

# Basic Organometallic Chemistry: 100+ New Problems and Exercises

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*While teaching organometallic chemistry to undergraduate and graduate students for the last two decades, the authors realized that solving problems in the classroom and giving them as assignments is an exciting and at the same time challenging methodology to generate interest in organometallic chemistry among students. This collection of new, original and literature supported problems in basic organometallic chemistry has been designed carefully by the authors, class tested at IIT Delhi and modified if found necessary. This collection is presented to interested faculty and students, all over the world to assist them in learning the basics of organometallic chemistry. This attempt is also a follow up of an earlier initiative by one of the authors entitled '100 problems and exercises in organometallic chemistry (2015)' which has been warmly accepted by teachers and students all over the world.*

*Each section of this new collection also has few solved problems at the outset to encourage students who are novices. The solutions to unsolved problems given in this collection can be obtained from the reference provided after each problem or by writing directly to any one of the authors by email: Prof. Anil J. Elias [eliasanil@gmail.com](mailto:eliasanil@gmail.com) or Prof. Selvarajan Nagendran [sisn@chemistry.iitd.ac.in](mailto:sisn@chemistry.iitd.ac.in)*

## Topics Covered

1. The 18-electron rule
2. Metal carbonyls
3. Metal alkyl and aryl complexes
4. Alkenes and alkynes as ligands
5. Phosphines and carbenes as ligands
6. Metal carbene and carbyne complexes
7. Metal sandwich complexes and metallocenes
8. Types of organometallic reactions
9. Ligand substitution reactions and fluxionality
10. Organometallics in catalysis: basics

***He who learns teaches, he who teaches learns.***

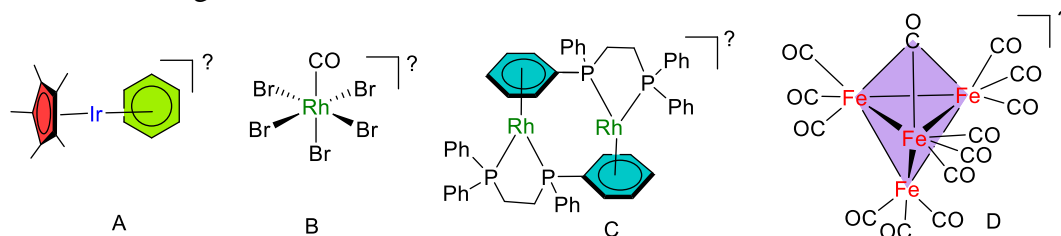
*Traditional Proverb*

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# 1. The 18-electron rule

## Solved Problems

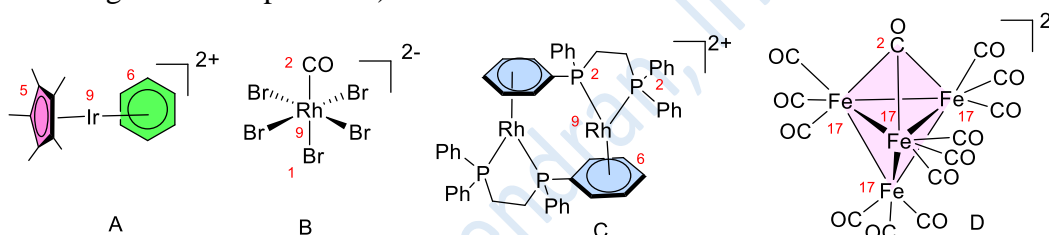
1. The given cationic / anionic complexes obey the 18 electron rule. The complexes having  $2^+$  overall charge are...



C. White, P. M. Maitlis, *J. Chem. Soc. A*, 1971, 3322-3326; D. Forster, *Inorg. Chem.*, 1969, 8, 2556; J. Halpern, D. P. Riley, A. S. C. Chan, J. J. Plutes, *J. Am. Chem. Soc.*, 1977, 91, 8055; N. N. Greenwood, *J. Chem. Soc., A*, 1969, 16, 2339-2345.

### Solution

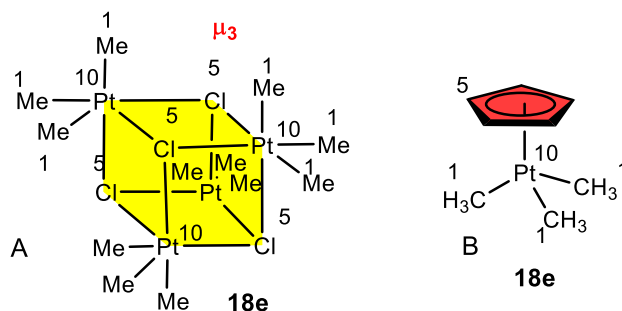
The compounds having  $2^+$  overall charge are A and C (Electron count as per neutral atom counting method is provided).



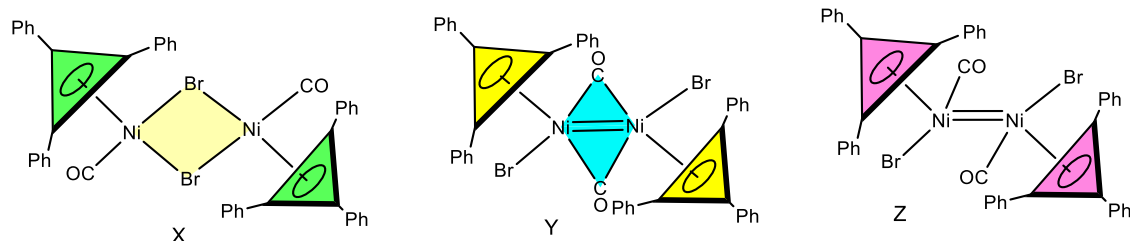
2. The reaction of  $\text{PtCl}_4$  with  $\text{MeMgBr}$  in 1:3 molar ratio resulted in an organometallic complex A having the formula  $[\text{Me}_3\text{PtCl}]_4$ . Compound A on reaction with 4 equivalents of cyclopentadienyl thallium (CpTl) resulted in a monomeric compound B. Given that both A and B obey the 18 electron rule and the coordination number around the metal does not exceed 6, arrive at the structures of compounds A and B.

R. E. Rundle, J. H. Sturdivent, *J. Am. Chem. Soc.*, 1947, 69, 1561.

### Solution



3. For the dimeric complex  $[(c\text{-Ph}_3\text{C}_3)\text{NiBr}(\text{CO})]_2$  which one among the given three possibilities is the most likely structure?



*E. W. Gowling, S.F. A Kettle, Inorg. Chem., 1964, 3, 604-605*

### Solution

Considering compliance with 18 e rule and nickel oxidation state (+2), all three structures seem possible. However, in reality, the compound has been found to adopt structure X having bridging bromines. It is generally observed that especially with first row transition metals, bridging ligands are favoured over metal-metal multiple bond formation for gaining 18 electrons. It is also observed that if anionic ligands and neutral ligands are present, most often the preference for bridging is more for the anionic ligand than the neutral ligand to gain 18 electrons as strain around the metal centre is also reduced in the process. The IR spectra of this compound gave a peak at  $2039\text{ cm}^{-1}$ .

4. The ligand that will make  $\text{Mo}(\text{NAr})(\text{CHR})(\text{OR}')_2$  (with a linear  $\text{Mo}=\text{N}-\text{Ar}$  moiety) stable is,  $[\text{Ar} = 2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3, \text{R} = \text{C}(\text{Ph})(\text{Me})_2$  and  $\text{R}' = \text{C}(\text{CH}_3)(\text{CF}_3)_2]$
- (i) bipyridine      (ii)  $\eta^6\text{-C}_6\text{H}_6$       (iii) pyridine      (iv)  $(\eta^8\text{-C}_8\text{H}_8)^{2-}$

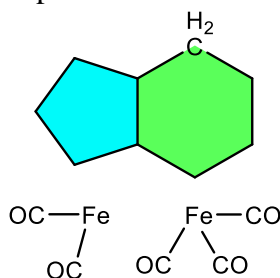
*Gulyás, H., Hayano, S., Madarász, Á. et al. Commun. Chem. 2021, 4, 71.*

### Solution

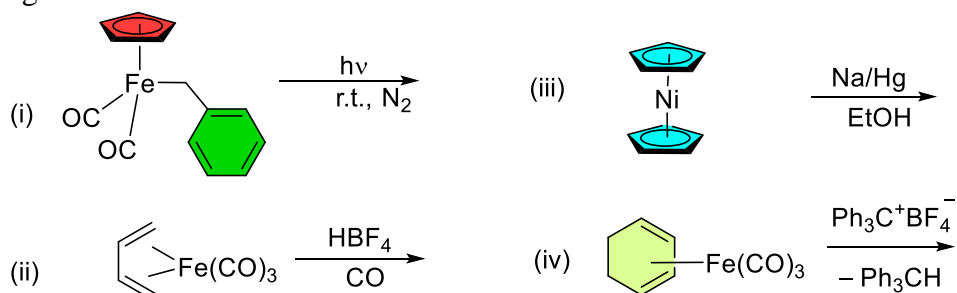
Imido ( $\text{Ar}-\text{N}^{2-}$ ) is a dianionic ligand having a lone pair on the nitrogen. So according to neutral atom counting method, similar to NO it will be a 2e donor in the bent form and 4e donor in the linear form. Given that it is linear, it will be 4e donor and total electron count of the complex will be 14. The correct option is (i) bipyridine which will make the complex an 18 e species.

## Unsolved Problems

5. The partial structure of compound  $(\text{C}_9\text{H}_8)\text{Fe}_2\text{CO}_5$  is given below. Using the 18-electron rule as the guide, complete its structure by finding out the hapticity of the rings and the nature of the (zero/single/double) metal-metal bond. **Hint:** the methylene carbon atom of the six-membered ring is not in the plane of the other ring carbon atoms.

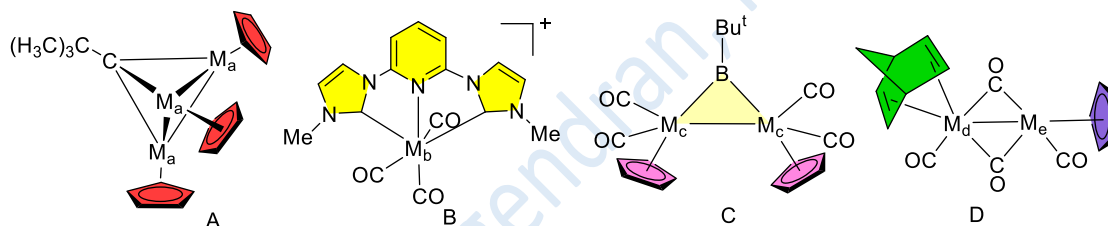


6. Given that the final products obey the 18 electron rule, which among the products of the given reactions have the metal NOT involved in an  $\eta^3$  coordination with one of the ligands?



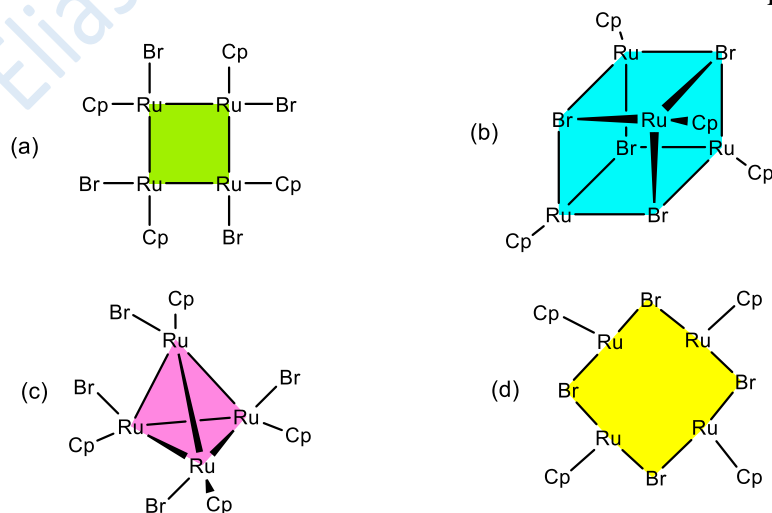
(a) J. P. Blaha, M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, 107, 2694-2702; (b) M. Dubeck, A. H. Filley, *J. Am. Chem. Soc.*, 1961, 83, 1257.

7. The following complexes obey the 18 electron rule and are made of first row transition metal ions. Determine those complexes having the same metal atoms.



(a) Booth B. L. *J. Organometal. Chem.*, 1979, 178, 371, (b) Luca O.R., *Organometallics*, 2019, 38, 1248 (c) H. Braunschweig, M. Mueller, *Chem. Ber.*, 1997, 130, 1295-1298 (d) Campbell I.L.C., *Dalton Trans.*, 1975, 226.

8. Reaction of  $[\eta^5\text{-CpRu}(\eta^6\text{-naphthalene})]^+\text{BF}_4^-$  with  $(\text{Bu}_4\text{N})\text{Br}$  resulted in the formation of a stable complex having four  $\eta^5\text{-CpRuBr}$  units. Naphthalene and  $(\text{Bu}_4\text{N})\text{BF}_4$  were the side products of this reaction. Choose the correct structure of this new compound.



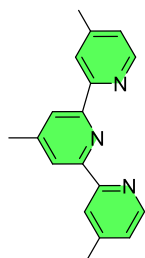
D. S. Perekalin, E. E. Karslyan, E. A. Trifanova, A. I. Kononov, N. L. Loskutova, Y. V. Nelyubina, A. R. Kudonov., *Eur. J. Inorg. Chem.*, 2013, 481-493.

9.  $\text{Ru}_2\text{Co}_2(\text{CO})_{13}$  (A) and  $\text{Fe}_2\text{Co}_2(\text{CO})_{11}\text{S}_2$  (B) are two bimetallic carbonyl complexes having 4 metal atoms each. In compound A, there are four  $\mu_2$  CO groups while in B there is one  $\mu_2$  CO and two  $\mu_4$  sulfur atoms present. The number of metal-metal bonds present in compounds A and B respectively are

(i) 6 and 6      (ii) 4 and 6      (iii) 6 and 4      (iv) 4 and 4

*H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 1981, 20, 679, 680*

10. The reaction of  $(\text{Br})\text{Re}(\text{CO})_5$  with the given ligand in refluxing toluene for four hours afforded product A with the evolution of a colorless gas. Heating compound A at  $270^\circ\text{C}$  for six hours gave compound B and the evolution of a colorless gas. Compound B's reaction with pyridine and  $\text{AgOTf}$  in refluxing toluene gave an ionic rhenium compound C without a gas's evolution ( $\text{OTf} = \text{CF}_3\text{SO}_3^-$ ; triflate). Considering that compounds A, B, and C are stable, choose all the correct statements.

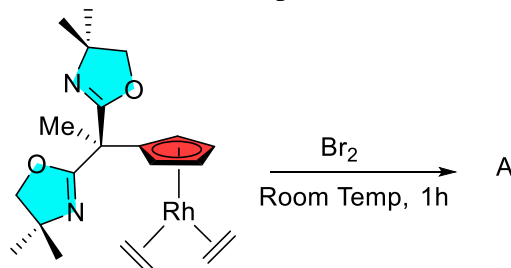


- (i) Compound B has three Re-N, one Re-Br, and three Re-CO bonds.  
 (ii) Compound A has three Re-N, one Re-Br, and four Re-CO bonds.  
 (iii) Compound B has three Re-N, one Re-Br, and two Re-CO bonds.  
 (iv) Compound C has four Re-N, one Re-Br, and two Re-CO bonds.  
 (v) Compound A has two Re-N, one Re-Br, and three Re-CO bonds.  
 (vi) Compound C has four Re-N and two Re-CO bonds.

*T. Auvray, B. D. Secco, A. Dubreuil, N. Zaccheroni, G. S. Hanan, Inorg. Chem. 2021, 60, 70–79*

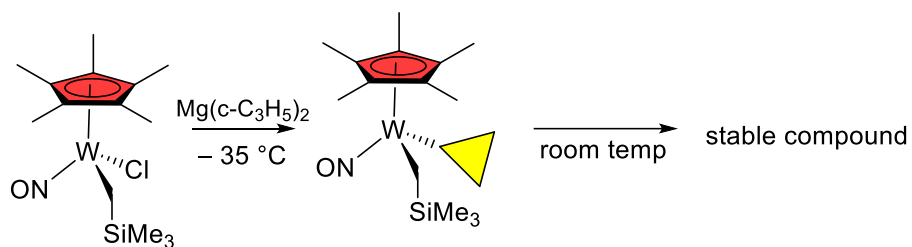
11. Reaction of the given complex with 1 mole of  $\text{Br}_2$  at room temperature gave compound A along with the release of a gas. A was found to obey the 18 electron rule. Structural analysis of compound A indicated presence of Rh-bromine and Rh-N bonds. Choose the correct statements from the following

- (i) The formal oxidation state of rhodium in A is +1  
 (ii) The formal oxidation state of rhodium in A is +3  
 (iii) 2 molecules of ethylene are released during the reaction  
 (iv) A has 2 Rh-N bonds present in it  
 (v) A has one Rh-N bond and 2 Rh-Br bonds present in it



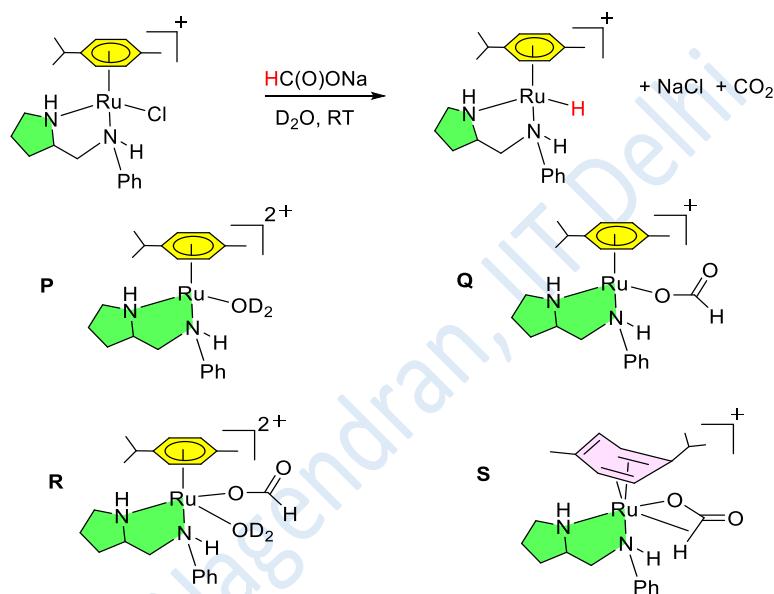
*B. M. Schmidt, H-A Ho, K. Basemann, A. Ellern, T. L. Windus, A. D. Sadow, Organometallics, 2018, 37, 4055-4069*

12. To prepare a cyclopropyl derivative of the given tungsten complex, it was reacted with cyclopropyl Grignard reagent and the expected compound was formed at  $-35^\circ\text{C}$ . However, on warming to room temperature, the molecule rearranged to give a more stable compound with the same molecular weight. Predict the structure of the new compound.



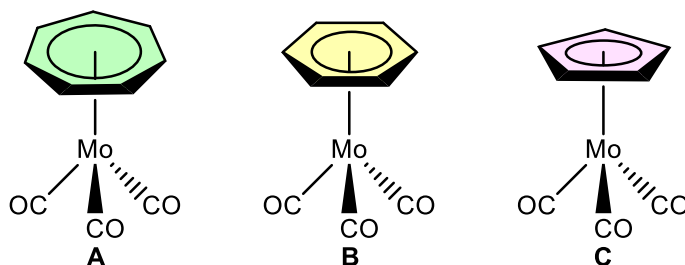
*K. D. J. Parker, L. Vendier, M. Etienne, Organometallics, 2018, 37, 1221-1224*

13. Given that ruthenium does not change its oxidation state during the reaction, identify the structure(s) for STABLE intermediates which are likely to be part of the reaction mechanism.



*A.K. Pandia Kumar, A. G. Samuelson, J. Chem. Sci., 2016, 128, 1405-1415.*

14. Find the unstable compounds among A–C. Then, stabilize the unstable compounds appropriately and draw three stable structures: two are charged, and one has no charge. **Note:** For stabilization, the addition of ligands, removal of ligands, and metal-metal bond formation are not allowed. However, modifying the existing ligand by adding hydrogen is permitted.



*T. Deganello, T. Boschi, J. Organometal. Chem., 97, C46-C48, 1975, E. W. Abel, M. A. Bennett, G. Wilkinson, Proc. Chem. Soc. London, 152-153, 1958,*

## 2. Metal carbonyls

## Solved Problems

15. For Vaska's complex,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  which among the given activities will decrease the  $\nu_{\text{CO}}$  stretching frequency of the coordinated CO ligand from  $1967 \text{ cm}^{-1}$  to lower value(s)? Justify your answer.

- Replacing both  $\text{PPh}_3$  by  $\text{PMe}_3$
- Oxidative addition by  $\text{MeI}$
- Replacing  $\text{Cl}^-$  by  $\text{CH}_3^-$
- Replacing  $\text{Cl}^-$  by  $\text{CH}_3\text{CN}$  (cationic complex)

*Organometallic compounds of cobalt, rhodium and iridium. Ed. C. White, Chapman and Hall chemistry source books, 1998.*

### Solution

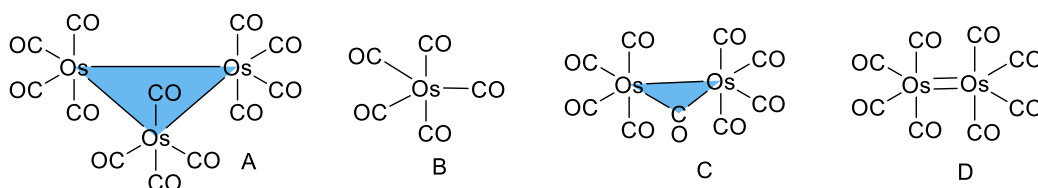
The correct options are (a) and (c) where electron density on the metal gets increased by the activity. The actual  $\nu_{\text{CO}}$  stretching frequencies are given below.

- |   |                        |
|---|------------------------|
| (i) Replacing both $\text{PPh}_3$ by $\text{PMe}_3$                       | $1938 \text{ cm}^{-1}$ |
| (ii) Oxidative addition by $\text{MeI}$                                   | $2047 \text{ cm}^{-1}$ |
| (iii) Replacing $\text{Cl}^-$ by $\text{CH}_3^-$                          | $1935 \text{ cm}^{-1}$ |
| (iv) Replacing $\text{Cl}^-$ by $\text{CH}_3\text{CN}$ (Cationic complex) | $1975 \text{ cm}^{-1}$ |

16. The reaction of  $\text{OsO}_4$  with CO (80 atm,  $175^\circ\text{C}$ ) resulted in an osmium carbonyl **A** with three osmium atoms. Heating **A** with a large excess of CO (200 atm,  $280^\circ\text{C}$ ) resulted in three moles of osmium carbonyl **B**. Two moles of compound **B** on UV photolysis resulted in a symmetrical diosmium carbonyl **C** with the evolution of a gas. The structure of compound **C** is different from the analogous iron carbonyl. Further, flash photolysis of compound **C** with UV radiation gave another dimeric osmium carbonyl **D** again with the evolution of a gas. Compounds **A** to **D** are homoleptic neutral carbonyls obeying the 18-electron rule; they all have at least 4 terminal CO groups attached to each Os atom. Given the IR spectral data of these compounds (**A**:  $2070, 2036, \text{ and } 2003 \text{ cm}^{-1}$ ; **B**:  $2035 \text{ and } 1993 \text{ cm}^{-1}$ ; **C**:  $1778, 2000, 2013, 2024, 2038, \text{ and } 2080 \text{ cm}^{-1}$ ; **D**:  $2057, 2023, \text{ and } 2006 \text{ cm}^{-1}$ ), arrive at their structures.

*S. R. Drake.; P. A. Loveday, Inorg. Synth., 1990, volume 28, pages 230–231. F. W. Grevels, W. E. Klotzbuecher, F. Seils, K. Schaffner, and J. Takats, J. Am. Chem. Soc. 1990, 112, 1995–1996. B. Xu, Q-S Li, Y. Xie, R. B. King, and H. F. Schaefer, Inorg. Chem. 2008, 47, 3869–3878*

### Solution



17. A neutral divanadium compound, **F**, is made of two interacting fragments,  $\text{Cp}_2\text{V}^1$  and  $\text{V}^2(\text{CO})_6$ . It has two different  $\text{V}^2\text{-C}$  and  $\text{C-O}$  bond lengths; however, all the  $\text{V}^2\text{-C-O}$

moieties are almost linear. Its  $V^2$  fragment obeys the 18-electron rule. The reaction of compound **F** with two moles of CO converted it into the ionic compound **G**, where both  $V^1$  (cation) and  $V^2$  (anion) units obey the 18-electron rule. Given the IR spectral data of compounds **F** and **G** (**F**: 2032, 1945, 1890, 1857, and  $1708\text{ cm}^{-1}$ ; **G**: 2008, 1954, and  $1853\text{ cm}^{-1}$ ), draw the structures of compounds **F** and **G**. Also, mention the oxidation states of  $V^1$  and  $V^2$  atoms in compounds **F** and **G**.

*J. H. Osborne, A. L. Rheingold, W.C. Trogler, J. Am. Chem. Soc., 1985, 107, 6292-6297*

### Solution



18. (i) The IR spectra of the following 18-electron complexes,  $[\text{Ir}(\text{CO})_6]^{3+}$  (**X**),  $[\text{Ir}(\text{CO})_3]^{3-}$  (**Y**), and  $\text{Ir}_4(\text{CO})_{12}$  (**Z**), were measured and compared with free CO. Match the complexes with the correct  $\nu_{\text{CO}}$  values (i) to (iv): (i)  $2060$  and  $2020\text{ cm}^{-1}$ ; (ii)  $1642\text{ cm}^{-1}$ ; (iii)  $2143\text{ cm}^{-1}$ ; (iv)  $2295$ ,  $2276$ , and  $2254\text{ cm}^{-1}$ .
- (ii) The total number of metal-metal bonds in complex **Z** is \_\_\_\_\_.

*J. E. Ellis et al., Inorg. Chem., 2001, 40, 5279; R. D. Pergola, G. Luigi, S. Martinengo, Inorg. Synth., 1990, 28, 245-247*

### Solution

$[\text{Ir}(\text{CO})_6]^{3+}$  (**X**) (iv)  $2295$ ,  $2276$ , and  $2254\text{ cm}^{-1}$

$[\text{Ir}(\text{CO})_3]^{3-}$  (**Y**) (ii)  $1642\text{ cm}^{-1}$

$\text{Ir}_4(\text{CO})_{12}$  (**Z**) (i)  $2060$  and  $2020\text{ cm}^{-1}$

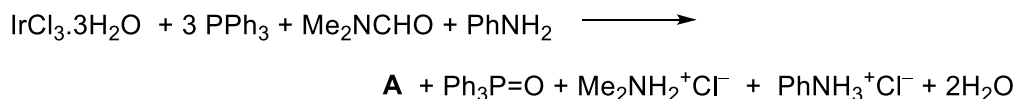
The total number of metal-metal bonds in complex **Z** is 6.

### Unsolved Problems

19. Reaction of 1 mole of  $\text{Fe}_2(\text{CO})_9$  with 1 mole of benzylidene acetone,  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}(\text{O})\text{CH}_3$  resulted in the formation of an iron carbonyl based 18 electron compound along with formation of another homoleptic 18 electron iron compound with the release of a colorless gas. NMR spectra of the compound with benzylidene acetone indicated that the phenyl group is not linked to the iron centre. Draw the structures of the two iron carbonyl compounds.

*B. F. G. Johnson, Inorg. Synth., 1990, 28, 52-55.*

20. From the given balanced equation find out the identity of compound **A** and draw its structure.





Which of the following statements are true with respect to compound A

- (i) Compound A shows an IR stretching band at  $1720\text{ cm}^{-1}$
- (ii) Compound A has iridium in +3 oxidation state
- (iii) Compound A is a dimeric compound
- (iv) The geometry of the complex A is square planar
- (v) Compound A obeys the 18 e rule
- (vi) Compound A can bind  $\text{O}_2$  reversibly

*R. J. Angelici, Synthesis and techniques in inorganic chemistry, 1999, University Science books, pp 190.*

21. The reaction of nickelocene ( $\eta^5\text{-Cp}_2\text{Ni}$ ) and  $\text{Ni}(\text{CO})_4$  in 1:1 molar ratio in benzene resulted in the dimeric compound A. A similar equimolar reaction of nickelocene with  $\text{Fe}(\text{CO})_5$  resulted in another dimeric compound B. Both compounds obey the 18 electron rule. Both reactions involve the release of a colorless gas and hapticity of Cp remains 5 in both compounds A and B. The infrared spectra of A gave a very strong band at  $1836\text{ cm}^{-1}$  while infrared spectra of B gave strong bands at 1801, 1887, 1969 and  $1989\text{ cm}^{-1}$ . Select the correct statements from the following with respect to compounds A and B.

- (i) Compound A has two bridging CO and no metal-metal bonds
- (ii) Compound A has two terminal CO and one metal-metal bond
- (iii) Compound A has two bridging CO and one metal-metal bond
- (iv) Compound B has two bridging and one terminal CO ligands
- (v) Compound B has two terminal and one bridging CO ligands
- (vi) Compound B has all terminal CO ligands

*P. McArdle and A. R. Manning, J. Chem. Soc. A, 1971, 717.*

22. Exposing  $\text{Fe}(\text{CO})_5$  to sunlight in acetic acid resulted in the formation of a new iron carbonyl A along with release of a colorless gas. Reactions of one mole of A with 2 moles of allyl bromide in hexane resulted in compound B (emp. formula  $\text{FeC}_6\text{H}_5\text{O}_3\text{Br}$ ) along with release of the same colourless gas. Treating B with excess Zn dust resulted in a new compound C (emp. formula  $\text{FeC}_6\text{H}_5\text{O}_3$ ) along with  $\text{ZnBr}_2$  as side product. The infra-red spectra of A showed bands at 2018 and  $1826\text{ cm}^{-1}$  while infra-red spectra of compounds B and C showed carbonyl bands in the range of  $1950$  to  $2050\text{ cm}^{-1}$ . Given that compounds A, B and C obey the 18 electron rule and B and C has allyl groups with the same hapticity, arrive at their structures.

Which among the following statements are **TRUE** for compounds A, B and C

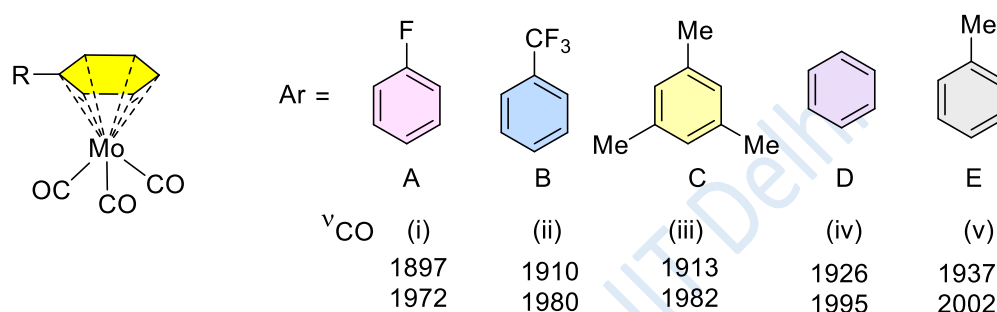
- (i) Compound B has terminal bromine and monohapto allyl groups present
- (ii) Compounds A and C have metal-metal single bonds present
- (iii) Only compound A has bridging carbonyls
- (iv) Compounds A and C have bridging carbonyls
- (v) Compound B has one allyl group while C has two allyl groups present
- (vi) Compound B has terminal bromine and trihapto allyl group present

*E. L. Muetterties, J. Am. Chem. Soc., 1978, 100, 4107.*

23. Reaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{Br}_2$  resulted in an orange colored powdery compound A. On keeping A under high vacuum in a sealed tube at room temperature for several days resulted in the formation of dark orange crystals of a new compound B. Analysis of A and B indicated only infra red bands in the range of  $2045\text{-}1950\text{ cm}^{-1}$ . A and B are stable compounds and both contain bromine atoms. Draw the structures of A and B.

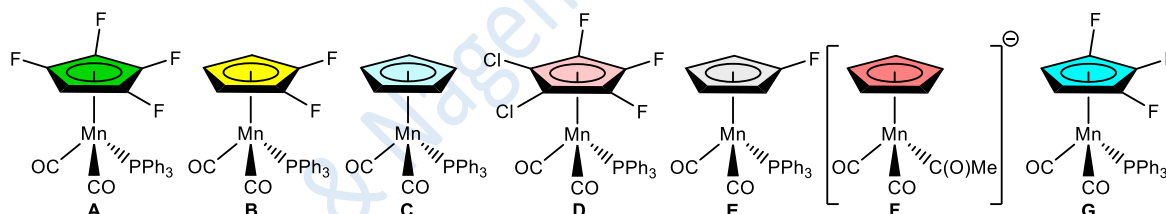
*A Hagihara, Acta Cryst, 2006, 62, i72*

24. The  $\nu_{\text{CO}}$  stretching bands of a series of piano stool complexes  $(\eta^6\text{-Ar})\text{Mo}(\text{CO})_3$  were obtained from their infrared spectra. Match the aryl rings with the correct spectral data given



*P. Zanello, J. Organomet. Chem., 2004, 689, 2158; A. N. Nesmeyanov, J. Organomet. Chem., 1975, 102, 185.*

25. Match the compounds A-G with their terminal carbonyl stretching bands I-VII (in  $\text{cm}^{-1}$ ).



Terminal carbonyl stretching bands (in  $\text{cm}^{-1}$ ): I: 1920, 1857; II: 1962, 1903; III: 1900, 1825; IV: 1940, 1878; V: 1957, 1900; VI: 1938, 1870; VII: 1946, 1887.

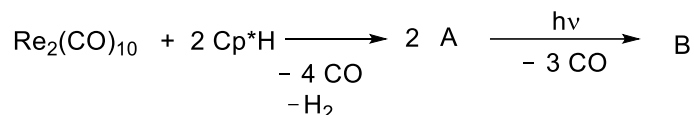
*C. Klein-Hessling, T. Blockhaus, K. Sunkel, J. Organometal. Chem., 2021, 943, 121833.*

26. Refluxing a mixture of  $\text{CpRh}(\text{CO})_2$  with  $\text{Me}_3\text{NO}$  in benzene for 2 hours followed by chromatographic separation resulted in three compounds, A, B and C having two, three and four  $\eta^5\text{-CpRh}$  units respectively along with the release of  $\text{CO}_2$  and  $\text{Me}_3\text{N}$ . Infrared spectra of red colored dimer A gave bands at  $1989$  and  $1841\text{ cm}^{-1}$  while that of green colored trimer B (major product) gave bands at  $1827$ ,  $1783$  and  $1766\text{ cm}^{-1}$ . The black colored tetramer C gave bands at  $1700$  and  $1671\text{ cm}^{-1}$ . Compounds A, B and C obey the 18 e rule. Arrive at their possible structures.

*J. R. Shapley, J. Am. Chem. Soc. 1976, 98, 7433-7435.*

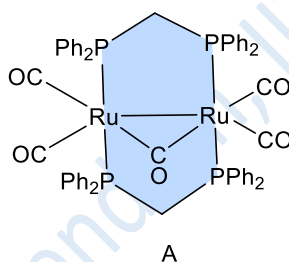
27. Reaction of  $\text{Re}_2(\text{CO})_{10}$  with 2 moles of  $\text{Cp}^*\text{H}$  resulted in the formation of a 18 electron monomeric rhenium compound A along with release of  $\text{CO}$  and  $\text{H}_2$ . The infrared spectrum

of A showed peaks at 2015 and 1915  $\text{cm}^{-1}$  and  $^1\text{H}$  NMR spectra gave a singlet at 2.21 ppm. Two moles of compound A on exposing to UV radiation resulted in the loss of three moles of CO and resulted in a new 18 electron compound B. Infrared spectra of B showed peaks at 1750  $\text{cm}^{-1}$  and  $^1\text{H}$  NMR spectra gave a singlet at 2.21 ppm. Arrive at the structures of compounds A and B.



*J. K. Hoyano, W. A. G. Graham, J. Chem. Soc., Chem Commun., 1982, 27.*

28. An equimolar reaction of compound **A** with  $\text{O}_2$  in the presence of two equivalents of  $\text{HBF}_4$  resulted in a symmetrical dicationic complex **B** with the evolution of a colorless gas. Compound **B** has two OH ligands, which form a four-membered  $\text{Ru}_2\text{O}_2$  ring. Given that compound **B** is stable and shows bands in the carbonyl stretching region (2072, 2061, 2025, 2007  $\text{cm}^{-1}$ ), draw its structure. Further, metal-phosphorus bonds are not affected during the reaction.

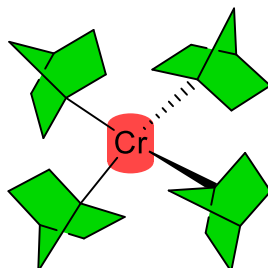


*J. Kuncheria, Y. Gao, R. J. Puddappatt, J. Organometal. Chem., 2016, 812, 183-189*

### 3. Metal-alkyl and aryl compounds

#### Solved Problems

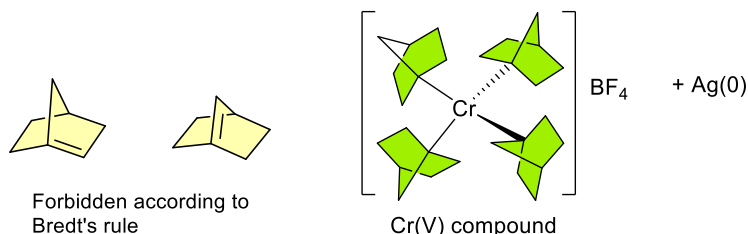
29. The chromium tetra-alkyl compound  $\text{Nor}_4\text{Cr}$  (Nor= norbornyl) is highly stable to air and moisture and to heating up to 250  $^\circ\text{C}$ . It does not degrade in the presence of dilute sulfuric acid as well. Give reasons for its unusual stability. What happens when  $\text{Nor}_4\text{Cr}$  is treated with  $\text{AgBF}_4$ ?



*Bower, B. K., J. Am. Chem. Soc., 1974, 94, 2512*

## Solution

According to Bredt's rule, a double bond cannot be placed at the bridgehead of a bridged bicyclic system, unless the rings are large enough. Although  $\beta$ -H elimination is a possible way of degradation for this molecule as the four membered intermediate required is quite possible, it will result in violation of the Bredt's rule of the resulting norbornene. Hence this compound is highly stable.



30. A solution of n-BuLi in decane on heating to 100 °C in the complete absence of air and moisture was found to decompose giving a gaseous hydrocarbon as the major product along with a decane insoluble solid. The solid on reaction with  $\text{AlCl}_3$  gave a well-known reagent having both Li and Al. The hydrocarbon gas formed is

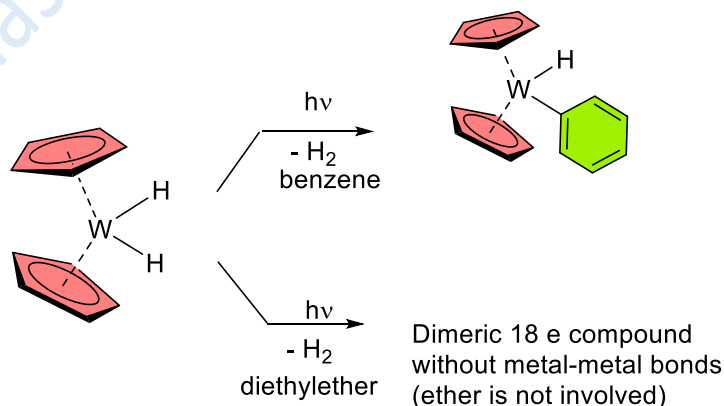
- (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$                       (ii)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$       (iii)  $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]_2$   
 (iv)  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3$

*R. A. Finnigen, J. Org. Chem., 1965, 30, 4138*

## Solution

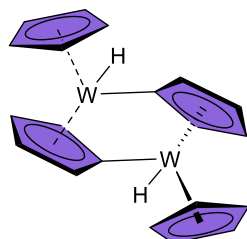
A= 1-butene; B =  $\text{LiAlH}_4$ . n-BuLi on heating undergoes  $\beta$ -hydrogen elimination to form LiH and 1-butene

31. UV irradiation of the given tungsten hydride in presence of benzene results in the reductive elimination of  $\text{H}_2$  and oxidative addition of benzene leading to the formation a new compound as shown. In the presence of diethylether as solvent, a similar reaction happens resulting in the formation of a dimeric 18 e compound without metal-metal bonds. Predict the structure of this new compound.

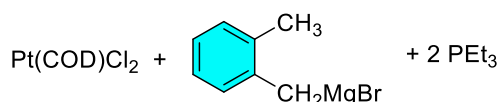


*M. Berry, S. G. Davies, M. L. H. Green, Chem. Commun., 1978, 3, 99-100*

## Solution:

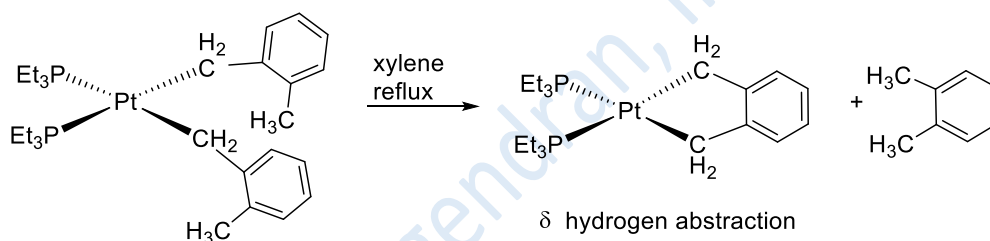


32. Reaction of  $\text{Pt}(\text{COD})\text{Cl}_2$  with 2 moles of the given Grignard reagent and 2 moles of  $\text{PEt}_3$  resulted in a square planar complex X having two  $\text{PEt}_3$  units. Heating compound X in refluxing xylene resulted in the release of o-xylene [ $\text{C}_6\text{H}_4(\text{CH}_3)_2$ ] and formation of a new square planar complex Y. Find out the structures of compound X and Y and indicate the type of reaction happening during the release of the o-xylene.



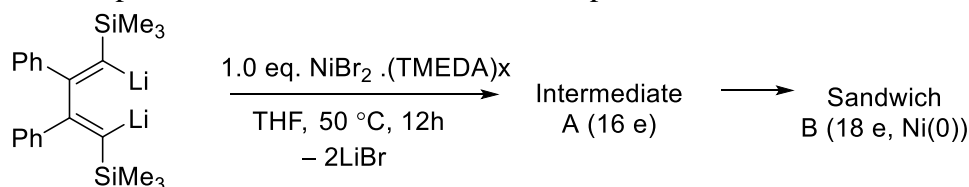
*J. Cole Hamilton, J. Chem. Soc., Chem. Comm., 1980, 238*

### Solution



### Unsolved Problems

33. Reaction of 2 eq. of the given dilithiated substituted butadiene with 1 eq.  $\text{NiBr}_2(\text{TMEDA})_x$  in THF at  $50^\circ\text{C}$  resulted in the formation of a sandwich compound B which obeys the 18 electron rule with nickel in the 0 oxidation state. The intermediate A, formed during this reaction was a 16 electron species with nickel in the +2 oxidation state which underwent reductive elimination to give B.  $^1\text{H}$  NMR of the intermediate A indicated presence of 4 Me groups and 2  $\text{CH}_2$  groups (in addition to  $\text{Me}_3\text{Si}$  groups) which were absent in the sandwich compound B. Draw the structures of compounds A and B.



*C. Yu, W-X Zhang, Z Xi, Organometallics, 2018, 37, 4100–4104*

34. Reaction of the given cationic cycloheptatrienyl molybdenum tricarbonyl with methoxide at low temperature was found to follow the given sequence of reactions. The methoxide first binds to the metal centre forming neutral complex A, followed by a migratory insertion involving one of the carbonyls to give the ester unit bound B. On bringing to

room temperature. B undergoes deinsertion of the carbonyl and transfer of the methoxy group to the cycloheptatrienyl ring forming a 7-exo substituted cycloheptatrienyl ring bound to  $\text{Mo}(\text{CO})_3$ .

Given that both A, B and C follow the 18 e rule, identify the hapticity of the cycloheptatrienyl ring in complexes A, B and C.

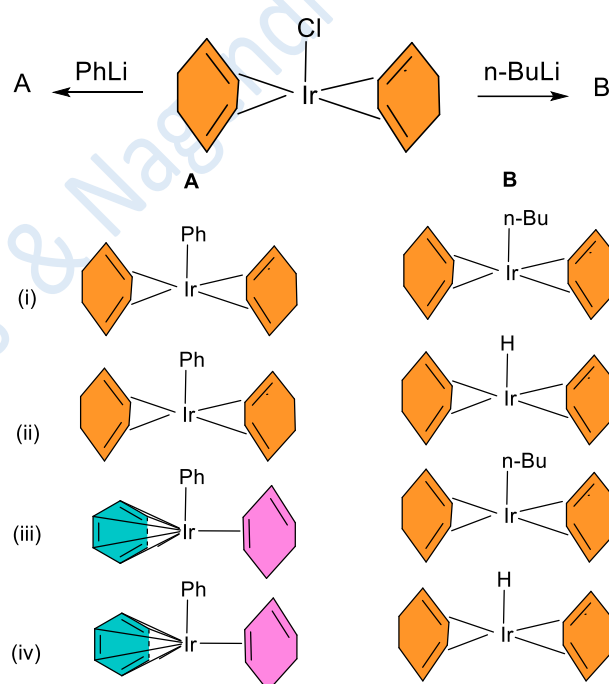
- (i) 6, 7, 6 (ii) 5, 7, 6 (iii) 5, 5, 6 (iv) 4, 7, 6

*M. L. H. Green, Chem. Rev., 1995, 95, 439.*

35. Irradiating  $\text{CpRh}(\text{C}_2\text{H}_4)_2$  in a mixture of hexane and benzene resulted in three products A, B and C with B being the major product. All compounds A, B and C obeyed the 18 electron rule and did not have ethylene in them but had one benzene unit in each of them showing different hapticities and deviation from planarity of the benzene ring in two cases. Compounds B and C had 2 and 3 rhodium atoms respectively connected by metal-metal bonds. Cp ring(s) was (were) present in all three showing only  $\eta^5$  hapticity. Arrive at the structures of A, B and C.

*J. Mueller, Angew. Chem. Int. Ed., 1993, 32, 1697.*

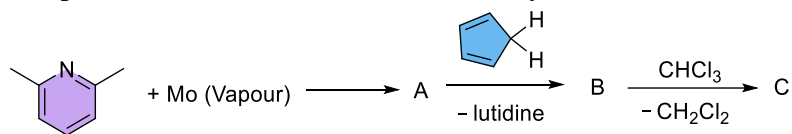
36. The compound  $\text{Ir}(\text{CHD})_2\text{Cl}$  (CHD = 1, 3-cyclohexadiene) was reacted with phenyllithium and n-butyllithium. The products obtained from these reactions A and B are



*J. Mueller, J. Organometal. Chem., 1994, 471, 249-258*

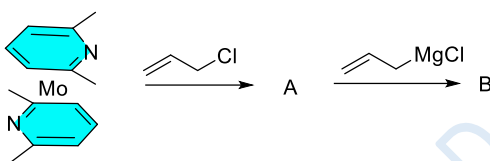
37. Reaction of lutidine with vapours of molybdenum metal was found to result in a stable sandwich compound A. A on reaction with freshly prepared cyclopentadiene (CpH) resulted in a bent sandwich compound B along with release of lutidine. Reaction of B with

chloroform resulted in compound C along with formation of dichloromethane. Suggest structures for compounds A, B and C all of which obeys the 18 electron rule.



*M. L. H. Green, J. Organometal. Chem. 1996, 513, 247-253*

38. The reaction of bis lutidine molybdenum with allyl chloride resulted in the formation of a complex A along with release of a lutidine molecule. Further reaction of complex A with allyl magnesium chloride resulted in the formation of complex B. Both A and B obey the 18 electron rule and analysis of A indicated presence of chlorine which was absent in B. Arrive at the structures of A and B.



*M. L. H. Green, J. Organometal. Chem., 1996, 513, 247-253*

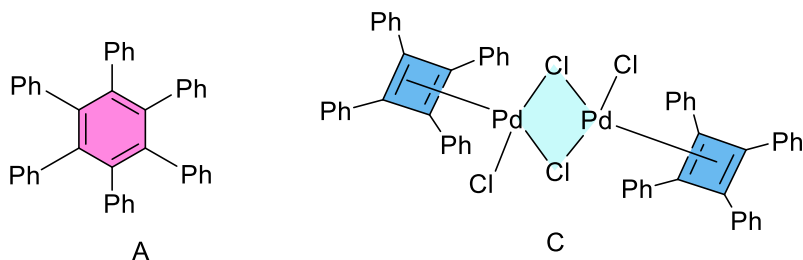
## 4. Metal-alkenes and alkynes

### Solved Problems

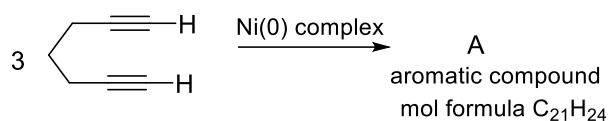
39. Reaction of catalytic amounts of  $\text{PdCl}_2(\text{benzonitrile})_2$  with excess diphenylacetylene in benzene solvent resulted in a metal free aromatic hydrocarbon A. The same reaction (but in 1:2 molar ratio) when performed in ethanol-chloroform mixture resulted in a 16 electron palladium compound B with empirical formula  $(\text{C}_{30}\text{H}_{25}\text{OPdCl})$  which on further reaction with HCl gave an 18 electron palladium compound C with the elimination of ethanol. Compound C has as ligands, chlorines and a cyclobutadiene derivative bound to palladium. Arrive at the structures of A and C

*Maitlis P M, J. Am. Chem. Soc. 1962, 84., 2329-2334*

**Solution:**

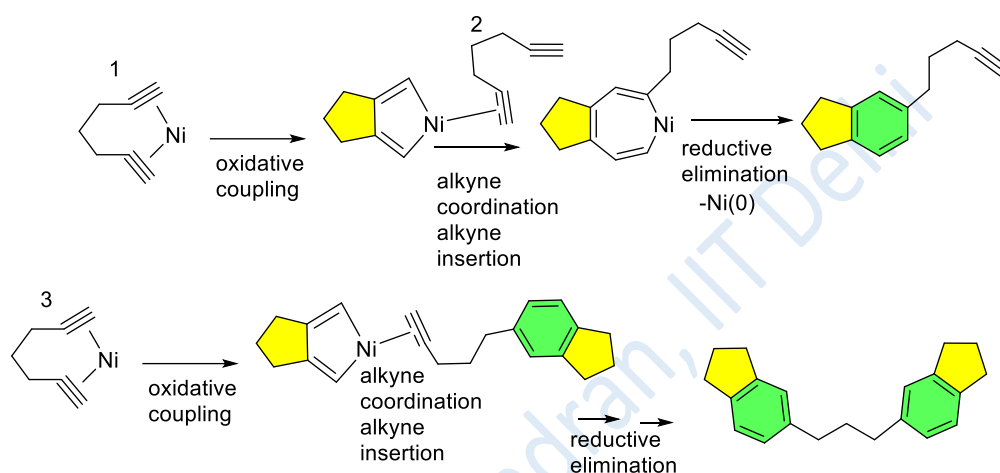


40. Three moles of the given dialkyne in the presence of a Ni(0) complex was found to result in a substituted aromatic hydrocarbon compound with molecular formula C<sub>21</sub>H<sub>24</sub>. Predict the structure this compound and propose a suitable mechanism.

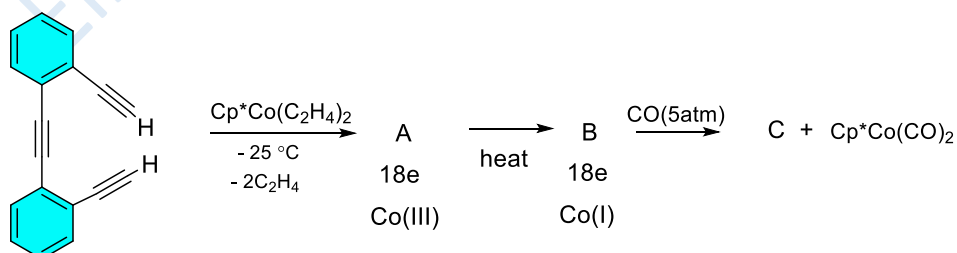


*S. Saito, M. Yamamoto, Chem Rev., 2000, 100, 2901-2915*

### Solution



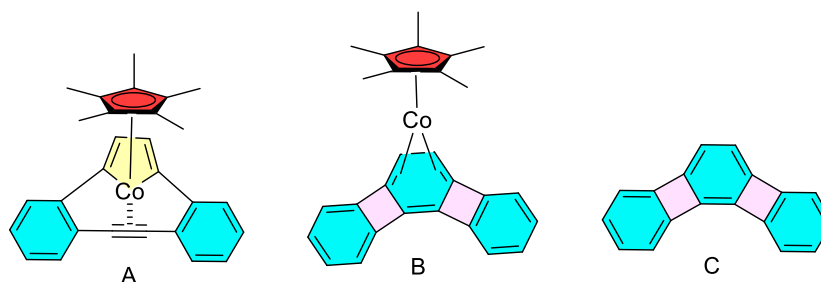
41. The equimolar reaction of the given trialkyne with Cp\*Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> at -25 °C was found to result in the release of two molecules of ethylene and the formation of a 18e Co(III) complex A. A on heating at 85 °C was found to rearrange to another 18e compound B having cobalt in the +1 oxidation state. B on heating with CO gas (5 atm) at 85 °C gave an organic compound C along with Cp\*Co(CO)<sub>2</sub>. Draw structures of compounds A, B and C. Molecular weights of A and B are same and infrared spectra of A showed a peak around 1922 cm<sup>-1</sup> which was absent in B and C.



*K. P. C. Vollhardt, J. Am. Chem. Soc. 1998, 120, 32, 8247-8248*

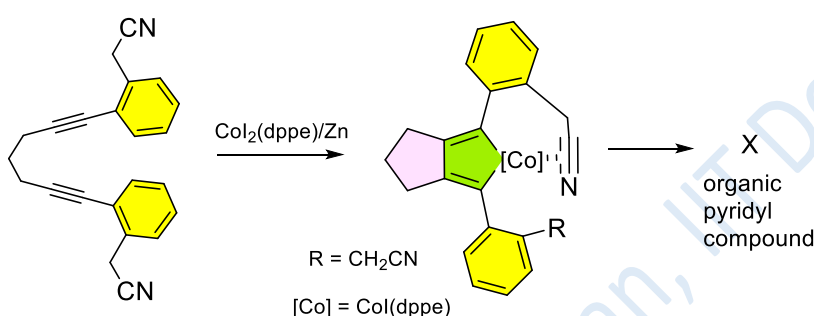
### Solution:





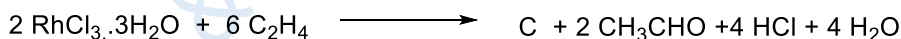
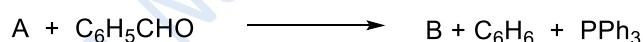
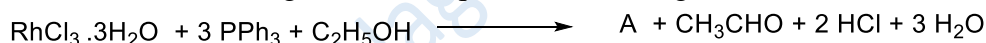
## Unsolved Problems

42. Predict the structure of organic pyridyl compound X which was formed from the cobalt catalysed cyclotrimerization reaction.



*H-T Chang, M. Jegannohan, C.H. Cheng, Org. Lett, 2007, 9, 505.*

43. Consider the following balanced equations involving RhCl<sub>3</sub>.3H<sub>2</sub>O



Which of the following statements are true with respect to compounds A, B and C

- (i) Compounds A, B and C are square planar 16 e complexes
- (ii) All of them are monomeric rhodium complexes
- (iii) All of them contain rhodium in the +1 oxidation state
- (iv) None of them contain CO as a ligand
- (v) A, B and C have at least one chlorine as terminal ligand
- (vi) All three reactions involve reduction/oxidation of the metal centre

*M. C. Baird, C. J. Nymen, G. Wilkinson, J. Chem. Soc. A., 1968, 348-351; R. Cramer, Inorg. Synth., 1974, 15, 14-18.*

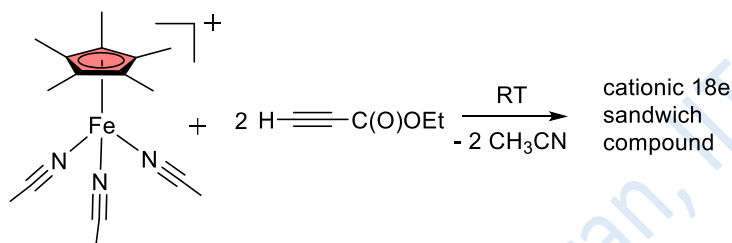
44. UV irradiation of CpRh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> with 3 moles of dimethyl acetylene was found to result in the formation of a stable 18 electron sandwich compound A. Neither ethylene nor dimethylacetylene are bound to compound A. <sup>1</sup>H NMR spectra of the compound showed a singlet at 4.3 ppm and a multiplet around 2.2 ppm the ratio between the signals being 5: 18. Arrive at the structure of the sandwich compound.

*J. Mueller, T. Akhnoukh, P. E. Gaede, A-L Guo, P. Moran, K. Qiao, J. Organometal. Chem., 1997, 541, 207-217*

45. Reaction of  $\text{Ni}(\text{C}_2\text{H}_4)_3$  with the diphosphine  $(\text{t-Bu})_2\text{PCH}_2\text{P}(\text{t-Bu})_2$  in 1:1 molar ratio resulted in a 16 e compound X along with release of one mole of ethylene gas. Compound X on reaction with 3 moles of acetylene resulted in an 18e compound Y. Neither ethylene nor acetylene was present in compound Y.  $^1\text{H}$  NMR of compound Y gave a singlet peak at 5.95 ppm, a second signal at 1.58 ppm and a third set of signals at 1.18 – 1.24 ppm. The integration ratio of these three signals were 3: 1: 18. Phosphorus NMR data of the compounds are given below. Arrive at the structures of X and Y.  
 $(\text{t-Bu})_2\text{PCH}_2\text{P}(\text{t-Bu})_2 + 20.5 \text{ ppm}; \text{ X} = +63.5 \text{ and } +23.8; \text{ Y} = +53.4 \text{ and } +19.1$

*K. R. Porschke, Angew. Chem. Int Ed., 1994, 33, 879*

46. The cationic  $\text{Cp}^*\text{Fe}(\text{CH}_3\text{CN})_3$  complex on reaction with 2 moles of the given alkyne at room temperature results in a new cationic 18 e sandwich compound. Predict the structure of the new complex formed which does not have the alkyne or  $\text{CH}_3\text{CN}$  as ligands bound to the iron centre.



*K. Ferré, L. Toupet and V. Guerchais, Organometallics, 2002, 21, 2578.*

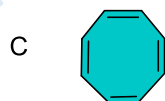
47. Match the compounds listed in column I obtained either from ethylene or acetylene with the suitable catalyst given in column II.



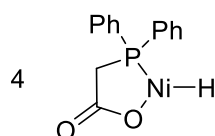
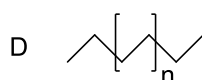
1  $\text{Ni}(\text{CN})_2, \text{CaC}_2$



2  $\text{Ni}(\text{COD})_2, \text{PPh}_3$



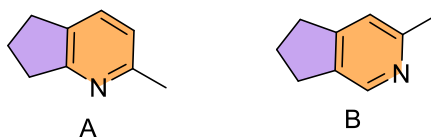
3  $\text{PdCl}_2, \text{CuCl}_2$



5  $\text{TiCl}_4 + \text{AlEt}_3$

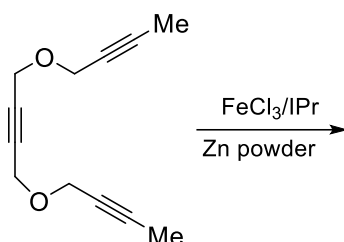
*B. F. Straub, C. Gollub, Chem. Eur. J, 2004, 10, 3081-3090; B. D. Gupta, A. J. Elias, Basic Organometallic Chemistry, Universities Press, 2010.*

48. Predict the starting materials required for preparing the given pyridyl derivatives by one step 2+2+2 cycloaddition reactions in presence of  $\text{CpCo}(\text{CO})_2$  as catalyst. Comment on formation of any other products from the same reactions.



*S. Saito, M. Yamamoto, Chem Rev., 2000, 100, 2901-2915*

49. Predict the product in the following reaction and propose steps in the formation of the product.



*S. Saito, M. Yamamoto, Chem Rev., 2000, 100, 2901-2915*

50. Determine the number of metal-carbon bonds present in the given compounds

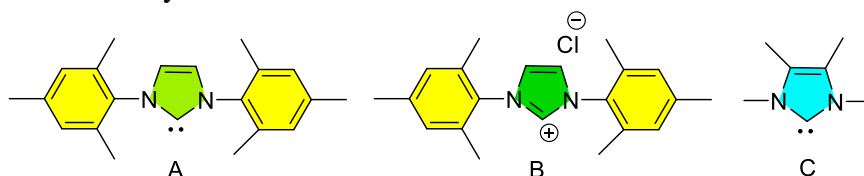
- (a)  $\text{Pd}(\text{dppf})\text{C}_{60}$  (Pd = Sq.Pl)
- (b)  $\text{Fe}(\text{Cp})(\text{Me}_5\text{C}_{60})$
- (c)  $\text{Ni}(\text{allyl})(\text{Me}_5\text{C}_{60})$
- (d)  $\text{IrClCO}(\text{PPh}_3)_2\text{C}_{60}$
- (e)  $\text{Ru}_3(\text{CO})_9\text{C}_{60}$  (has 3 Ru-Ru bonds)

*A. J. Elias, Chemistry of the p-Block Elements, Chapter 5, Universities Press, Hyderabad, 2018*

## 5. Metal-Phosphines and Carbenes

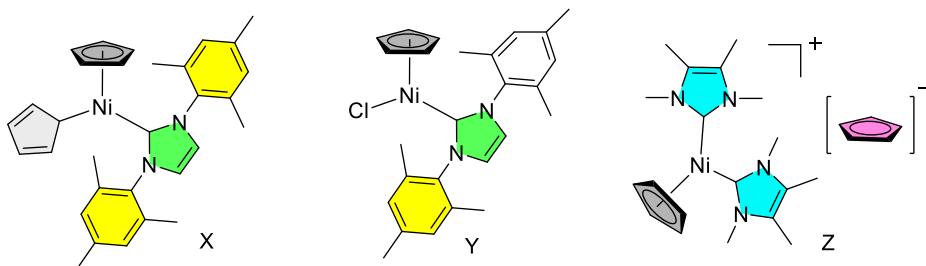
### Solved Problems

51. Reaction of  $\text{Cp}_2\text{Ni}$  with 1 mole of the given NHC (A) gave a compound X. Reaction of 1 mole of the NHC precursor salt (B) with  $\text{Cp}_2\text{Ni}$  gave another compound Y with the release of  $\text{CpH}$ . Both X and Y are neutral compounds. Reaction of  $\text{Cp}_2\text{Ni}$  with excess of the less hindered NHC (C) gave a cationic compound Z with  $\text{Cp}^-$  as the anion. All compounds X, Y and Z obey the 18 electron rule. Draw the structures of each.

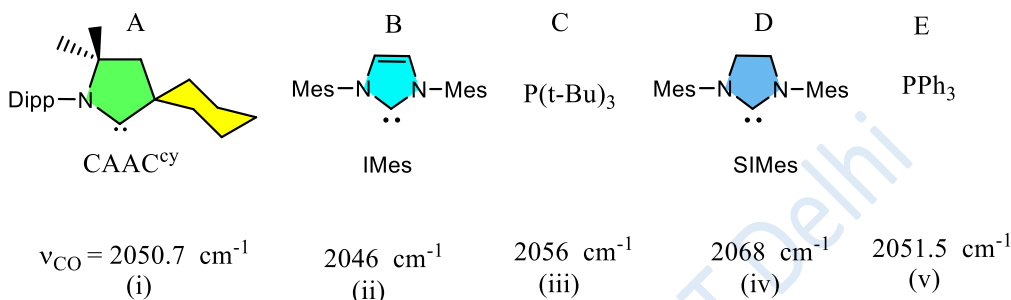


*L. Banach, P. A. Gunca, J. Zachara, W. Buchowicz, Coord. Chem. Rev., 2019, 389, 19-58*

### **Solution**

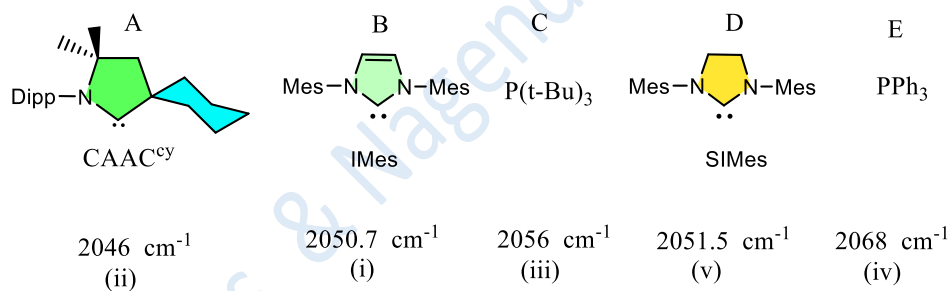


52. Infrared spectra ( $\nu_{\text{CO}}$  (A1) stretching bands) of a set of  $\text{Ni}(\text{CO})_3\text{L}$  complexes where L= a phosphine or carbene is provided. Match the spectral bands with the correct phosphine/ carbene ligand.



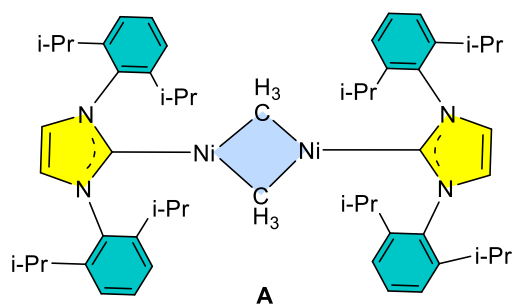
*U. S. D. Paul, U. Radius, Organometallics, 2017, 36, 1398-1407; S. P. Nolan, D. J. Nelson, S. P. Nolan, Chem. Soc. Rev., 2013, 42, 6723-6753*

### Solution

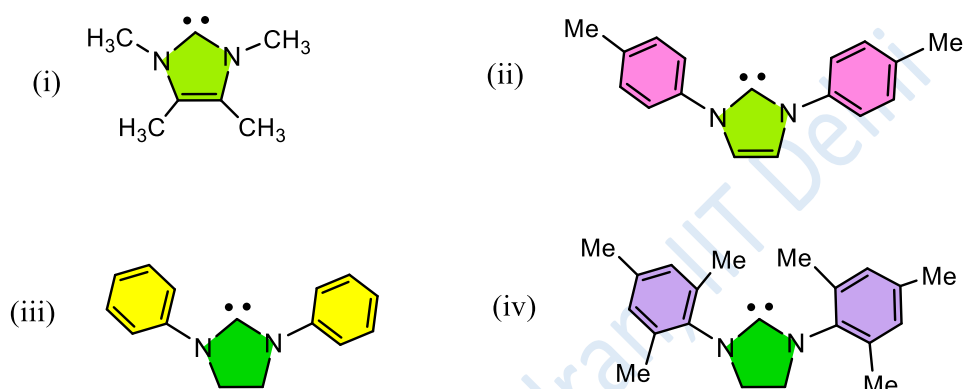


### Unsolved Problems

53. When heated in benzene, the Ni(I) complex **A** gave a mixture of mononuclear **B** and dinuclear **C** Ni(0) complexes and eliminated ethane. The reaction of compound **A** with dihydrogen in benzene also gave the same products (**B** and **C**) but with methane being the side product. If compounds **B** and **C** are stable, have no bond between metal atoms, and the metal:carbene ratio remains the same as compound **A**, draw their structures.



54. Which among the given N- heterocyclic carbenes is unstable and is most likely to undergo dimerization?



Arduengo, A. J, *J. Am. Chem. Soc.*, 1992, 114, 5530-5534, 1995, 117, 11027-11028

55. A reaction of  $\text{Na}_2\text{PdCl}_4$  with ethylene in water followed by reaction with allyl chloride resulted in the formation of a 16 electron compound A along with acetaldehyde, NaCl and HCl. Palladium underwent a reduction followed by oxidation during this reaction. Ethylene is not present in compound A and its analysis indicated presence of chlorine. Compound A on reaction with sodium cyclopentadienyl ( $\text{NaCp}$ ) was found to form an 18 electron compound B. Reaction of A with two moles of the NHC, IMes formed another 16 electron compound C. Write balanced chemical equations and arrive at the structures of compounds A, B and C.

Choose the correct statements from those given below

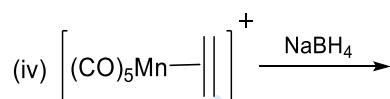
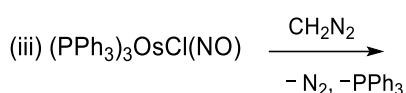
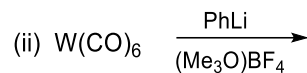
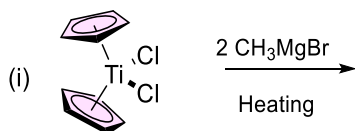
- (i) The role of ethylene is to reduce palladium(II) to palladium(0)
- (ii) The allyl chloride reacts with the generated Pd(0) by oxidative addition to form A
- (iii) The hapticity of the allyl group is 3 in all the three compounds A, B and C
- (iv) Both A and B have two palladium atoms in the molecule.
- (v) CO can be used instead of ethylene in the first step of the reaction
- (vi) Compound A can also be obtained by reacting a Pd(0) complex with allyl chloride

F. R. Hartley, *J. Organometal. Chem.*, 1974, 66, 465-473; R. B. King, *Inorg. Chem.* 1963, 2, 528. S. P. Nolan, *Organometallics*, 2004, 23, 1629-1635

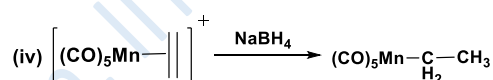
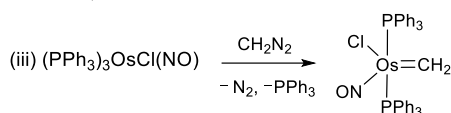
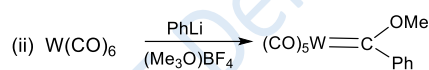
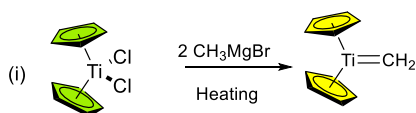
## 6. Metal carbene and carbyne complexes

### Solved Problems

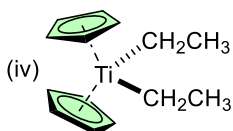
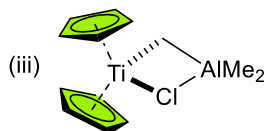
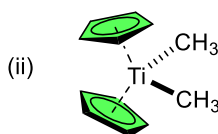
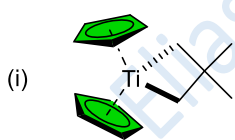
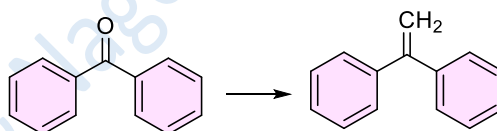
56. Choose from the given reactions the reaction which does not lead to the formation of a metal-carbene complex



### Solution

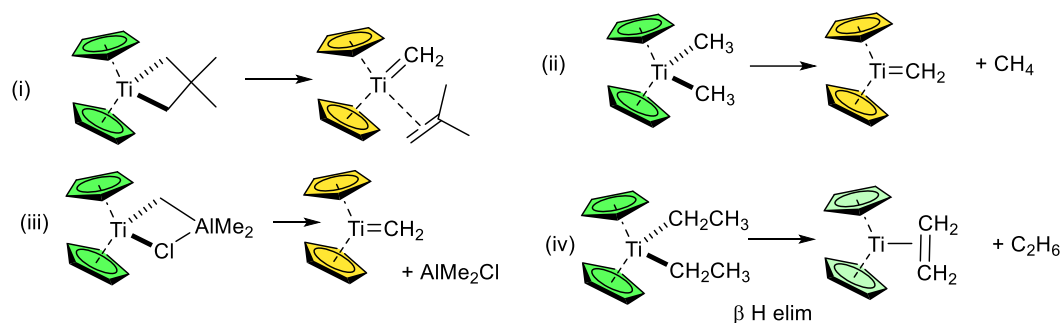


57. Select the most likely compound(s) which upon heating along with benzophenone will not convert it to 1, 1-diphenylethene?



R. C. Hartley, G. J. McKiernan, *J. Chem. Soc., Perkin Trans.1*, 2002, 2763-2793

### Solution

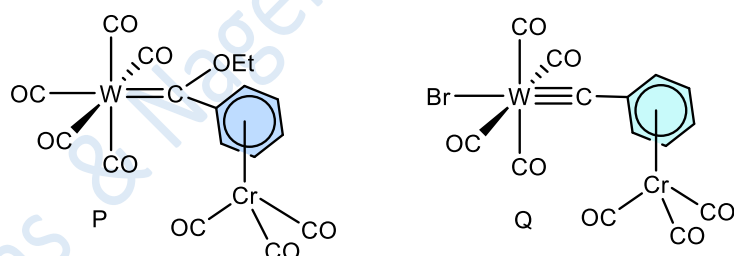


58. Reaction of  $W(CO)_6$  with the lithiated piano-stool complex,  $LiC_6H_5Cr(CO)_3$ , followed by Meerwein's salt resulted in a carbene complex P. Compound P on reaction with  $BBr_3$  resulted in a carbyne complex Q. (a) Draw structures of P and Q, both having  $W(CO)$  and  $Cr(CO)$  bonds (b). Infrared spectral analysis of P and Q gave two sets of bands for the A1 and E carbonyl stretching modes for each of the complexes which are provided below. Assign the complexes to the correct set of bands. Also determine which metal is  $M^1$  and which metal is  $M^2$ .

	$M^1(CO)_x$		$M^2(CO)_y$	
	A1	E	A1	E
Set 1.(for one complex)	1942	1934	1978	1918
Set 2.(for the other complex)	2132	2047	1980	1916

*E. O. Fischer, Chem Ber, 1980, 113, 1010.*

### Solution

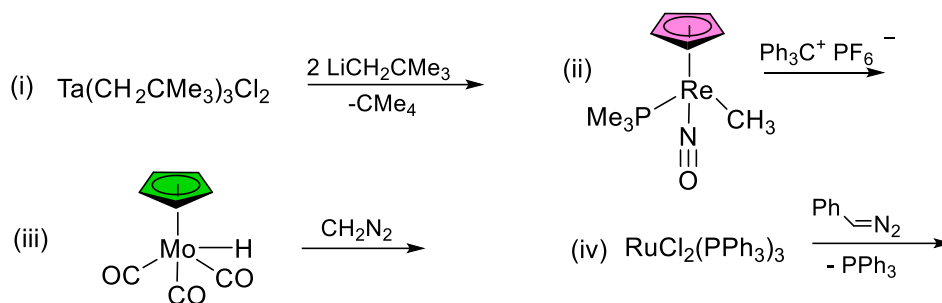


$M^1 = W$ ;  $M^2 = Cr$

Set 1 = Carbene complex P; Set 2 = Carbyne complex Q : Carbyne Q has metal in higher oxidation state compared to carbene P and therefore less electron density for back bonding of CO.

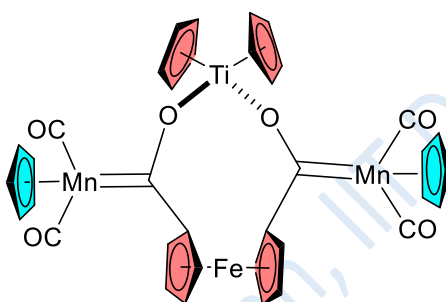
### Unsolved Problems

59. Choose from the given reactions the reaction which does not lead to the formation of a metal-carbene complex



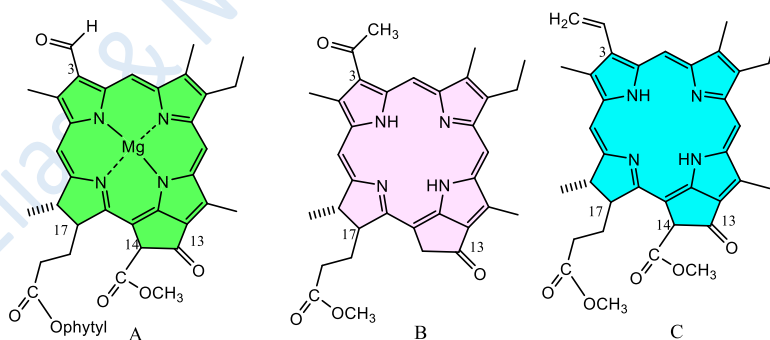
W. A. Kiel, W. E. Buhro, J. A. Gladysz, *Organometallics*, 1984, 3, 879-886; T. S. Piper, G. Wilkinson, *Naturwissenschaften*, 1955, 42, 625.

60. Given ferrocene,  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{CpMn}(\text{CO})_3$  and  $n\text{-BuLi}$  as primary reactants, suggest a reaction route to make the following Fischer carbene complex having three different types of sandwich units.



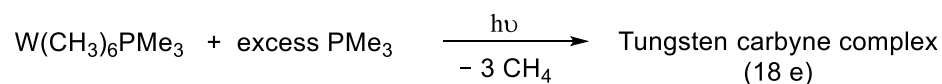
Bezuidenhout, D. I, S. Lotz, M. Landman, D. C. Liles, *Inorg. Chem.*, 2011, 50, 1521

61. Given that only one of the carbonyl groups of the given chlorophyll and its precursors get methylenated by a controlled reaction with Tebbe's reagent, predict the products in the given reactions by identifying the carbonyl which will get methylenated.



H. Tamiaki, *Tetrahedron Lett.*, 2016, 57, 788-790

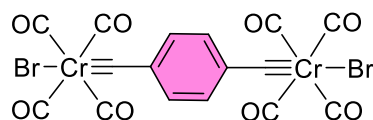
62. Reaction of  $\text{WMe}_6(\text{PMe}_3)$  with excess of  $\text{PMe}_3$  under UV irradiation resulted in the loss of 3 moles of  $\text{CH}_4$  and formation of an octahedral carbyne complex which obeys the 18 electron rule. Draw the structure of this tungsten carbyne complex. What is the formal oxidation state of tungsten in this complex?



G. Wilkinson, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans*, 1204, 1981.



63. Using p-phenylenedilithium ( $\text{LiC}_6\text{H}_4\text{Li}$ ),  $\text{Cr}(\text{CO})_6$ ,  $\text{Et}_3\text{OBF}_4$  and  $\text{BBr}_3$ , show steps and intermediates formed during the formation of the given trans dicarbonyl complex.

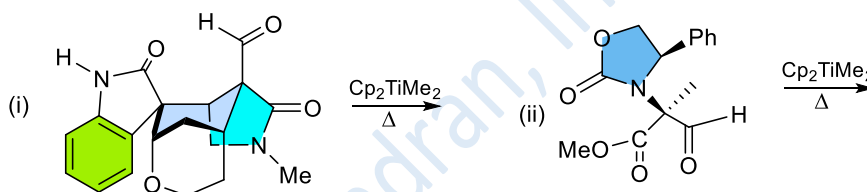


*E. O. Fischer, Chem Ber, 1982, 115, 2951*

64. Reaction of  $\text{Fe}(\text{CO})_5$  with lithium diisopropylamide (LDA) followed by Meerwein's salt ( $\text{Et}_3\text{OBF}_4$ ) resulted in compound A. Compound A on reaction with one mole of  $\text{PPh}_3$  resulted in compound B along with the release of CO. Reaction of B with 2 moles of  $\text{BCl}_3$  resulted in an ionic complex  $[\text{C}]\text{BCl}_4$  along with one mole of  $\text{BCl}_2\text{OEt}$  as the side product. Given that complexes A, B and C obey the 18e rule, draw their structures.

*E. O. Fischer, Angew. Chem. Int. Ed., 1984, 23, 820*

65. Given that only one of the carbonyl groups is methylenated in the following natural products on controlled reaction with Petasis reagent, predict the products.

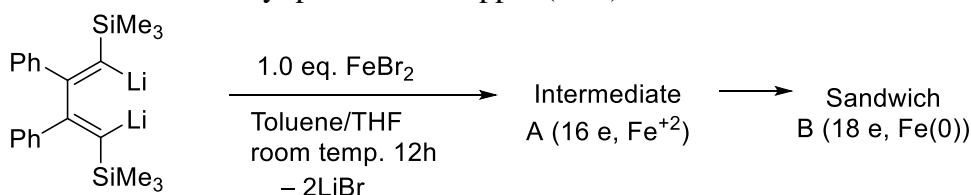


*R. C. Hartley, G. J. McKiernan, J. Chem. Soc. Perkin Trans 1, 2002, 2763-2793*

## 7. Metal- sandwich compounds and metallocenes

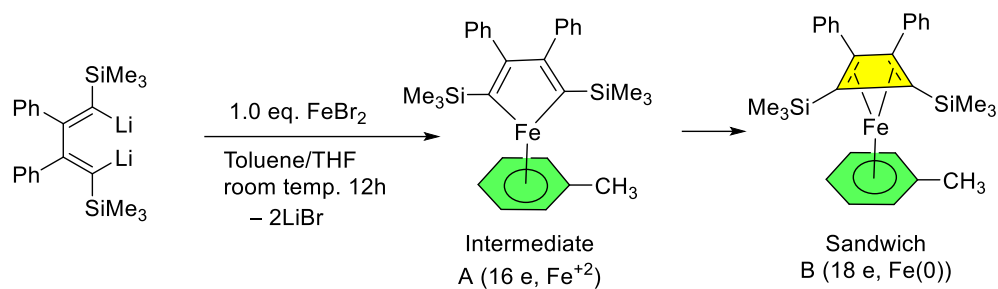
### Solved Problems

66. Reaction of the given dilithiated substituted butadiene with 1.0 eq. of  $\text{FeBr}_2$  in a mixture of toluene and THF at room temp. resulted in an 18 electron iron sandwich compound B where iron is in the zero oxidation state along with formation of  $\text{LiBr}$ . The intermediate A, formed during this reaction was a 16 electron species with iron in the +2 oxidation state which underwent reductive elimination to give B. Both compounds A and B gave peaks indicating the presence of a methyl group in their  $^1\text{H}$  NMR at 1.73 ppm (3H) in addition to the TMS methyl peaks at 0.19 ppm (18H). Draw the structures of A and B.

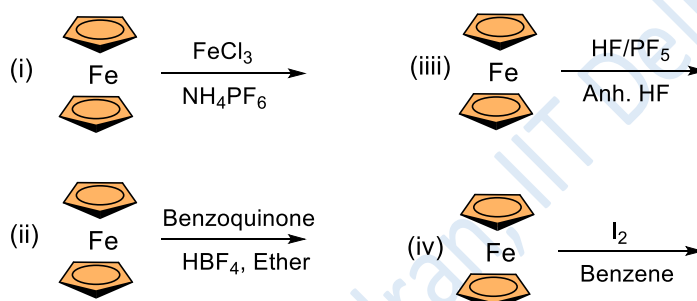


*C. Yu, W-X Zhang, Z Xi, Organometallics 2018, 37, 4100-4104*

### Solution

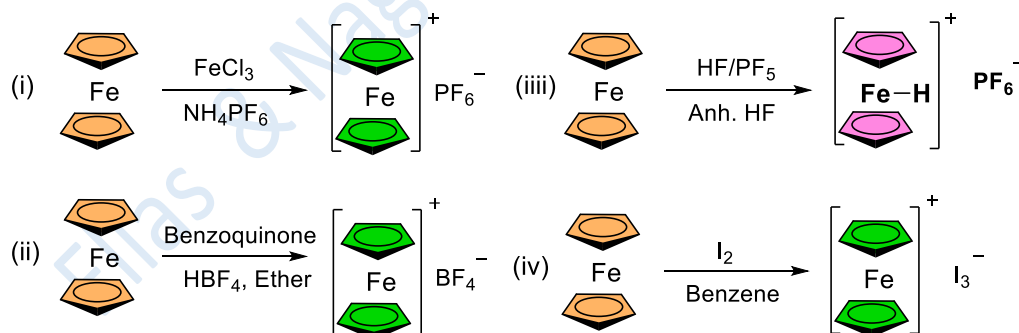


67. Which one among the given reactions of ferrocene performed in the absence of air does not lead to the formation of ferrocenium cation,  $(\text{Cp}_2\text{Fe})^+$ .

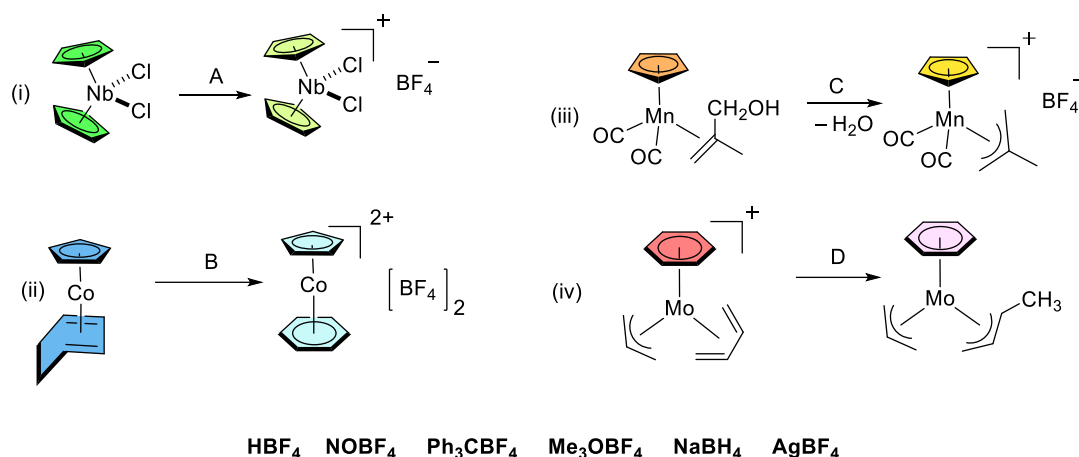


*K. Meyer Angew.Chem.2017,129,13557–13561, S. Toma, Synthesis, 2015, 47, 1683-1695*

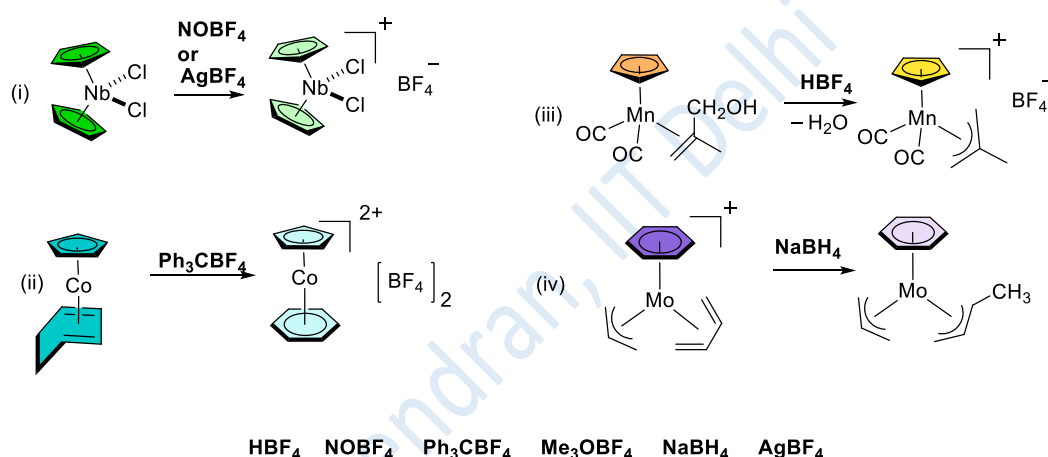
### Solution



68. Choose from the list of reagents provided the most suitable reagents A, B, C and D for the given transformations



### Solution



### Unsolved Problems

69. Reaction of one mole of ironcyclopentadienyldicarbonyl dimer,  $[\text{CpFe}(\text{CO})_2]_2$  with one mole of  $\text{I}_2$  gave a monomeric compound A with the molecular formula  $\text{C}_7\text{H}_5\text{O}_2\text{IFe}$ . Compound A on reaction with pyrrole ( $\text{C}_4\text{H}_5\text{N}$ ) and diisopropyl amine under visible light radiation from a tungsten lamp gave compound B along with  $i\text{Pr}_2\text{NH}_2^+\text{I}^-$ . Heating compound B in a mixture of hydrocarbon solvents resulted in the evolution of a gas and formation of a new compound C. Compounds A, B and C obey the 18 electron rule and C does not have CO as a ligand. Arrive at the structures of A, B and C.

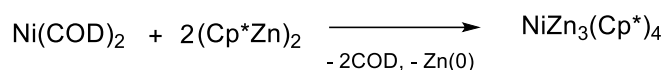
*J. Zakrzewski, J. Organometal. Chem., 1987, 327, C41-C42*

70. Reaction of  $\text{ReCl}_5$  with excess of  $\text{NaCp}$  in THF solvent resulted in a stable compound A. The  $^1\text{H}$  NMR of A showed two peaks at 4.34 ppm and -13.3 ppm in the ratio 10:1. On reacting A with  $n\text{-BuLi}$  at  $-50^\circ\text{C}$ , the peak at -13.3 ppm disappeared forming a new compound which on reaction with acetaldehyde gave another compound B (mol formula  $\text{C}_{20}\text{H}_{20}\text{Re}_2$ ) with a single peak in  $^1\text{H}$  NMR at 4.33 ppm. Compound B on heating gave another compound C (Mol formula  $\text{C}_{20}\text{H}_{18}\text{Re}_2$ ) along with A (in 1:2 molar ratio). The  $^1\text{H}$  NMR of C gave two sets of peaks at 4.46 (5H) and 4.05-4.28 (4H). Compound B on reaction with benzyl bromide in 1:1 ratio gave two compounds D and E in equal amounts.

Compound E gave a single peak at 3.80 ppm (mol formula  $C_{10}H_{10}ReBr$ ) while D gave three sets of peaks at 7.10 (5H), 3.76 (10H) and 2.70 (2H) ppm. Given that all compounds A-E obey the 18 e rule. Arrive at their structures.

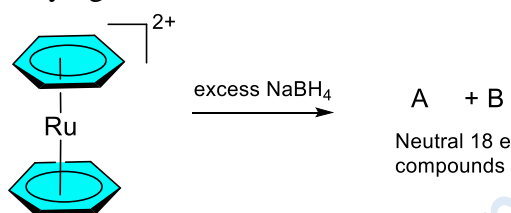
*J. J. M. Snell, J. Organometal. Chem., 1984, 276, 387-392*

71. Reaction of one mole of  $Ni(COD)_2$  with two moles of  $(Cp^*Zn)_2$  resulted in the formation of a new complex  $NiZn_3(Cp^*)_4$  along with side products COD and  $Zn(0)$ . Given that the central atom nickel has a tetrahedral arrangement of groups around it and the molecule obeys 18 e rule with respect to both Ni and Zn arrive at its structure. Indicate the formal oxidation state of both Ni and Zn ions in the complex.



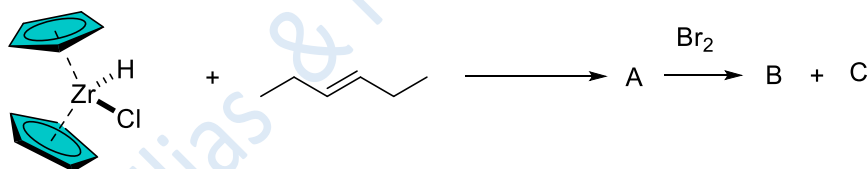
*T. Bollermann, K. Freitag, C. Gemel, R. W. Seidel, R. A. Fischer, Organometallics, 2011, 30, 4123.*

72. Reduction of  $[(C_6H_6)_2Ru](ClO_4)_2$  with excess of  $NaBH_4$  resulted in two neutral ruthenium compounds A and B but having ruthenium in different formal oxidation states both obeying the 18 e rule. Predict the structures of A and B.



*G. Wilkinson, J. Chem. Soc., 1962, 4458*

73. For the given reaction predict the most likely products A, B and C

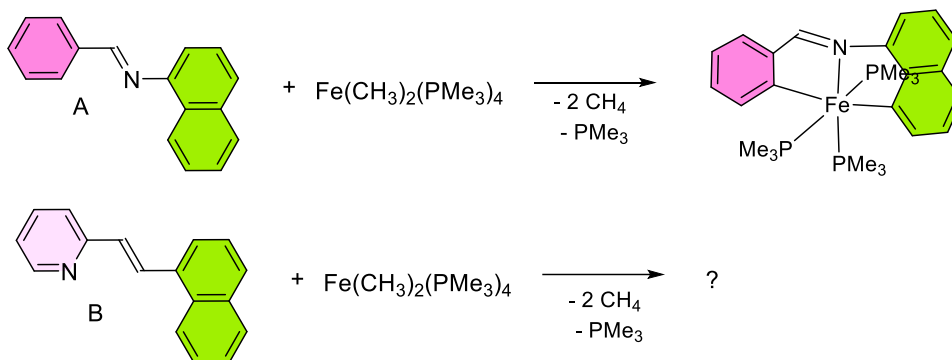


*J. Schwartz, J. A. Labinger, Angew. Chem. Int. Ed. Engl., 1976, 15, 333-340*

## 8. Types of organometallic reactions

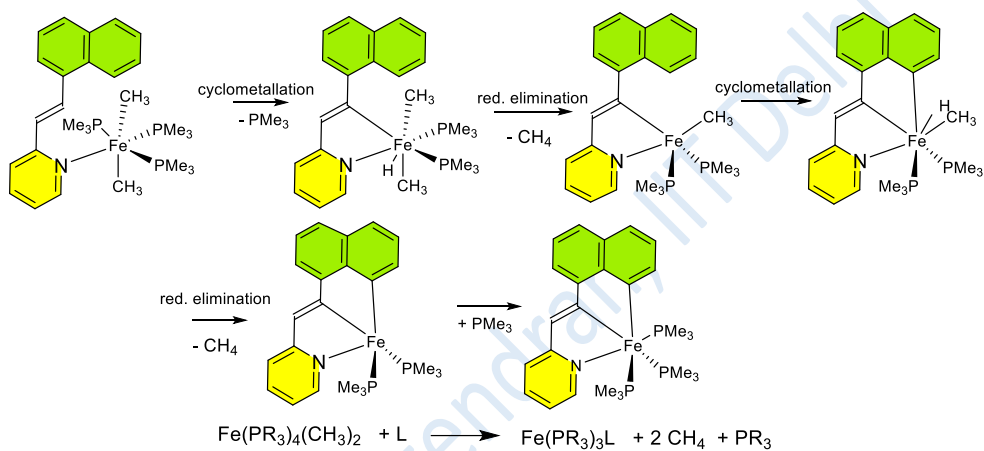
### Solved Problems

74. Reactions of an imine based ligand (A) and an isomeric pyridine based ligand (B) with the same iron complex are depicted below. Provide the mechanism of the second reaction clearly indicating the correct sequence of steps involved leading to the final product.

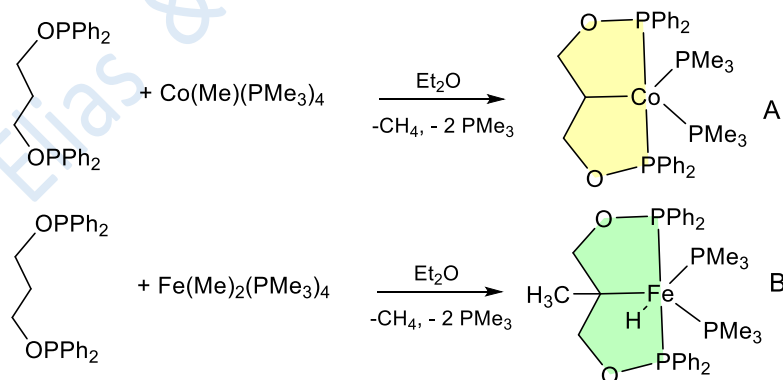


H. F. Klein, S. Camadanli, R. Beck, U. Flourke, *Chem Commun.*, 2005, 381

### Solution

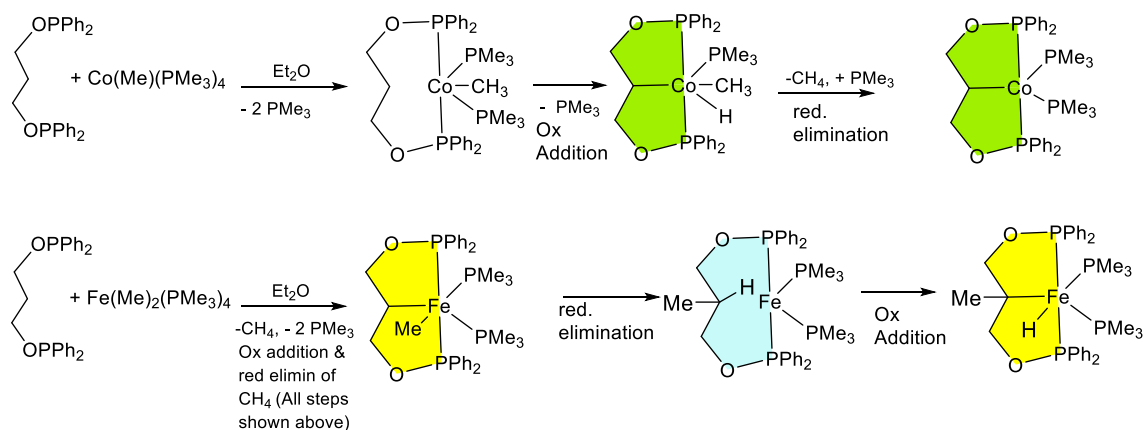


75. Write a suitable mechanism for the following reactions

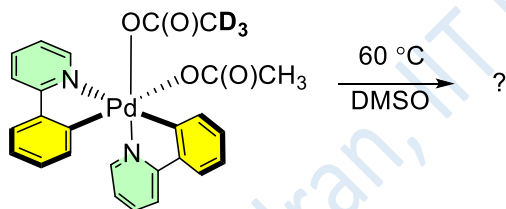


G. Xu, H. Sun, X. Li, *Organometallics*, 2009, 28, 6090

### Solution

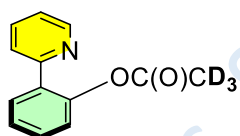


76. The given Pd(IV) complex undergoes reductive elimination upon heating, leading to more than one stable **organic** products. List all such organic compounds and predict which one among them will be the major product [Note: Square planar palladium (II) complexes having one or two DMSO as ligands are also formed in this reaction even displacing pyridyl rings ]

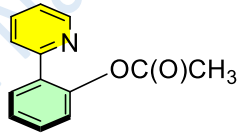


*J. M. Racowski, A. R. Dick, M. S. Sanford, J. Am. Chem. Soc., 2009, 131, 10974*

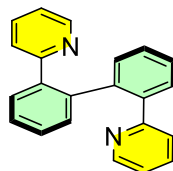
### Solution



Major product as the acetyl group is cis to both aryl rings for red. elimination



Minor product as the acetyl group is cis to only one aryl ring



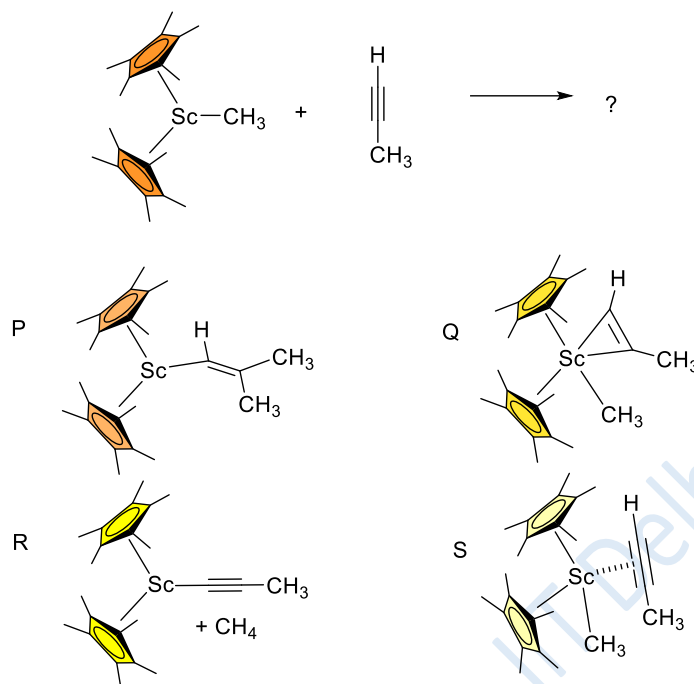
Minor product as removal requires breaking two Pd-N bonds

### Unsolved Problems

77. Reaction of  $(\text{Cp}^*)_2\text{ScCH}_3$  with (a) benzene and (b) toluene at  $80^\circ\text{C}$  in the absence of any solvent resulted in the formation of new organometallic compounds along with the elimination of  $\text{CH}_4$  in both the reactions. Predict the structures of the new compounds formed from both reactions. Name the type specific of reaction happening.

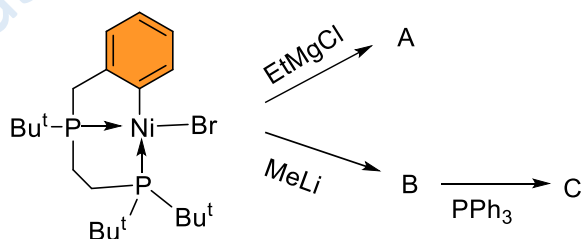
*M. E. Thompson, S. M. Baxter, A. R. Bulls, B.J. Burga, M. C. Nolan, B.D. Santarsiero, W. P. Schafer, J. E. Bercaw, J. Am. Chem. Soc., 1987, 109, 203-218*

78. Indicate the most likely product which can result from the given reaction. Justify your choice



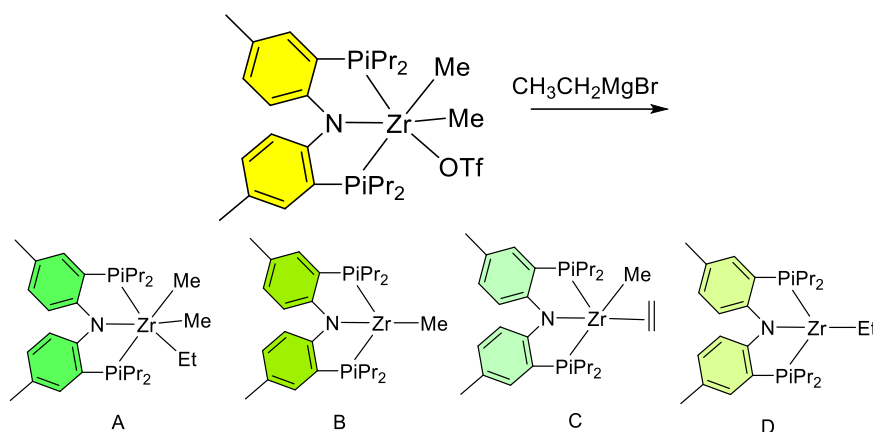
*M. E. Thompson, S. M. Baxter, A. R. Bulls, B.J. Burga, M. C. Nolan, B.D. Santarsiero, W. P. Schafer, J. E. Bercaw, J. Am. Chem. Soc., 1987, 109, 203-218*

79. Reaction of the given nickel(II) complex with ethyl Grignard reagent EtMgCl did not result in the expected N-ethyl containing product but another 16 electron Ni(0) species A. The reaction did give MgBrCl as the Grignard reaction side product. On the other hand, reaction of the same Ni(II) complex with methyllithium resulted in the replacement of Br by Me forming B along with LiBr as side product. Reaction of B with PPh<sub>3</sub> at 50 °C resulted in a new complex C with nickel in the 0 oxidation state and retaining the Me group elsewhere in the new molecule. Draw the structures of A, B and C. Indicate the type of reaction(s) happening during formation of A and formation of C from B.



*A.C. Zimmermann, M. D. Fryzuk, Organometallics, 2018, 37, 14, 2305–2318*

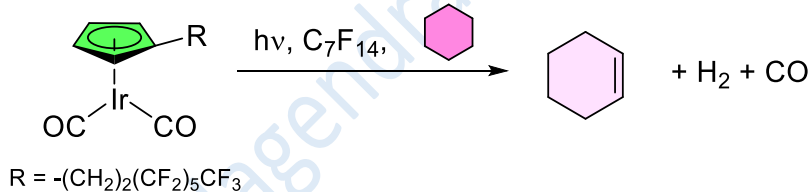
80. The reaction of the given Zr(PNP) complex with one mole of the ethyl Grignard reagent was found to result in the evolution of a gas and formation of a new complex. The complex formed is



*M. Kamitani, K. Searles, C-H Chen, P. J. Carroll, D. J. Mindiola. Organometallics 2015, 34, 2558-2566*

81. Cyclohexane was found to get converted to cyclohexene as the major product when it was exposed to UV radiation in the presence of catalytic amounts of the given iridium complex in a fluorocarbon solvent. Additional products of the reaction were  $\text{H}_2$  and traces of  $\text{CO}$ , cyclohexadiene and benzene. Write a suitable mechanism (catalytic cycle). From the given options select the correct sequence of steps in the mechanism.

*B. Rabay, T. Braun, J. P. Falkenhgen, Dalton Trans., 2013, 42, 8058-8065*

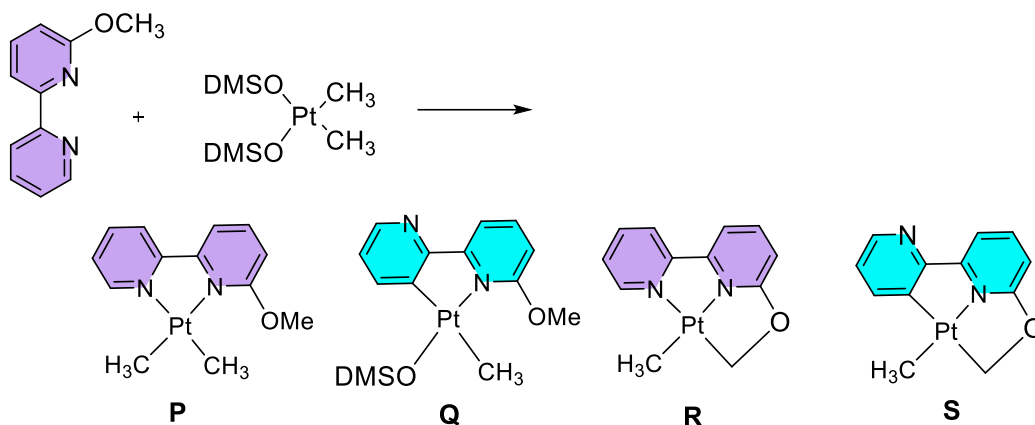


The is

- (i) (a) CO dissociation, (b) Oxidative addition of cyclohexane, (c)  $\beta$  hydrogen elimination (d) displacement of cyclohexene, (e) reductive elimination of  $\text{H}_2$ , and (f) oxidative addition of cyclohexane
- (ii) (a) CO dissociation, (b) Oxidative addition of cyclohexane, (c) CO dissociation, (d)  $\beta$  hydrogen elimination, (e) CO association with displacement of alkene, (f) reductive elimination of  $\text{H}_2$  and (g) oxidative addition of cyclohexane
- (iii) (a) Oxidative addition of cyclohexane, (b) CO dissociation, (c)  $\beta$  hydrogen elimination, (d) CO displacement of alkene, (e) reductive elimination of  $\text{H}_2$  and (f) oxidative addition of alkane
- (iv) (a) CO dissociation, (b) CO dissociation, (c) Oxidative addition of cyclohexane, (d)  $\beta$  hydrogen elimination, (e) displacement of alkene, (f) reductive elimination of  $\text{H}_2$  and (g) oxidative addition of alkane.

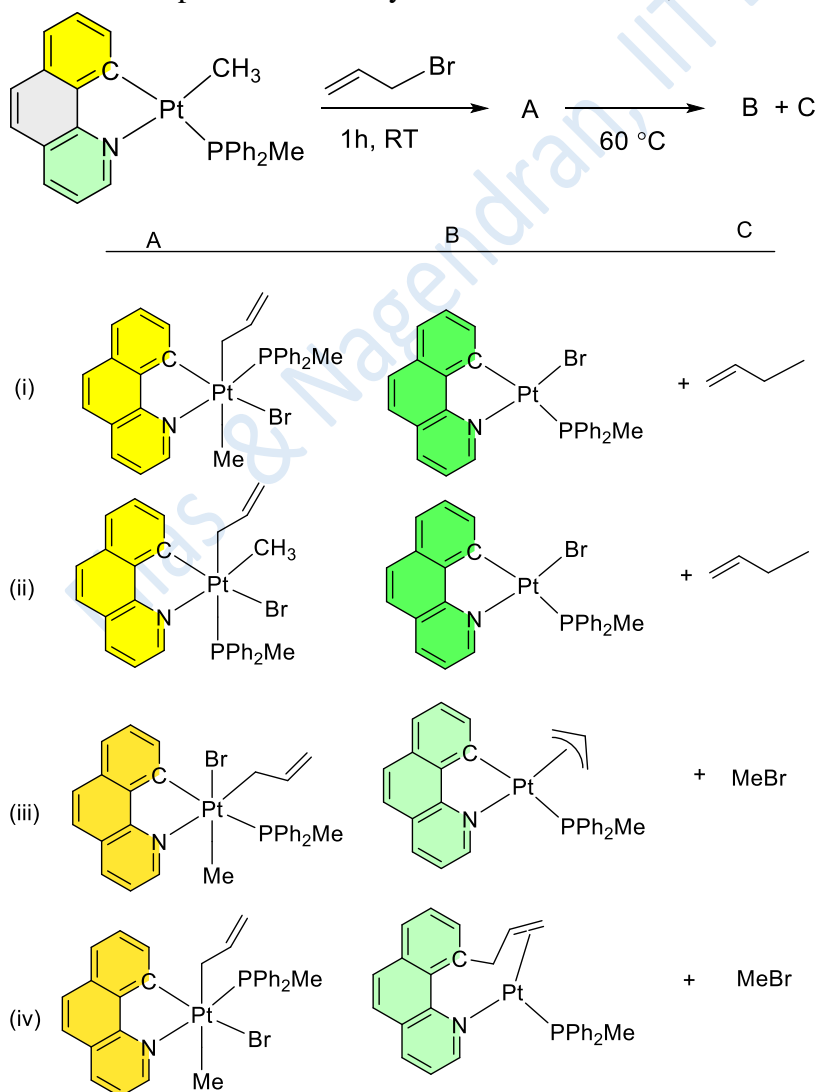
82. For the given reaction, select the most unlikely product from the given options.





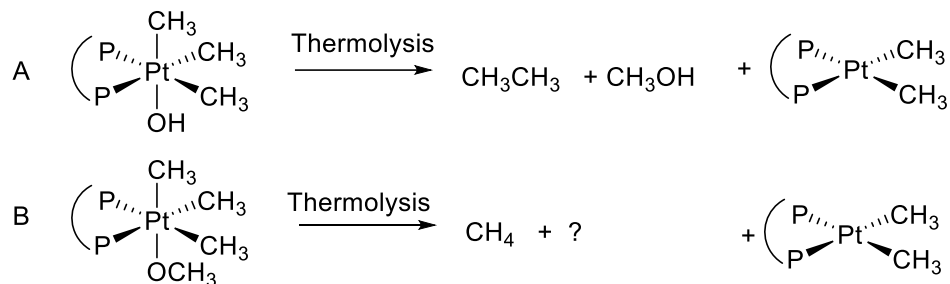
*G. Minghetti, S. Stoccoro, M. A. Cinellu, B. Soro, A. Zucca, Organometallics, 2003, 22, 4770-4777.*

83. Reaction of the given square planar platinum complex with allyl bromide resulted in the formation of an octahedral complex A at room temperature. On warming to 60 °C the compound A underwent a rearrangement, gave off a stable organic compound C and converted to compound B. Identify the correct set of A, B and C from the given options.



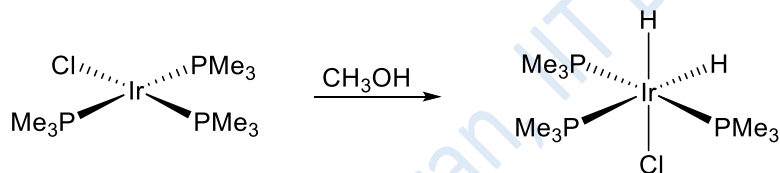
*M. Zanganeh, S. J. Hoseini, M. Rashidi, S. M. Nabavisadeh, M. R. Halwagar J. Organomet. Chem., 2018, 856, 1-12*

84. The complexes A and B were subjected to undergo thermolysis and both gave the same platinum complex as the metal containing compound after reductive elimination. However the major organic products of A were methanol and ethane while that of B was methane. Indicate how methane is formed. Is there any other product likely to form during this reaction from B?



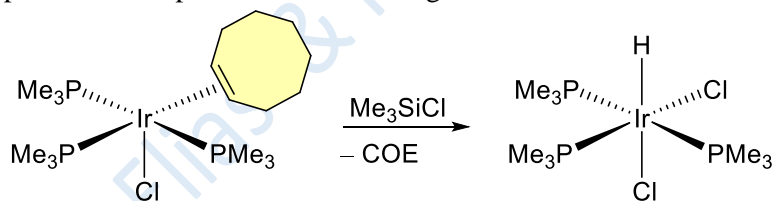
*N. A. Smythe, K. A. Grice, B. C. Williams, K. I. Goldberg, Organometallics 2009, 28, 277–288*

85. Reaction of  $\text{IrCl}(\text{PMe}_3)_3$  with  $\text{CH}_3\text{OH}$  was found to result in  $\text{IrCl}(\text{H})_2(\text{PMe}_3)_3$ . Show steps indicating how this compound is formed. What is the other product obtained from this reaction?



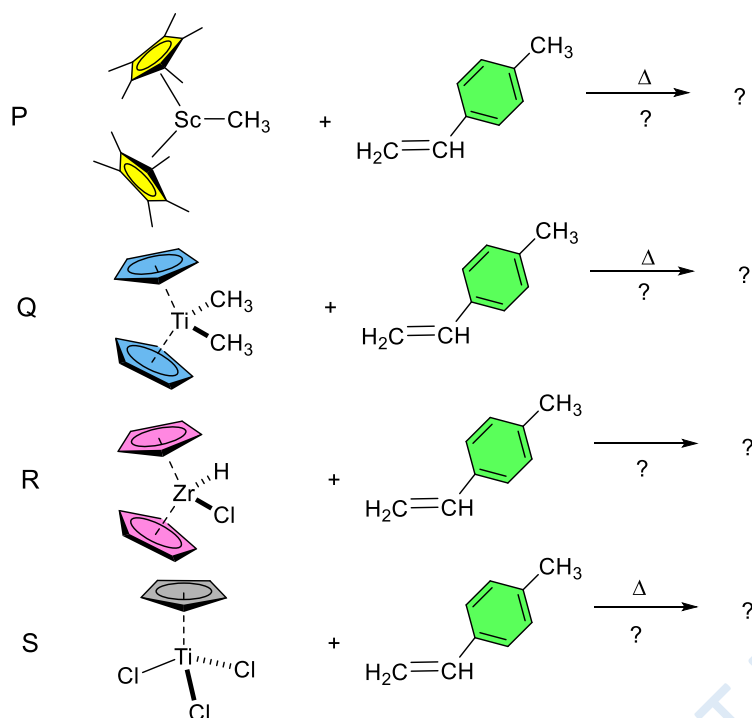
*O. Blum, D. Milstein, Angew. Chem. Int. Ed., 1995, 34, 229*

86. Reaction of  $\text{IrCl}(\text{COE})(\text{PMe}_3)_3$  with  $\text{Me}_3\text{SiCl}$  was found to result in  $\text{IrCl}_2\text{H}(\text{PMe}_3)_3$ . Show steps indicating how this compound is formed. Given that this is an unusual reaction, predict the possible other product formed during this reaction?



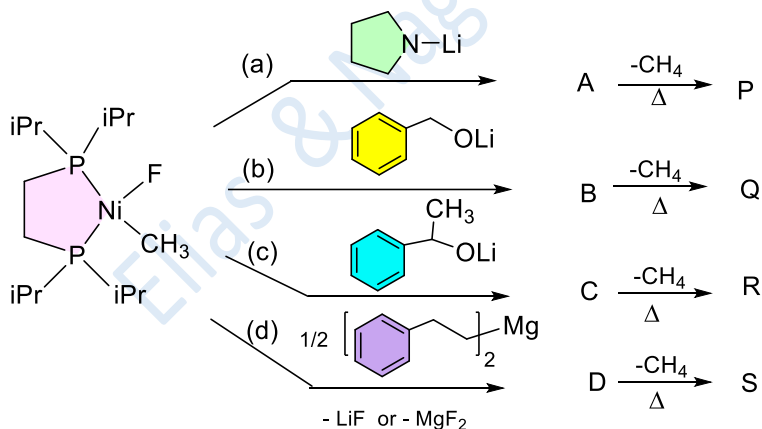
*A.A. Slota, F. Frolow, D. Milstein, J. Chem. Soc. Chem. Commun., 1989, 1826*

87. Predict the most likely product(s) from the following proposed reactions. Indicate the specific type of reaction happening in each case.



M. E. Thompson, S. M. Baxter, A. R. Bulls, B.J. Burga, M. C. Nolan, B.D. Santarsiero, W. P. Schafer, J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, 109, 203-218, R. Po, N. Cardi, *Prog. Polym. Sci.*, 1996, 21, 47-88.

88. Reactions of the given Ni(dippe)(Me)(F) complex with four different metalated reagents are shown. The products A, B, C and D which are formed initially, when heated, converts to compounds P, Q, R and S respectively along with the release of methane gas. Identify the type of reactions happening and provide the structural formulae of A, B, C, D and P, Q, R, S.

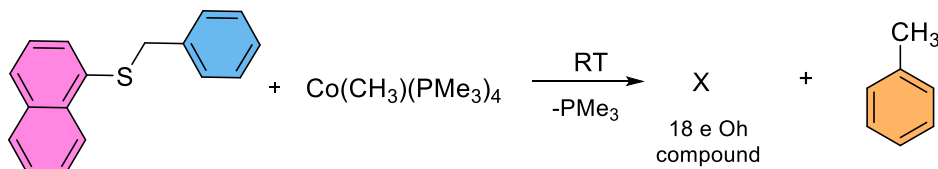


I. Matas, J. Campora, P. Palma, E. Alvarez, *Organometallics*, 2009, 28, 6515

89. Reaction of Wilkinson's catalyst with MeMgBr resulted in a new 16 electron complex P. On heating complex P, a gas was released resulting in the formation of another 16 e complex Q. Compound Q on reacting with one mole of H<sub>2</sub> gas and one mole of PPh<sub>3</sub> was found to result in a 18 electron complex R. Complex R gave a band at 2156 cm<sup>-1</sup> which was absent in P and Q. Predict the structures of compounds P, Q and R and indicate the type of reactions happening on converting P to Q and to R.

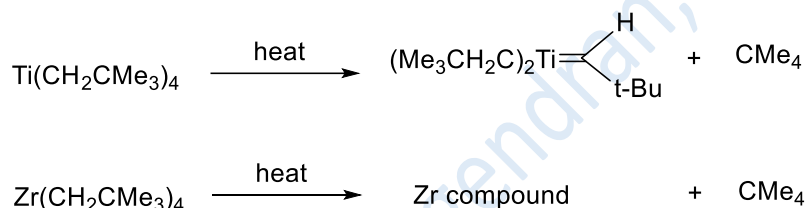
W. Kaim, *J. Organometal. Chem.*, 1968, 14, 179.

90. Reaction of the given benzyl sulfide with  $\text{Co}(\text{CH}_3)(\text{PMe}_3)_4$  results in the formation of a 18 e octahedral  $\text{Co}(\text{III})$  complex, X along with liberation of toluene and one mole of  $\text{PMe}_3$ . Formation of X involves an oxidative insertion of the Co unit into a C-S bond and cyclometallation resulting in a 5 membered ring. Draw the structure of complex X and show steps leading to its formation. Predict what other organic products could have formed from the reaction similar to toluene.



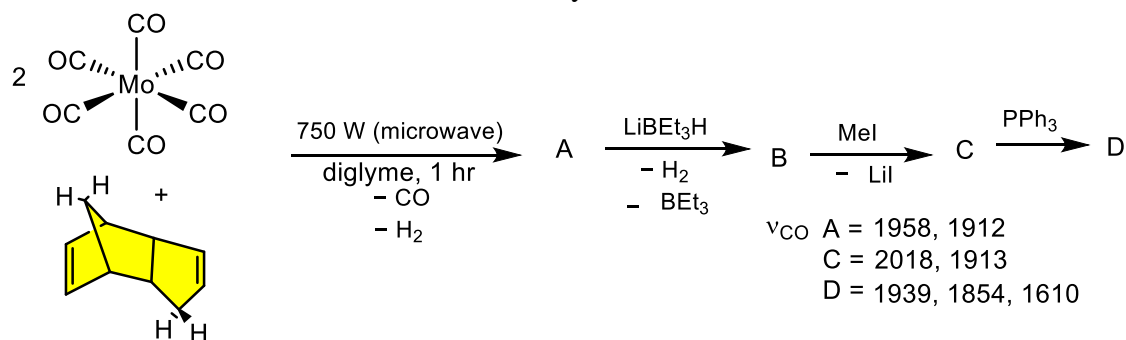
*R. Beck, M. Frey, S. Camdanli, H-F Klein, Dalton Trans, 2008, 4981*

91. Heating of  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  resulted in the formation of a titanium carbene complex along with the release of one mole of neopentane. Heating of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$  also released one mole of neopentane but a organometallic monomeric compound different from the titanium carbene was found to form which had the metal centre in tetrahedral geometry and did not possess a metal-carbene bond. Predict the structure of the Zr compound and indicate the type of reactions by which it is formed.



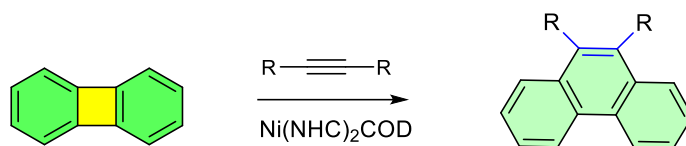
*Y-D. Wu, Z-H Peng, K. W. K. Chan, X. Liu, A. A. Tuinman, Z. Xue, Organometallics 1999, 18, 2081-2090.*

92. Reaction of  $\text{Mo}(\text{CO})_6$  with dicyclopentadiene under microwave conditions results in compound A along with release of CO and  $\text{H}_2$ . A on reaction with  $\text{LiBEt}_3\text{H}$  gives the lithium salt of an anionic complex B which on reaction with  $\text{MeI}$  gives a neutral complex C. Complex C on reaction with  $\text{PPh}_3$  gives a new compound D where no side product was formed. The  $\nu_{\text{CO}}$  stretching frequencies for A, C and D are provided. Arrive at the structures of A, B, C and D all of which obey the 18 e rule.



*M. T. Whited and G. E. Hofmeister, J. Chem. Educ., 2014, 91, 1050*

93. Provide a suitable reaction mechanism for the following reaction



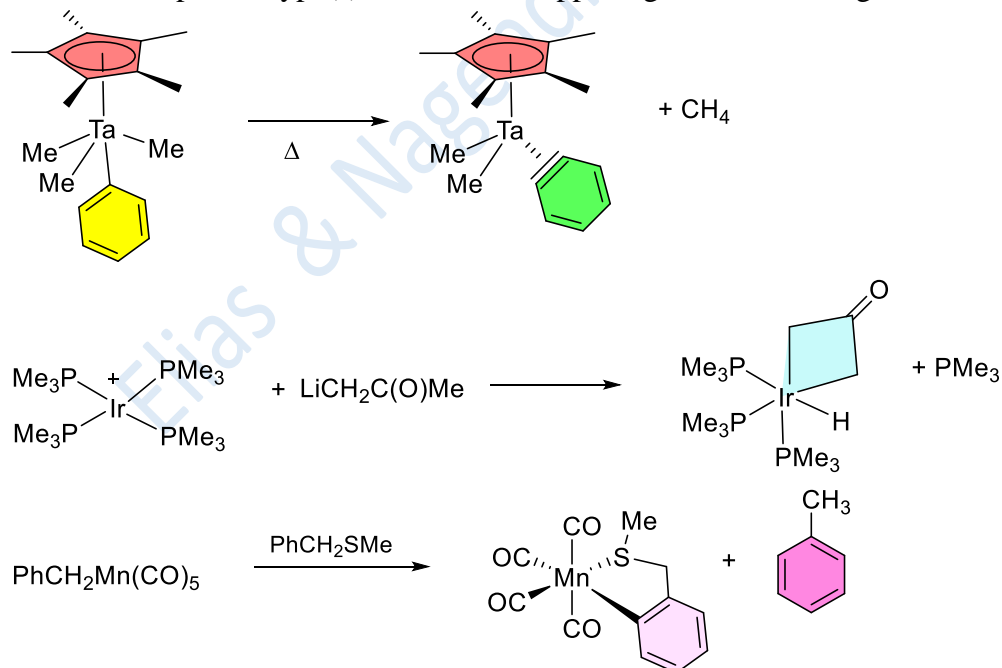
*L. Souillart, N. Cramer, Chem Rev., 2015, 115, 9410-9464*

94. Write the mechanism for the following ring expansion reaction using Wilkinson's catalyst.



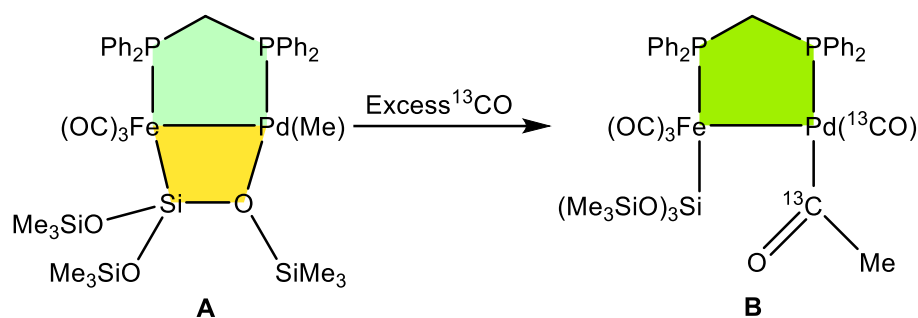
*T. Matsuda, T. Matsumoto, Org. Biomol. Chem., 2016, 14, 5023*

95. Indicate the specific type(s) of reactions happening in the following reactions



*S. J. McLain, R. R. Schrock, P. R. Sharp, M. R. Churchill, Youngs W. J., J Am. Chem. Soc., 1979, 101, 263-265; R. L. Bennett, M. I. Bruce, I. Matsuda, Aust. J. Chem., 1975, 28, 2307-2310; T.H. Tulip, D. L. Thorne, J Am. Chem. Soc., 1981, 103, 2448-2450,*

96. The reaction of compound **A** with excess  $^{13}CO$  resulted in an intermediate **B**. Show the steps involved in forming intermediate **B** from compound **A** (along with the name of the reaction in each step). The Fe center obeys the 18-electron rule, and the electron count on the Pd center should not exceed 16. (3 marks)

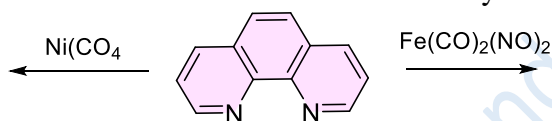


*M. Knorr, P. Brunstein, A. Tiripicchio, F. Ugozzoli, Organometallics, 1995, 14, 4910-4919*

## 9. Ligand substitution reactions and fluxionality

### Solved Problems

97. Kinetic studies indicate that the reaction of  $\text{Ni}(\text{CO})_4$  with phenanthroline follows two consecutive first order reactions while the reaction of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  follows purely second order kinetics. It has also been observed that the attachment of the first donor atom of phenanthroline is the rate determining step. Give reasons for the difference in the kinetics of these reactions and identify the type of mechanism in each case.

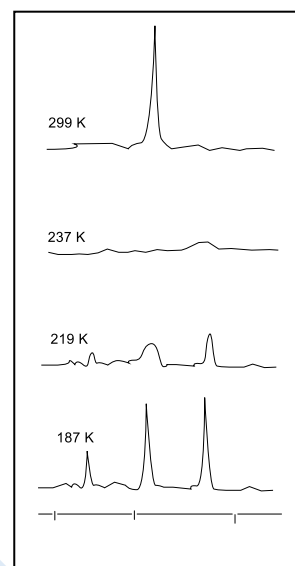
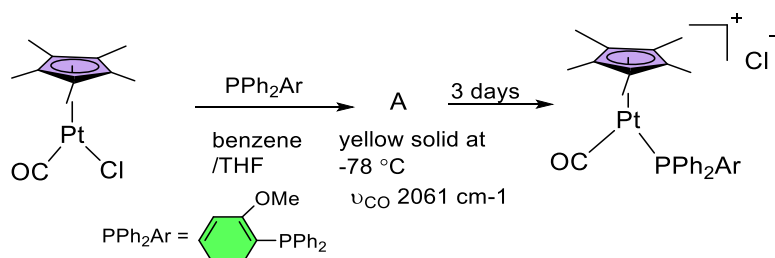


*B. J. Plankey, J.V Rund, Inorg. Chem. 1979, 18, 957-960.*

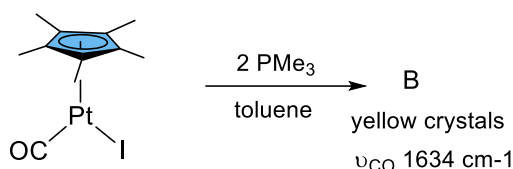
### Solution

Both the complexes are 18 e species.  $\text{Ni}(\text{CO})_4$  reaction proceeds by the dissociative mechanism while the  $\text{Fe}(\text{CO})_2(\text{NO})_2$  reaction proceeds by the associative mechanism (second order kinetics) since the ligand NO can change from linear to bent mode and vice versa.

98. The 18e Cp\*Pt(CO)Cl complex on reaction with the phosphine PPh<sub>2</sub>(o-OMeC<sub>6</sub>H<sub>4</sub>) gave a yellow solid A which was isolated by rapid cooling at -78 °C. Compound A showed stereochemical nonrigidity. The <sup>13</sup>C(<sup>1</sup>H) NMR spectra of A recorded at 187K showed three broad peaks in the methyl region which when brought to 299K coalesced to a single peak. Provide the structure of A and explain its spectra. [4]



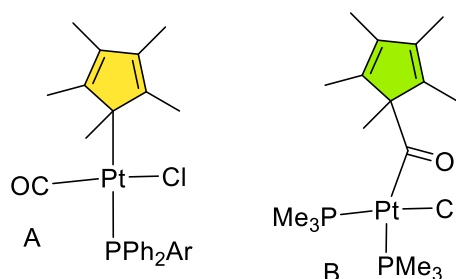
The analogous 18e Cp\*Pt(CO)I complex on reaction with 2 moles of PMe<sub>3</sub> gave another highly unexpected yellow solid B which did not show stereochemical nonrigidity. The IR spectra of this compound gave a peak at 1634 cm<sup>-1</sup>. The <sup>1</sup>H NMR of B showed 4 signals in the region 1.12 to 1.62 ppm in the ratio 1:2:2:6. Provide the structure of B. Compound A and B are both 16 e species.



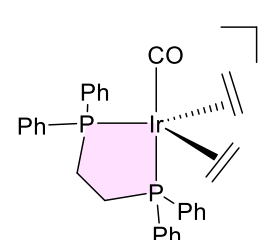
Boag, N. M., Quayum, R., Rao K. M., *Chem. Comm*, 1992, 114-115; L. Lyudmila, Huges R. P., Rheingold A. L., *Organometallics*, 2007, 26, 5735-5736

### Solution

Ring whizzing occurs on the  $\eta^1$  bound Cp\* ring for compound A, whose 16 e structure is shown below. The IR spectra band of compound B indicates that it is an acyl group. The NMR data suggests presence of 2 PMe<sub>3</sub> groups and an  $\eta^1$  bound Cp\* which is not involved in ring whizzing.



99. Variable temperature <sup>1</sup>H NMR and <sup>31</sup>P NMR studies indicated that the given iridium complex was found to show multiple fluxionality as a consequence of which a single peak at 2.6 ppm for the ethylene hydrogen atoms (<sup>1</sup>H NMR) and a single peak at 23 ppm (<sup>31</sup>P NMR) for the two phosphorus atoms of dppe were observed at room temperature. On lowering the temperature both these peaks were found to split into multiplets. Dynamic processes, not involving bond breaking, have



been identified which leads to this multiple fluxionality. Name these dynamic processes.

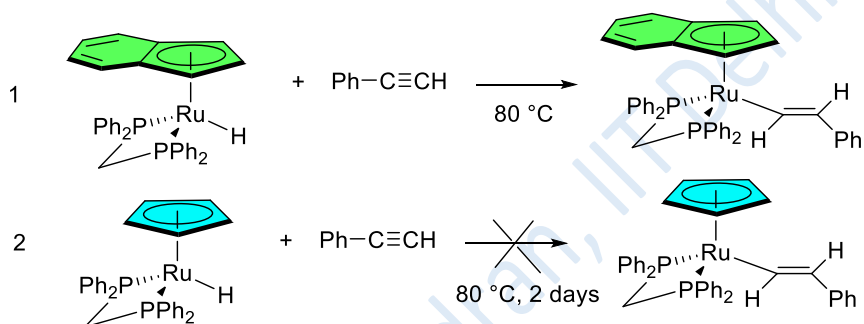
*P. J. Albietz, B. P. Cleary, W. Paw, R. Eisenberg, Inorg. Chem. 2002, 41, 2095-2108*

### Solution

The dynamic processes are (i) propeller rotation of the ethylene units and (ii) Berry pseudorotation type bond movement as a result of which the axial and equatorial groups keep exchanging.

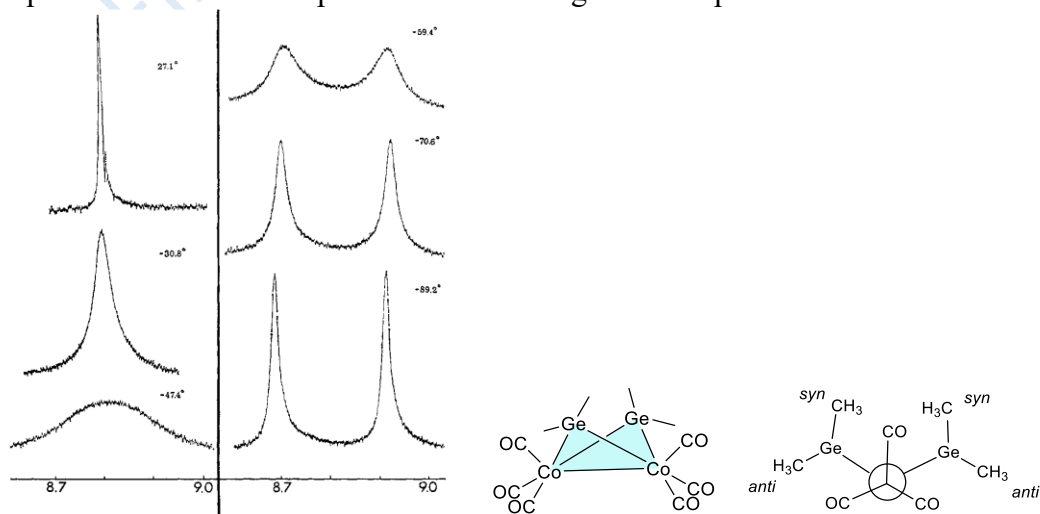
### Unsolved Problems

100. Give reason why the second reaction does not proceed. Provide steps involved for the first reaction whose kinetic studies indicate an activation entropy of  $-21 \pm 4 \text{ cal mol}^{-1} \text{ K}^{-1}$  (e.u).



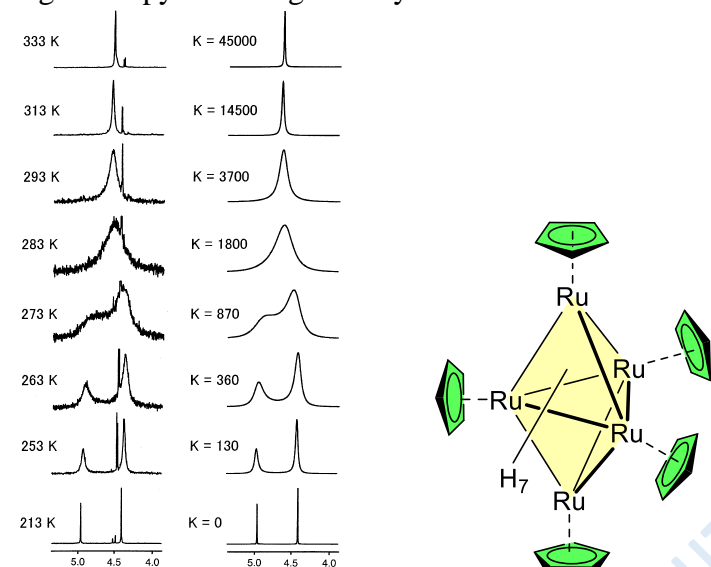
*M. Basetti, P. Casellato, M. P. Gamasa, J. Gimeno, C-G Bernado, B. Martin Vaca Organometallics, 1997, 16, 5470-5477*

101. The reaction of  $\text{Me}_2\text{GeH}_2$  with  $\text{Co}_2(\text{CO})_8$  gave the compound  $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ . The  $^1\text{H}$  NMR of this compound gave a single sharp peak for all the methyl groups at room temperature. This line broadens and collapses and is eventually replaced by two sharp singlets at  $-89^\circ\text{C}$ . The structure of this compound is shown which is analogous to the structure of  $\text{Co}_2(\text{CO})_8$  where the methyl groups of a given germanium atom lie in different environments which is similar to the Newman projections of an ethane like structure. Explain the observed temperature based changes in the spectra.





102. The reaction of the ruthenium diamine complex  $\text{CpRu}(\text{tmeda})\text{Cl}$  with  $\text{LiAlH}_4$  afforded the novel pentaruthenium cluster  $\text{Cp}_5\text{Ru}_5\text{H}_7$  having five CpRu units present in a trigonal bipyramidal geometry.



In the  $^1\text{H}$  NMR spectrum recorded at  $-60\text{ }^\circ\text{C}$ , the cluster exhibited two kinds of  $\text{C}_5\text{H}_5$  signals one at  $\delta$  4.40 and another at 4.95 ppm in 3:2 integration ratio. At  $\delta$  -13.67 ppm, a signal assignable to the hydride was observed as a singlet peak with an intensity of 7H. The resonance signals of the hydrides are observed to be equivalent in the temperature range from  $-60\text{ }^\circ\text{C}$  to ambient temperature, probably due to fast site exchange. With an increase in the temperature, the two  $\text{C}_5\text{H}_5$  signals broadened and consequently combined to a single peak at  $\delta$  4.57 ppm at  $10\text{ }^\circ\text{C}$ . Explain the dynamic  $^1\text{H}$  NMR spectra.

Y. Ohki, N. Uehara, H. Suzuki, *Organometallics*, 2003, 22, 59-64

103. The reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}((\eta^3\text{-2-Me-C}_3\text{H}_4))$  with  $\text{P}(\text{i-Pr})_3$  gave a compound whose  $^1\text{H}$ -NMR when measured indicated presence of two isomers at low temperature. The room temperature spectra, in addition to  $\text{P}(\text{iPr})_3$  peaks gave a broad singlet at 6.42 ppm (5H), 4 peaks for the allyl-C-H bonds (4H) and one singlet for the Me (3H) group at 1.49 ppm. The below  $-60\text{ }^\circ\text{C}$  spectra, in addition to  $\text{P}(\text{iPr})_3$  peaks gave a broad singlet at 5.53 ppm (5H), 4 peaks for allyl CH hydrogens (4H) and a singlet for methyl group at 2.12 ppm (3H). Given that one of them is an 18e species and the other a 16e species, propose the structures of the two species which have the same molecular weight and convert from one to another. Indicate what type(s) of fluxionality is(are) found to operate based on the spectral data.

A	$-60\text{ }^\circ\text{C}$	5.53 bs	5.05 s	4.75 bs	2.90 bs	2.90 bs	2.12 s
B	Room temp	6.42 bs	3.56 d	-	1.81 s	2.54 s	1.49 s

H. Werner, A. Kuhn, *Angew. Chem. Int. Ed.*, 1979, 18, 416

104. The  $^1\text{H}$  NMR spectra of  $\text{CpRh}(\text{C}_2\text{H}_4)_2$  when measured at  $57\text{ }^\circ\text{C}$  indicated a broad singlet at 1.93 ppm (8H) along with a sharp singlet at 5.15 ppm (5H). The spectra when measured at  $-20\text{ }^\circ\text{C}$  showed the broad singlet at 1.92 ppm getting resolved into 2 pairs

of doublets of equal intensity one around 1.12 ppm and the other around 2.77 ppm. This difference in the temp dependant NMR is due to

- (a) Ring whizzing of the Cp ring
- (b) Rotation of the ethylenes around the Rh- alkene axis
- (c) Rotation of the ethylenes around the ethylene C=C axis
- (d) Ethylene units dissociating from rhodium and re joining

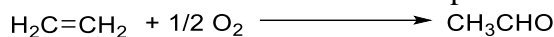
*R. Cramer, J. Am. Chem. Soc., 1964, 86, 217- 222*

## 10. Organometallics in Catalysis: Basics

105. Which one among the given reactions is not part of the reactions of Fisher-Tropsch process of converting coal to gasoline?

- (i) Water gas shift reaction
- (ii) Steam reforming
- (iii) Coal gasification
- (iv) Coal hydrogenation

106. The overall reaction of Wacker oxidation is expressed as follows



The wrong statement with respect to Wacker oxidation is

- (i) Wacker oxidation uses palladium (II) as the catalyst
- (ii) Cocatalyst  $\text{CuCl}_2$  oxidizes Pd(0) formed during the reaction to Pd(II)
- (iii) Acetaldehyde is obtained from ethylene when reaction is carried out in water
- (iv) The oxygen gas used becomes part of the acetaldehyde product

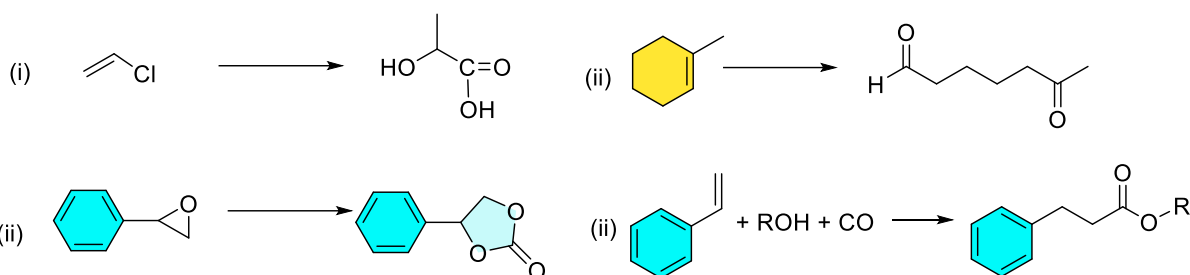
107. Which one of the following reactions happen during the propagation step of a Ziegler Natta polymerization?

- (i) Migratory insertion
- (ii) Oxidative addition
- (iii) Reductive elimination
- (iv)  $\beta$ - hydrogen elimination
- (v)

108. The type of polypropylene which can be produced using Ziegler Natta polymerization using titanium and aluminium based catalysts is

- (i) Atactic polypropylene
- (ii) Isotactic polypropylene
- (iii) Syndiotactic polypropylene
- (iv) Both isotactic and syndiotactic polypropylene

109. Which of the following reactions involves hydroformylation?



110. Which of the following statements are true for hydroformylation?

- Hydroformylation can occur as a side reaction during Fischer-Tropsch process using a cobalt catalyst.
- Hydrogenation of alkenes to alkanes can be a competing reaction during hydroformylation using rhodium catalysts.
- Branched aldehydes are more favoured to form during hydroformylation than linear aldehydes.
- Hydroformylation is an atom economic reaction.

111. Which of the following statements are true for Fischer-Tropsch Process?

- Fischer-Tropsch process can be considered as a process which indirectly converts coal to gasoline.
- Depending upon the catalyst used, the F-T process can be used for synthesizing hydrocarbons, methanol and higher alcohols.
- The major side product of gasoline synthesis by the F-T process is carbon dioxide
- Iron and cobalt are the most common catalysts used in the F-T process.

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