Problems

14.1 Predict the transition metal-containing products of the following reactions:

a. $[Mn(CO)_5]^- + H_2C{=}CH{-}CH_2Cl \rightarrow$ initial product $\xrightarrow{-CO}$ final product

b. *trans*-$Ir(CO)Cl(PPh_3)_2 + CH_3I \rightarrow$

c. $Ir(PPh_3)_3Cl \xrightarrow{\Delta}$

d. $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_3) + PPh_3 \rightarrow$

e. $(\eta^5\text{-}C_5H_5)Mo(CO)_3[C({=}O)CH_3] \xrightarrow{\Delta}$

f. $H_3C{-}Mn(CO)_5 + SO_2 \rightarrow$ (no gases are evolved)

14.2 Predict the transition metal–containing products of the following reactions:

a. $H_3C{-}Mn(CO)_5 + P(CH_3)(C_6H_5)_2 \rightarrow$ (no gases are evolved)

b. $[Mn(CO)_5]^- + (\eta^5\text{-}C_5H_5)Fe(CO)_2Br \xrightarrow{\Delta}$

c. *trans*-$Ir(CO)Cl(PPh_3)_2 + H_2 \rightarrow$

d. $W(CO)_6 + C_6H_5Li \rightarrow$

e. *cis*-$Re(CH_3)(PEt_3)(CO)_4 + {}^{13}CO \rightarrow$(show all expected products, percentage of each)

f. *fac*-$Mn(CO)_3(CH_3)(PMe_3)_2 + {}^{13}CO \rightarrow$(show all expected products, percentage of each)

14.3 Predict the transition metal–containing products of the following reactions:

a. *cis*-$Mn(CO)_4({}^{13}CO)(COCH_3) \xrightarrow{\Delta}$

(show all expected products, percentage of each)

b. $C_6H_5CH_2\text{-}Mn(CO)_5 \overset{hv}{\rightarrow} CO +$

c. $V(CO)_6 + NO \rightarrow$
d. $Cr(CO)_6 + Na/NH_3 \rightarrow$
e. $Fe(CO)_5 + NaC_5H_5 \rightarrow$
f. $[Fe(CO)_4]^{2-} + CH_3I \rightarrow$
g. $H_3C\text{-}Rh(PPh_3)_3 \overset{\Delta}{\rightarrow} CH_4+$

14.4 Heating $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ with NaH in solution gives **A**, which has the empirical formula $C_7H_6O_2Fe$.**A** reacts rapidly at room temperature to eliminate a colorless gas **B**, forming a purple-brown solid **C** having the empirical formula $C_7H_5O_2Fe$. Treatment of **C** with iodine generates a brown solid **D** with the empirical formula $C_7H_5O_2FeI$, which on treatment with TlC_5H_5 gives a solid **E** with the formula $C_{12}H_{10}O_2Fe$. **E**, on heating, gives off a colorless gas, leaving an orange solid **F** with the formula $C_{10}H_{10}Fe$. Propose structural formulas for **A** through **F**.

14.5 $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ reacts with $ClCH_2CH_2SCH_3$ to give **A**, a monomeric and diamagnetic substance of stoichiometry $C_{10}H_{12}FeO_2S$ having two strong IR bands at 1980 and 1940 cm^{-1} . Heating of **A** gives **B**, a monomeric, diamagnetic substance having strong IR bands at 1920 and 1630 cm^{-1}. Identify **A** and **B**.

14.6 The reaction of $V(CO)_5(NO)$ with $P(OCH_3)_3$ to give $V(CO)_4[P(OCH_3)_3](NO)$ has the rate law

$$\frac{-d[V(CO)_5(NO)]}{dt} = k_1[V(CO)_5(NO)] + k_2[P(OCH_3)_3][V(CO)_5(NO)]$$

a. Suggest a mechanism for this reaction consistent with the rate law.
b. One possible mechanism consistent with the last term in the rate includes a transition state of formula $V(CO)_5[P(OCH_3)_3](NO)$. Would this necessarily be a 20-electron species? Explain.

14.7 The rate law for the reaction
$H_2 + Co_2(CO)_8 \rightarrow 2\ HCo(CO)_4$ is is

$$\text{Rate} = \frac{k[Co_2(CO)_8][H_2]}{[CO]}$$

Propose a mechanism consistent with this rate law.

14.8 Which of the following *trans* complexes would you expect to react most rapidly with CO? Which would you expect to react least rapidly? Briefly explain your choices.

$Cr(CO)_4(PPh_3)_2$
$Cr(CO)_4(PPh_3)(PBu_3)$ (Bu=*n*-butyl)
$Cr(CO)_4(PPh_3)[P(OMe)_3]$
$Cr(CO)_4(PPh_3)[P(OPh)_3]$

(See M. J. Wovkulich, J. D. Atwood, *Organometallics*, **1982**, *1*, 1316.)

14.9 The equilibrium constants for the ligand dissociation reaction $NiL_4 \leftrightharpoons NiL_3 + L$ have been determined for a variety of phosphines. (See C. A. Tolman, W. C. Seidel, L. W. Gosser, *J. Am. Chem. Soc.*, **1974**, *96*, 53). For L = PMe_3, PEt_3, $PMePh_2$, and PPh_3, arrange these equilibria in order of the expected magnitudes of their equilibrium constants (from largest *K* to smallest).

14.10 In addition to pioneering the cone angle concept, C. A. Tolman proposed a parameter χ (chi) as a measure of the electronic effect of phosphine and related ligands, based on infrared spectra of complexes containing these ligands (C. A. Tolman, *J. Am. Chem. Soc.*, **1970**, *92*, 2953).

a. What was the general formula of the complexes used by Tolman?
b. How was χ defined?
c. What types of ligands had high values of χ?
d. To what extent does this approach distinguish between the sigma donor and pi acceptor nature of the ligands studied?

14.11 The nickel(II) pincer complexes $[N(o\text{-}C_6H_4PR_2)_2]NiX$ (**1**: R = Ph, X = H; **2**: R = Ph, X = Me) undergo different reactions with CO on the basis of the R and X groups, but the phosphine arms remain attached to the Ni center (See L.-C. Liang, Y.-T. Hung, Y.-L. Huang, P.-Y. Lee, W.-C. Chen, *Organometallics*, **2012**, *31*, 700 for structural details of these complexes.)

a. When R = Ph and X = H, the addition of CO results in the disappearance of a ^1H NMR resonance at -18 ppm, with the corresponding new signal (that also integrates to one H) at 8.61 ppm. Two *v*(CO) stretching bands appear in the IR spectrum at 1993 and 1924 cm^{-1}. Propose a structure for this product and a mechanism for its formation.
b. When R = Ph and X = Me, the addition of CO results in the appearance of an intermediate with a single (CO) infrared band at 1621 cm^{-1}. This

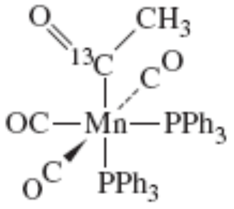
intermediate subsequently provides another nickel complex with three (CO) infrared bands (2002, 1943, 1695 cm^{-1}). Propose the structures of the intermediate and final product, and the reaction mechanisms involved in these reactions.

c. Why do the reactions proceed differently when X = H or X = Me?

14.12 The *N*, *N*-dibenzylcyclam ligand supports a novel double-cyclometallation reaction of zirconium(IV) (R = ^{t}Bu, Me, CH_2Ph) in the presence of 4 atm H_2 as depicted in Scheme 1 of R. F. Munhá, J. Ballmann, L. F. Veiros, B. O. Patrick, M. D. Fryzuk, *Organometallics*, **2012**, *31*, 4937.

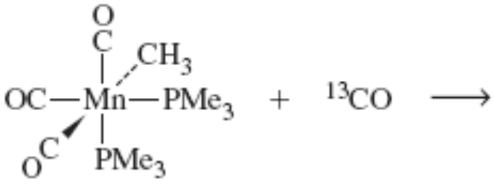
a. Propose a mechanism for this reaction, which proceeds most slowly for R = CH_2Ph, that is consistent with the rate being independent of H_2 pressure.
b. Explain the reasoning for your selection. Why might the reaction be slowest with R = CH_2Ph)?

14.13 The complex shown below loses carbon monoxide on heating. Would you expect this carbon monoxide to be ^{12}CO, ^{13}CO, or a mixture of both? Why?



14.14

a. Predict the products of the following reaction, showing clearly the structure of each:



b. Each product of this reaction has a new, rather strong IR band that is distinctly different in energy from any bands in the reactants. Account for this band, and predict its approximate location (in cm^{-1}) in the IR spectrum.

14.15 Give structural formulas for **A** through **D**:

$$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4 \xrightarrow{Na/Hg} A \xrightarrow{Br_2} B \xrightarrow{LiAlH_4} C \xrightarrow{PhNa} A + D(\text{a hydrocarbon})$$

*v*CO = 1942, 1790 cm^{-1} for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$

A has strong IR bands at 1880 and 1830 cm^{-1}; **C** has a ^{1}H spectrum consisting of two singlets of relative intensity 1:5 at approximately δ -12 and δ 5 respectively. (Hint: Metal hydrides often have protons with negative chemical shifts.)

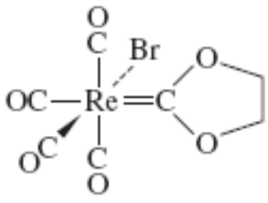
14.16 $Re(CO)_5Br$ reacts with the ion Br — CH_2 CH_2 — O^- to give compound Y + Br^-.

a. What is the most likely site of attack of this ion on $Re(CO)_5Br$? (Hint: Consider the hardness (see **Chapter 6**) of the Lewis base.)
b. Using the following information, propose a structural formula of Y, and account for each of the following:
   Y obeys the 18-electron rule.
   No gas is evolved in the reaction.
   ^{13}C NMR indicates that there are five distinct magnetic environments for carbon in **Y**.
   Addition of a solution of Ag^+ to a solution of **Y** gives a white precipitate.

(See M. M. Singh, R. J. Angelici, *Inorg. Chem.*, **1984**, *23*, 2699.)

14.17 What is a *nitrenium* ligand? How does it compare with an *N*-heterocyclic carbene? Which of these types of ligand is viewed as a stronger sigma donor, and what experimental evidence supports this view? What role do pincer ligands play in nitrenium complexes? (See Y. Tulchinsky, M. A. Iron, M. Botoshansky, M. Gandelman, *Nature Chem.*, **2011**, *3*, 525.)

14.18 The carbene complex **I** shown below undergoes the following reactions. Propose structural formulas for the reaction products.



a. When a toluene solution containing **I** and excess triphenylphosphine is heated to reflux, compound **II** is formed first, and then compound **III. II** has infrared bands at 2038, 1958, and 1906 cm^{-1} and **III** at 1944 and 1860 cm^{-1}. ^{1}H NMR data δ values (relative area) are as follows:

II: 7.62, 7.41 multiplets (15)

4.19 multiplet (4)

III: 7.70, 7.32 multiplets (15)

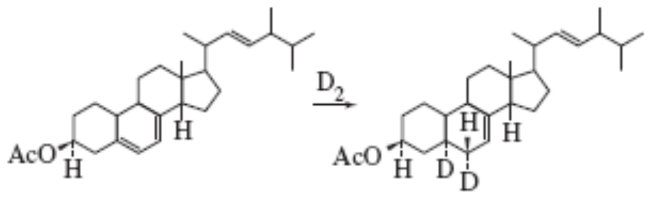
3.39 singlet (2)

b. When a solution of **I** in toluene is heated to reflux with 1,1-bis(diphenylphosphino)methane, a colorless product **IV** is formed that has the following properties:
IR: 2036, 1959, 1914 cm^{-1}
Elemental analysis (accurate to ±0.3%): 35.87% C, 2.73% H
c. **I** reacts rapidly with the dimethyldithiocarbamate ion $S_2CN(CH_3)_2^-$ in solution to form $Re(CO)_5Br$ + V, a product that does not contain a metal atom. This product has no infrared bands between 1700 and 2300 cm^{-1}. However, it does show moderately intense bands at 1500 and 977 cm^{-1}. The ^1H NMR spectrum of **V** shows bands at δ3.91 (triplet), 3.60 (triplet), 3.57 (singlet), and 3.41 (singlet).
(See G. L. Miessler, S. Kim, R. A. Jacobson, R. J. Angelici, *Inorg. Chem.*, **1987**, *26*, 1690.)

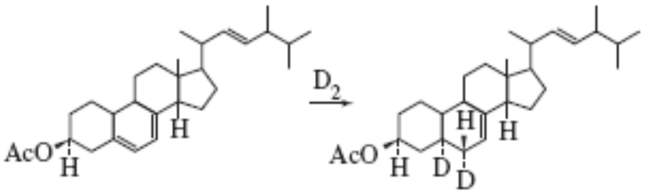
14.19 The complex **I** in the preceding problem can be synthesized from $Re(CO)_5Br$ and 2-bromoethanol in ethylene oxide solution with solid NaBr present. Suggest a mechanism for the formation of the carbene ligand.
14.20 $BrCH_2CH_2CH_2Mn(CO)_5$ is formed by reaction of $[Mn(CO)_5]^-$ with 1,3-dibromopropane. However, the reaction does not stop here; the product reacts with additional $[Mn(CO)_5]^-$ to yield a carbene complex. Propose a structure for this complex, and suggest a mechanism for its formation.
14.21 An acyl metal carbonyl ($R{-}C({=}O)M(CO)_x$) is generally easier to protonate than either a metal carbonyl or an organic ketone, such as acetone. Suggest an explanation.
14.22 Show how transition-metal complexes could be used to effect the following syntheses:

a. Acetaldehyde from ethylene
b. $CH_3CH_2COOCH_3$ from CH_3CH_2Cl
c. $CH_3CH_2CH_2CH_2CHO$ from $CH_3CH_2CH{=}CH_2$

d. $PhCH_2CH_2CH_2CHO$ from an alkene (Ph = phenyl)



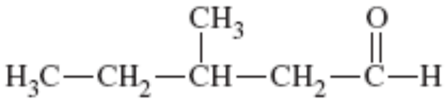
e.

- 

- $C_6D_5CH_3$ from toluene, $C_6H_5CH_3$.

- **14.23** The complex $Rh(H)(CO)_2(PPh_3)_2$ can be used in the catalytic synthesis of *n*-pentanal from an alkene having one less carbon. Propose a mechanism for this process. Give an appropriate designation for each type of reaction step (such as oxidative addition or alkyl migration), and identify the catalytic species.

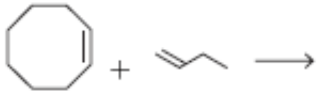
- **14.24** It is possible to synthesize the following aldehyde from an appropriate 5-carbon alkene by using an appropriate transition-metal catalyst:

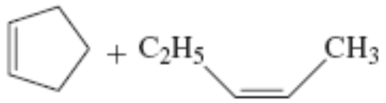


$$H_3C-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

Show how this synthesis could be effected catalytically. Identify the catalytic species.

- **14.25** Predict the products if the following compounds undergo metathesis:

  a. 

  b. 

  c. 1-butene + 2-butene

d. 1,7-octadiene

- **14.26** The complex $(CO)_5M{=}C(C_6H_5)_2$ [**M** = third row transition metal] can catalyze ROMP of 1–methylcyclobutene. Identify M, show the initial steps in this process, and clearly identify the structure of the polymer.

- **14.27** One of the classical experiments in the development of olefin metathesis was the “double cross” metathesis in which a mixture of cyclooctene, 2-butene, and 4-octene underwent metathesis.

  a. What products would be expected from this metathesis?
  b. How would the formation of these products differ in the pairwise and non-pairwise mechanisms? (See T. J. Katz, J. McGinness, *J. Am. Chem. Soc.*, **1975**, *97*, 1592.)

- **14.28** The complex $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ reacts with the highly electrophilic borane $HB(C_6F_5)_2$ to form a product having stoichiometry $(CH_2)[HB(C_6F_5)_2]_2[(C_5H_5)_2Zr]$, and the product is a rare example of pentacoordinate carbon.

  a. Suggest a structure for this product.
  b. An isomer of this product,$[(C_5H_5)_2ZrH]^+[CH_2\ \{B(C_6F_5)_2\}_2\ (\mu\text{-}H)]^-$, has been proposed as a potential Ziegler–Natta catalyst. Suggest a mechanism by which this isomer might serve as such a catalyst.

(See R. E. von H. Spence, D. J. Parks, W. E. Piers, M. MacDonald, M. J. Zaworotko, S. J. Rettig, *Angew. Chem., Int. Ed.*, **1995**, *34*, 1230.)

- **14.29** Terminal tungsten nitride complexes containing W ≡ N bonds have been reported to catalyze nitrile–alkyne cross-metathesis (NACM) by a mechanism that has parallels with the non-pairwise mechanism for olefin metathesis (A. M. Geyer, E. S. Weidner, J. B. Gary, R. L. Gdula, N. C. Kuhlmann, M. J. A. Johnson, B. D. Dunietz, J. W. Kampf, *J. Am. Chem. Soc.*, **2008**, *130*, 8984.) When *p*-methoxybenzonitrile and 3-hexyne were mixed in the presence of catalyst candidate $N \equiv W(OC(CF_3)_2Me)_3(DME)$, two principal products attributable to metathesis were observed.

  a. Outline the NACM mechanism, as described in the reference.
  b. Account for the formation of the two products, and suggest which was formed first.

- **14.30** At low temperature and pressure, a gas-phase reaction can occur between iron atoms and toluene. The product, a rather unstable sandwich compound, reacts with ethylene to give compound **X**. Compound **X** decomposes at room temperature to liberate ethylene; at -20 °C it reacts with $P(OCH_3)_3$ to give $[P(OCH_3)_3]_2$. Suggest a structure for compound **X**. (See U. Zenneck, W. Frank, *Angew. Chem., Int. Ed.*, **1986**, *25*, 831.)

- **14.31** The reaction of $RhCl_3 \cdot 3H_2O$ with tri-*o*-tolylphosphine in ethanol at 25 °C gives a blue-green complex **I** ($C_{42}H_{42}P_2Cl_2Rh$) that has ν(Rh—Cl) at 351 $cm^{-1}$and μ_{eff} = 2.3 BM. At a higher temperature, a diamagnetic yellow complex **II** that has an Rh:Cl ratio of 1:1 is formed that has an intense band near 920 cm^{-1}. Addition of NaSCN to **II** replaces Cl with SCN to give a product **III** having the following ^1H NMR spectrum:

Chemical Shift	Relative Area	Type
6.9–7.5	12	Aromatic
3.50	1	Doublet of 1:2:1 triplets
2.84	3	Singlet
2.40	3	Singlet

Treatment of **II** with NaCN gives a phosphine ligand **IV** with the empirical formula $C_{21}H_{19}P$ and a molecular weight of 604. **IV** has an absorption band at 965 cm^{-1} and the following ^1H NMR spectrum:

Chemical Shift	Relative Area	Type
7.64	1	Singlet
6.9–7.5	12	Aromatic
2.37	6	Singlet

Determine the structural formulas of compounds **I** through **IV**, and account for as much of the data as possible. (See M. A. Bennett, P. A. Longstaff, *J. Am. Chem. Soc.*, **1969**, *91*, 6266.)

- **14.32** Ring-closing metathesis (RCM) is not restricted to alkenes; similar reactions are also known for alkynes. The tungsten alkylidyne complex $W(\equiv CCMe_3)(OCMe_3)_3$ has been used to catalyze such reactions. Predict the structures of the cyclic products for metathesis of

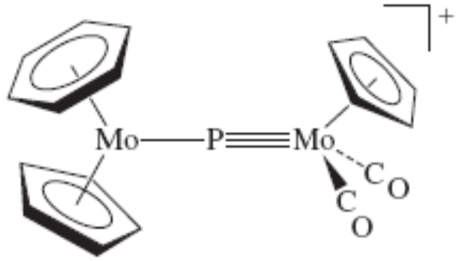
  a. $[MeC\equiv C(CH_2)_2OOC(CH_2)]_2$
  b. $MeC\equiv C(CH_2)_8COO(CH_2)_9C\equiv CMe$

(See A FÜrstner, G. Seidel, *Angew. Chem., Int. Ed.,* **1998**, *37*, 1734.)

- **14.33** More than two decades elapsed between the development of a homogeneous catalytic process for producing acetic acid in the late 1960s and convincing experimental evidence for the key intermediate $[CH_3Rh(CO)_2I_3]^-$ (**Figure 14.20**). Describe the evidence presented for this intermediate. (A. Haynes, B. E. Mann, D. J. Gulliver, G. E. Morris, P. M. Maitlis, *J. Am. Chem. Soc.,* **1991**, *113*, 8567.)

- **14.34** The compound $Fe(CO)_4I_2$ reacts with cyanide in methanol solution to form complex **A**, which has intense IR bands at 2096 and 2121 cm^{-1} and less intense bands at 2140 and 2162 cm^{-1} Reaction of **A** with additional cyanide yields **B**. Ion **B** also has two pairs of infrared bands, a more intense pair at 1967 and 2022 cm^{-1} and a less intense pair at 2080 and 2106 cm^{-1} Neither **A** nor **B** contains iodine. Propose structures of **A** and **B**. (See J. Jiang, S. A. Koch, *Inorg. Chem.*, **2002**, *41*, 158.)

- **14.35** Cation **1** reacts with the ion $HB(sec\text{-}C_4H_9)_3^-$, a potential source of hydride, to form **2**. The following data are reported for **2**:



1

IR: strong bands at 1920, 1857 cm^{-1} .

^1H NMR : chemical shift (relative area):

5.46 (2)

5.28 (5)

5.15 (3)

4.22 (2)

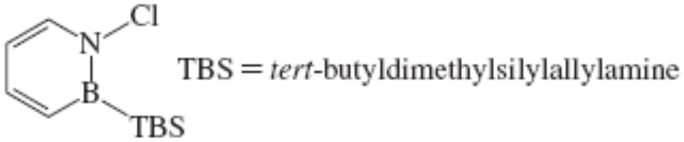
1.31 (27)

In addition, a small peak is believed to be hidden under other peaks.

^{13}C NMR : resonance at 236.9 ppm, seven additional peaks and clusters of peaks between 32.4 and 115.7 ppm.

Propose a structure for **2**, and account for as much of the experimental data as possible. (See I. Amor, D. García-Vivó, M. E. García, M. A. Ruiz, D. Sáez, H. Hamidov, J. C. Jeffery, *Organometallics*, **2007**, *26*, 466.)

- **14.36** Sometimes an organometallic complex can act as the intermediate in the synthesis of organic compounds. The heterocyclic compound (TBS) shown below was reacted with $LiBH(C_2H_5)_3$ to form **X**, a halogen-free heterocycle. When **X** was treated with $Cr(CO)_3(CH_3CN)_3$, followed by reaction with HF · pyridine, transition-metal complex **Y**, which had strong absorptions at 1898 and 1975 cm^{-1}, formed. Addition of triphenylphosphine gave a new transition-metal complex plus heterocycle **Z**. The ^1H NMR spectrum of **Z** showed four single peaks of equal intensity between δ 6.4 and 7.8 ppm, a quartet at 4.9 ppm, and a triplet at 8.44 ppm. Propose structures for **X**, **Y**, and **Z**. (See A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S-H. Liu, *Angew. Chem., Int. Ed.*, **2009**, *48*, 973.)



- **14.37** When hexaiodobenzene, C_6I_6, reacts with diferrocenylzinc, $[(\eta^5\text{-}C_5H_5)FeC_5H_4]_2Zn$, one of the products has a C to Fe atom ratio exactly 10 percent higher than in ferrocene and an H to Fe atom ratio 10 percent lower than in ferrocene. The product contains no elements other than those that occur in ferrocene. Suggest a structure of this product. (See Y. Yu, A. D. Bond,

P. W. Leonard, U. J. Lorenz, T. V. Timofeeva, K. P. C. Vollhardt, G. D. Whitener, A. A. Yakovenko, *Chem. Commun.*, **2006**, 2572.)