Ch 154

Due January 29, 2008 before class

Problem Set 2

General Instructions: Do not use primary literature.

1. Assign the oxidation state of all the transition metal complexes in the following reactions. Identify the reactions that involve oxidative-addition and/or reductive-elimination.

a) $2\ HCo(CO)_3PPh_3 \rightarrow Co_2(CO)_6(PPh_3)_2 + H_2$

b) $CH_3Mn(CO)_5 + PMe_3 \rightarrow CH_3C(O)Mn(CO)_4PMe_3$

c) $HCo(N_2)(PPh_3)_3 + C_2H_4 \rightarrow HCo(C_2H_4)(PPh_3)_3 + N_2$

d) $HCo(N_2)(PPh_3)_3 + H_2 \rightarrow H_3Co(PPh_3)_3 + N_2$

e) $2\ [Co(CN)_5]^{3-} + CH_3I \rightarrow [CH_3Co(CN)_5]^{3-} + [Co(CN)_5I]^{3-}$

f) *trans*-$HPt(PMe_3)_2Cl + CH_3I \rightarrow$ *trans*-$Pt(PMe_3)_2ICl + CH_4$

2. Certain metal complexes are found to undergo hydrolysis (replacement of an anionic ligand by water or hydroxide) much faster in base than in acid. For example,

$[Co(NH_3)_5Cl]^{2+}$ + OH^- -----> $[Co(NH_3)_5(OH)]^{2+}$ + Cl^-

is as much as 10^6 times faster than

$[Co(NH_3)_5Cl]^{2+}$ + H_2O -----> $[Co(NH_3)_5(OH_2)]^{3+}$ + Cl^-

The rate depends linearly on hydroxide concentration: rate = $k_{obs}[Co(NH_3)_5Cl]^{2+}[OH]^-$

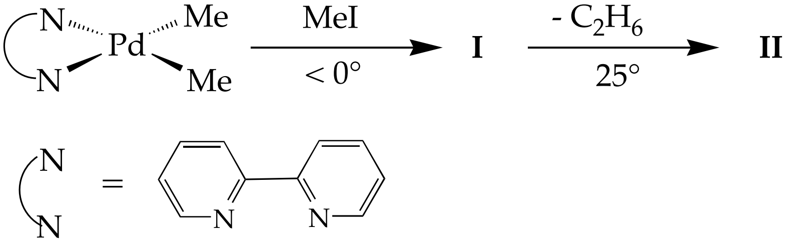
In contrast, for

trans-$[Co(py)_4Cl_2]^+$ + OH^- -----> $[Co(py)_4(Cl)(OH)]^{2+}$ + Cl^- (py = pyridine)

no rate enhancement compared to acid hydrolysis is observed, and the rate doesn't depend on hydroxide concentration at all.

Propose mechanisms that can account for the differing kinetic behaviors, including rate law expressions for each case.

3. Reaction of CH_3I with (bpy)$PdMe_2$ (bpy = 2,2'-bipyridine) in acetone at low temperatures (<0°C) forms a product **I**, which is soluble in non-polar organic solvents such as benzene. At room temperature in solution, **I** decomposes slowly to give off ethane and a new palladium complex **II**.



Consider the following additional observations:

a) The same reaction carried out in CD_3CN at low T gives **III** which is soluble in polar solvents but not in non-polar solvents.

b) The ^1H NMR spectra of both **I** and **III**, recorded at low temperature, show two separate signals in the region expected for Pt-Me groups in intensity ratio 2:1. However, on warming to around -5°, the signals for **III** broaden and coalesce, whereas those for **I** remain sharp and distinct.

c) Kinetics studies show the first reaction (formation of **I**) is first-order in both [(bpy)$PdMe_2$] and [MeI]. The decomposition of **I** is first-order in [**I**] but is inhibited by the addition of excess I^-.

Explain all of these observations, including proposed structures for all three complexes, interpretation of the NMR behavior, mechanisms for the reactions, and a rate law expression for decomposition of **I** that accounts for the dependence on [I^-].

4. The reaction of an analog of Zeise's salt with tetramethylallene (TMA) followed by pyridine gives *trans*-$PtCl_2$(py)(TMA). The ^1H NMR at room temperature shows a single peak for the TMA protons, with satellite peaks (coupling to ^{195}Pt, 33% abundant) corresponding to $J_{Pt\text{-}H}$ = 22 Hz. On cooling to -70° that signal broadens, collapses, and grows up into three separate signals, with relative intensities in the ratio of 2:1:1; only the first of these shows satellites ($J_{Pt\text{-}H}$ = 44 Hz). At

intermediate temperatures the rate of the process causing the NMR changes can be determined by line-shape analysis; this was done not only for the parent py complex but for analogs with *para*-substituted pyridines as well, with the following results:

X in *p*-XC_5H_5N	rate (s^{-1})
-NH_2	5
-CH_3	16
-H	30
-Br	75
-CN	200

Propose a structure for the TMA complex that accounts for the low-T NMR spectrum, a mechanism for the process that is responsible for the temperature dependence, and an explanation for the dependence of the rate on the pyridine substituent.

5. Both $Pt(PPh_3)_4$ and $[Ir(cod)(PPh_3)_2]^+$ (where cod = 1,5-cyclooctadiene) react with HCl, to give addition products, respectively, *trans*-$PtHCl(PPh_3)_2$ and $[IrHCl(cod)(PPh_3)_2]^+$. By using additional reagents (HBF_4 and LiCl) to vary the concentrations of $[H^+]$ and $[Cl^-]$ independently, it was found that the rate of the Pt reaction is first order in $[H^+]$ but independent of $[Cl^-]$, whereas the reverse is true for the Ir reaction. When treated with HBF_4 alone the Pt complex reacts readily while the Ir complex does not react at all. Suggest mechanisms for the two HCl additions that account for the different rate laws, and explain the difference(s) between the two complexes responsible for the different behavior.