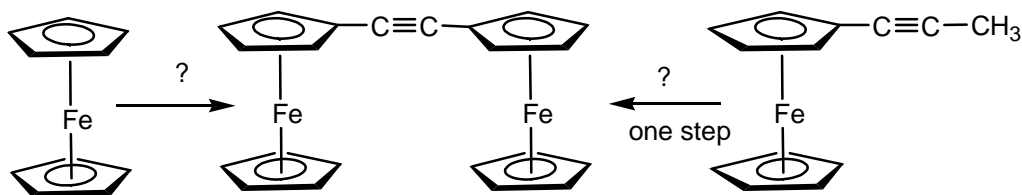


94. Starting from ferrocene show minimum steps with reagents used for the synthesis of the following compounds.



(Moritani, I., *J. Organomet. Chem.*, 1971, 26, 133.; Hillman, M., *Organometallics*, 1987, 6, 1737)

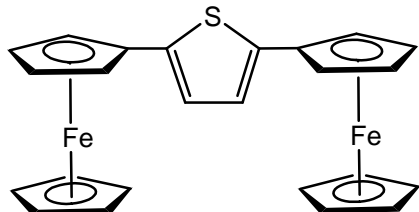
95. Starting from ferrocene give steps for the synthesis of the diferrocenyl alkyne X. Can compound X be prepared also from 3-ferrocenylprop-2-yne in a single step?



X

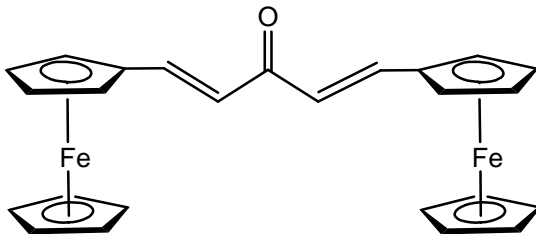
(Li, C., *Catal. Commun.*, 2009, 10, 1006)

96. The given 2,5-bis ferrocenyl thiophene has been prepared by Negishi coupling in good yields. Given thiophene, N-bromosuccinimide, t-BuLi, ZnCl₂, and PdCl₂(PPh₃)₂ provide schemes for the synthesis of this compound starting from ferrocene



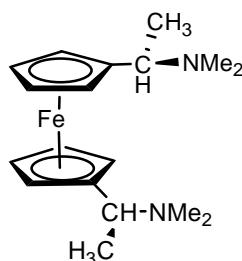
(Lang, H., *Inorg. Chem.*, 2011, 50, 10623)

97. Dibenzylidene acetone (dba) prepared by cross aldol condensation (Claisen-Schmidt reaction) is an excellent ligand used for stabilizing metals like Pd in zero oxidation state. Suggest a scheme to make the ferrocene analogue of this compound (phenyl groups replaced by ferrocene) starting from ferrocene and acetone.



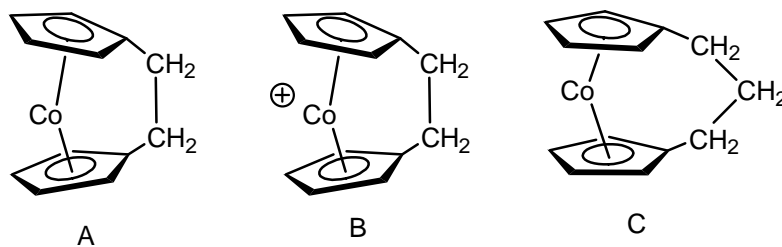
(Tolbert, L. M., *J. Am. Chem. Soc.*, 2010, 132, 10374)

98. Starting from ferrocene show reagents and steps towards the synthesis of the given 1, 1'-bis aminomethyl ferrocenyl derivative which is the precursor for the chiral biphosphine Mandyphos.



Chapter 19: Organometallic polymers

99. (a) Suggest synthetic routes for the preparation of the given cobalt based metallocenophanes
 (b) The tilt angles of the given metallocenophanes have been found to be 12.9, 27.1 and 21.4° (not in the order). Assign the tilt angles to the respective compounds. Also only one among these have been found to undergo ROP. Predict which one is it. [Given: The distance between the parallel Cp rings of normal cobaltocene is 3.44 Å while the same for $[\text{CoCp}_2]^+$ is 3.24 Å]
 (Manners *et al.* *J. Am. Chem. Soc.*, 2009, 131, 10382)



100. List the unique features of a ferrocenophane which helps one to decide whether it is likely to undergo thermal ring opening polymerization. Which among these is the most important?