T4. OMCh Problems

1   Give structural formulas and electron count for A and B:


A: Rh(I) alkene binuclear complex
B: Rh(I) Cp mononuclear complex
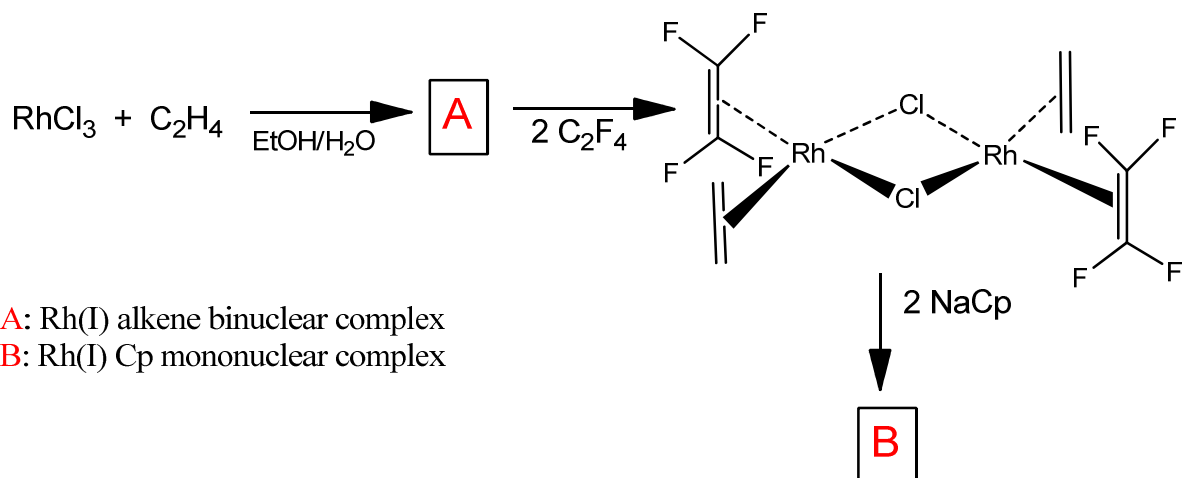
a) Explain the configuration of olefin ligand in compound A
b) ^{19}F NMR for compound B gives two signals between 20 and -50 ºC. However, ^1H NMR spectrum shows a single signal at 20ºC and two signals at -44ºC. Explain these facts.

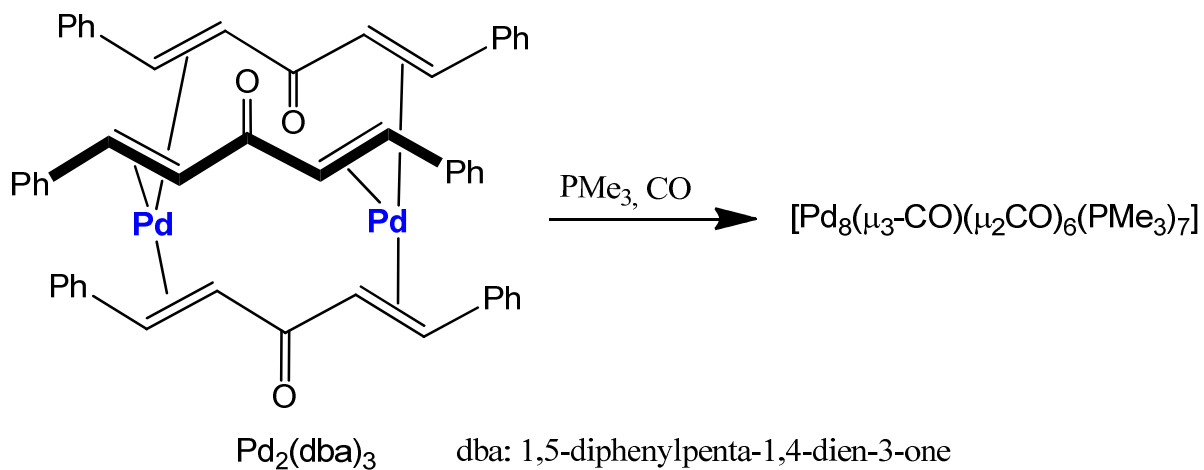| Ligand	Bond distance C-C (Å)	Bond distance Rh-C (Å)
C_2H_4	1.358	2.169
C_2F_4	1.405	2.026

VOE & OP, 2010

2   Cyclododecatriene (CDT) forms labile complex with Ni(0), which serves as a starting material for other Ni(0) olefin complexes. Determine electron count and structural formulas for A and B. Indicate the coordination of central atom.
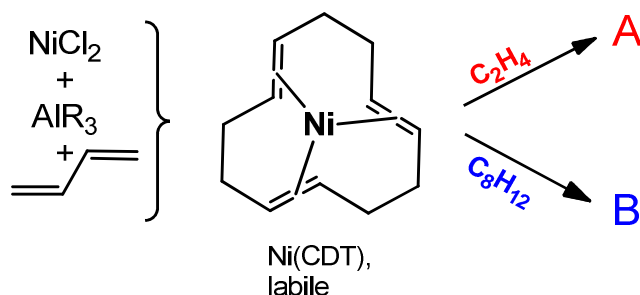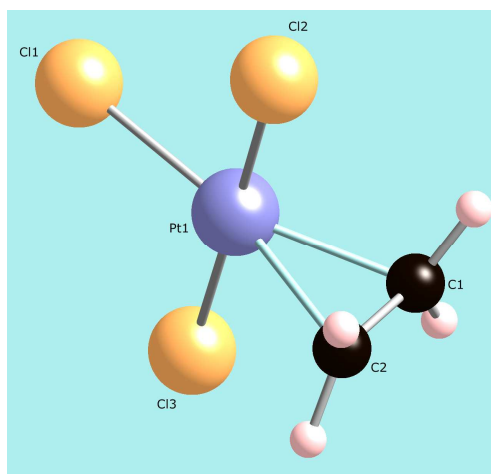

3   For butadiene

a. Draw the frontier orbitals (HOMO-1 to LUMO+1)

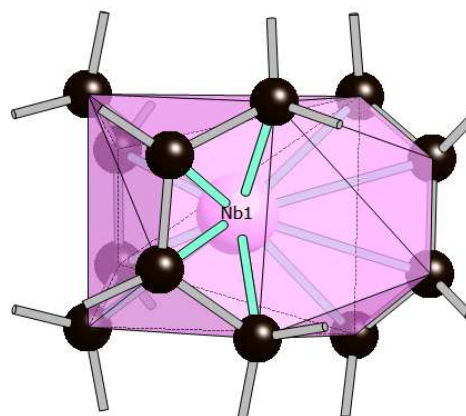b. Sketch its coordination modes to metal centers.

4 $Pd_2(dba)_3$ is a ready source of palladium(0). Draw the molecular structure of the reaction product. Indicate the coordination polyhedron of each palladium center:

$$\xrightarrow{\text{PMe}_3,\text{ CO}} [Pd_8(\mu_3\text{-CO})(\mu_2CO)_6(PMe_3)_7]$$

$Pd_2(dba)_3$ dba: 1,5-diphenylpenta-1,4-dien-3-one

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5 Describe the synthesis of the following compounds:

$PtCl_3(C_2H_4)$ $[Nb(C_4H_6)_3]^-$

6 Resonance forms for olefin coordination:

Dative (planar)   Metallacyclopropane (bent)
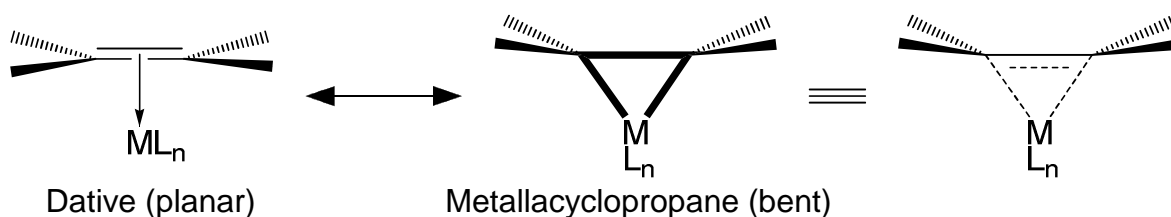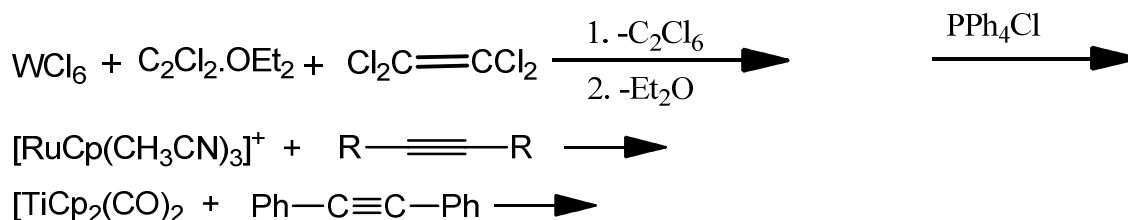
According to the geometrical date, indicate which compounds of the following table are genuine olefin complexes and which ones are rather metallacyclopropanes:

Complex		C=C	M-C	Angle
[Pt $(C_2H_4)_2(C_2F_4)$]	ETFEPT11	136.5 137.9 143.4	219-227 219-225 202-204	14-17 15-16 34-36
[Au$(C_2H_4)_3$]$^+$	KISVOY	135-137	226-227	36
[Cu$(C_2H_4)_3$]$^+$	NITYUL	129-132	212-218	2-36
[RhCp$(C_2H_4)(C_2F_4)$]	CPEFRH	135.8 140.5	216-217 202-203	20-22 37
[CoCp(PMe$_3$)(C_2H_4)]	MOHWUC	142.0	198	23-26
[RhCp(PMe$_3$)(C_2H_4)]	COHBAC	144.5	208-209	11-28
[RhCp(PPh$_3$)(C_2H_4)]	XEPJIM	140-141	209-211	35
[VCp(PMe$_3$)$_2(C_2H_4)$]	GEXNAY10	136.5	215-217	21-25
[CrCp(PMe$_3$)$_2(C_2H_4)$]	NABXIX	141.5	213	29-32

7 Predict the products of the following reactions:

$$WCl_6 + C_2Cl_2.OEt_2 + Cl_2C\!=\!\!=\!CCl_2 \xrightarrow[\text{2. -Et}_2\text{O}]{\text{1. -C}_2\text{Cl}_6} \xrightarrow{\text{PPh}_4\text{Cl}}$$

$$[RuCp(CH_3CN)_3]^+ + R\!-\!\!\equiv\!\!-R \longrightarrow$$

$$[TiCp_2(CO)_2 + Ph\!-\!C\!\equiv\!C\!-\!Ph \longrightarrow$$

Additional problems
Butler, Harrod, *Inorganic Chemistry. Principles and applications,* Benjamin Cummings, Redwood City, 1989. 22.17.