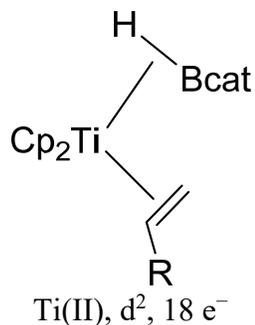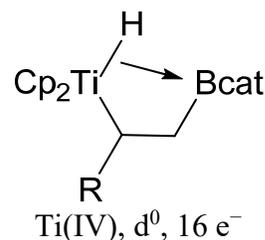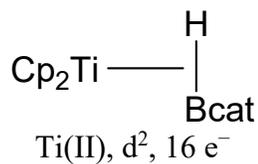**Recommended Reading: 24**, 27.1-27.7 (3rd edition); **24**, 25.1-25.7 (4th edition)

Ch 102 – Problem Set 8
Due: Thursday, June 8 – *Before Class*

Problem 1 (1 point)

a)

Cp_2Ti —— H
Bcat
Ti(II), d^2, 16 e$^-$

H
Cp_2Ti —→ Bcat
R
Ti(IV), d^0, 16 e$^-$
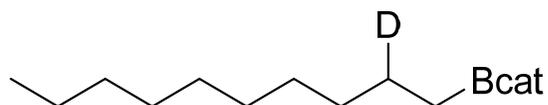
H
Bcat
Cp_2Ti
R
Ti(II), d^2, 18 e$^-$

A: ligand association
C: reductive elimination

b)

D
Bcat

Problem 2 (2 points)

A) The bisphosphine borane nickel compound pictured below reacts reversibly with diphenyl silane to do oxidative addition and reductive elimination of one of the Si-H bonds. Give the valence electron count, d-electron count and formal oxidation state for each of the Ni compounds. (Hint: 4 coordinate boron has a formal charge that must be accounted when counting e-.)

Ph$_2$P PPh$_2$
Ni
B

Ph$_2$SiH$_2$

PPh$_2$
B—H Ni—SiHPh$_2$
PPh$_2$

Ni (0), d^{10}, 16 e-

Ni(II), d^8, 16 e-
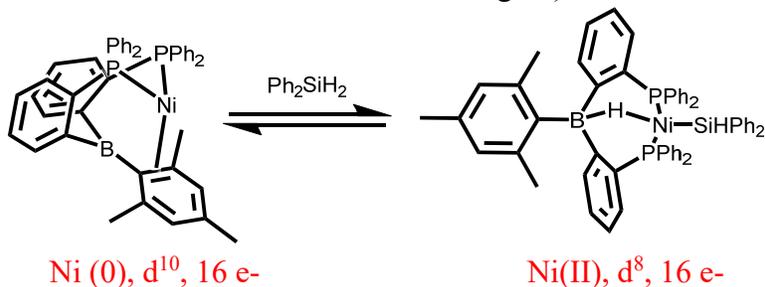
B) The Ni compound pictured above also acts as a catalyst for the hydrosilylation of benzaldehydes (overall reaction shown below). Kinetic measurements showed a linear dependence of the reaction rate on the concentration of the Ni catalyst at 3 different catalyst loadings (1.25 mol%, 2.5 mol% and 5 mol%). Kinetic measurements also showed that the reaction rate was invariant with changing concentrations of Ph_2SiH_2 and *p*-dimethylaminobenzaldehyde. Write a rate law for this reaction consistent with the provided kinetic data.
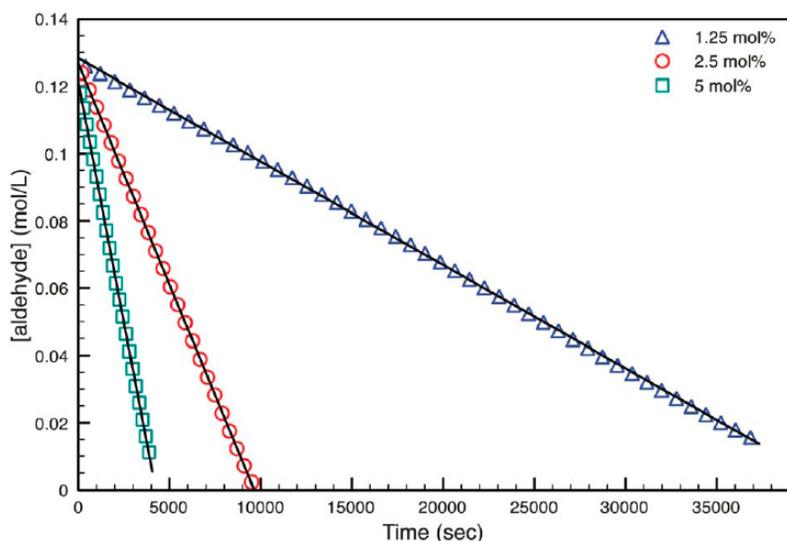
Rate = k[Ni] where Ni is Ni(0) species from part A

5 mol % [Ni]

H_2SiPh_2, C_6D_6

X = H, Me, OMe, NMe_2, CF_3

Fig. 4   Plot of aldehyde concentration *versus* time for the hydro-silylation of *p*-dimethylaminobenzaldehyde by 1.25, 2.5, and 5 mol% 1.

C) ^1H, ^{13}C and ^{31}P NMR studies of the catalytic hydrosilylation of benzaldehyde under turnover conditions revealed a diamagnetic intermediate species that displays peaks corresponding to the Ni-diphosphine motif bound to the two reagents upon some chemical transformations. This species was observed to have an up-field resonance consistent with a metal hydride. Using benzaldehyde with a ^{13}C label on the carbonyl carbon a doublet (corresponding to single bond C-H coupling) was observed specifically for this carbon position in the proton-coupled ^{13}C NMR spectrum. Three possible mechanisms are outlined below for the hydrosilylation of benzaldehyde, with proposed structures of the detectible intermediate labeled as Intermediate A, B, or C. Which of the mechanisms is consistent with the experimental data? Explain how you can rule out the other two choices.

Cycle A can be ruled out because the intermediate does not have a hydridic proton. Cycles A and C can be ruled out because the ^{13}C labelled carbon would appear as a triplet rather than the observed doublet because it is bonded directly to two protons. The only cycle consistent with all the data is B where the intermediate has a borohydride ligand (accounts for the hydridic resonance in the ^1H NMR) and the ^{13}C labelled carbon would appear as a doublet since it is directly bonded to only one ^1H.
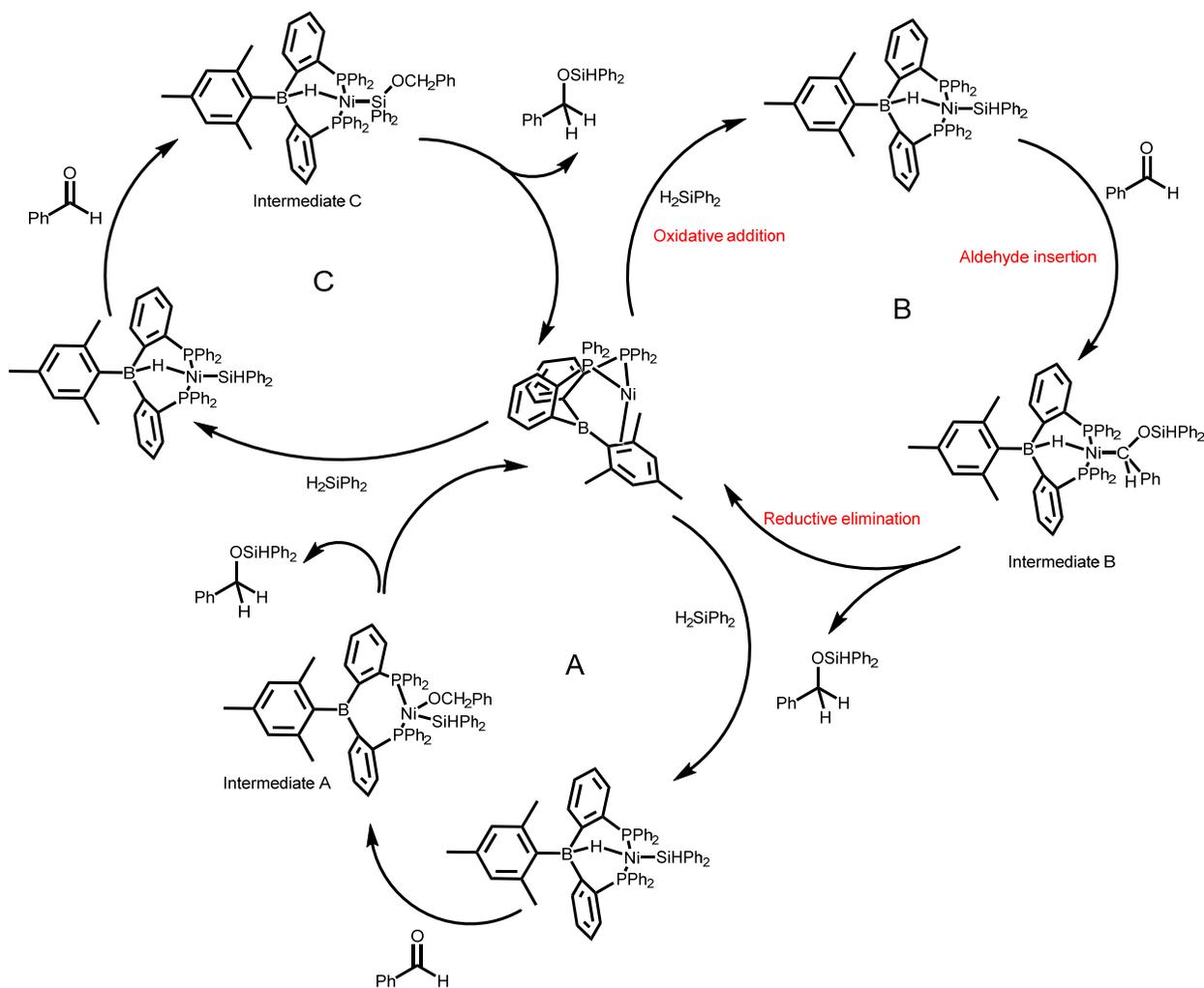
D) For the catalytic cycle you chose in part C identify which step is the rate determining step using your rate law from part B. Label all the elementary steps on your chosen cycle with the type of transformation (sigma-bond metathesis, insertion, α-H abstraction etc…)

Reductive elimination of the silyl-ether must be the rate limiting step since the oxidative addition and aldehyde insertion steps should show a first order dependence on Ph_2SiH_2 and benzaldehyde respectively.
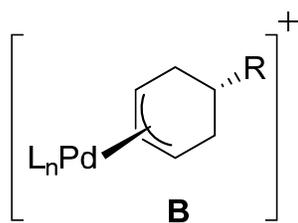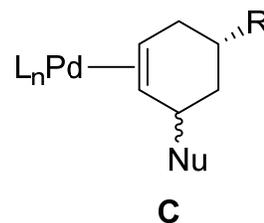
Problem 3 (2 points)

Part I

a)
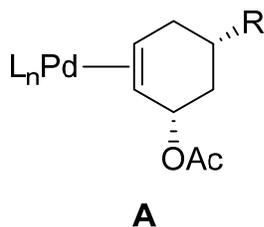
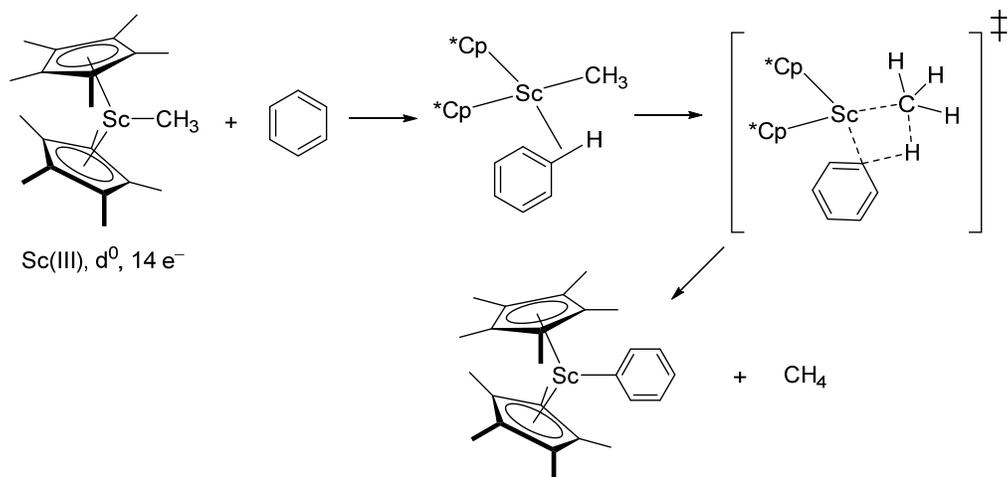| A	B	C
16 e$^-$, Pd(0), d^{10}	16 e$^-$, Pd(II), d^8	16 e$^-$, Pd(0), d^{10}

b)
Step (a): reductive elimination
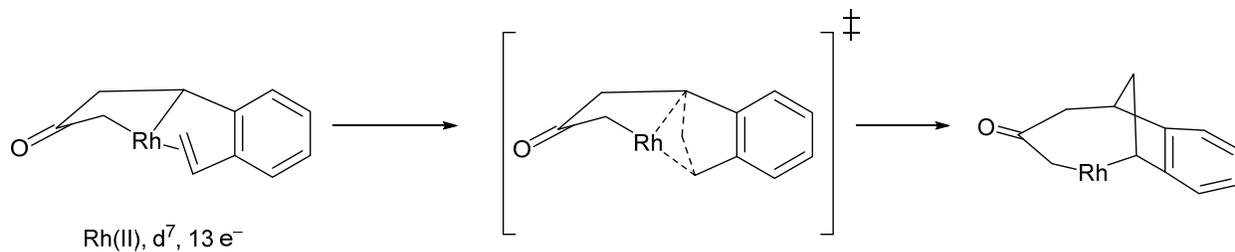Step (b): nucleophilic attack on the allyl ligand

Part II
a) σ-bond metathesis
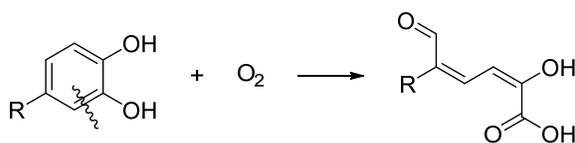

Sc(III), d⁰, 14 e⁻

b) alkyne metathesis

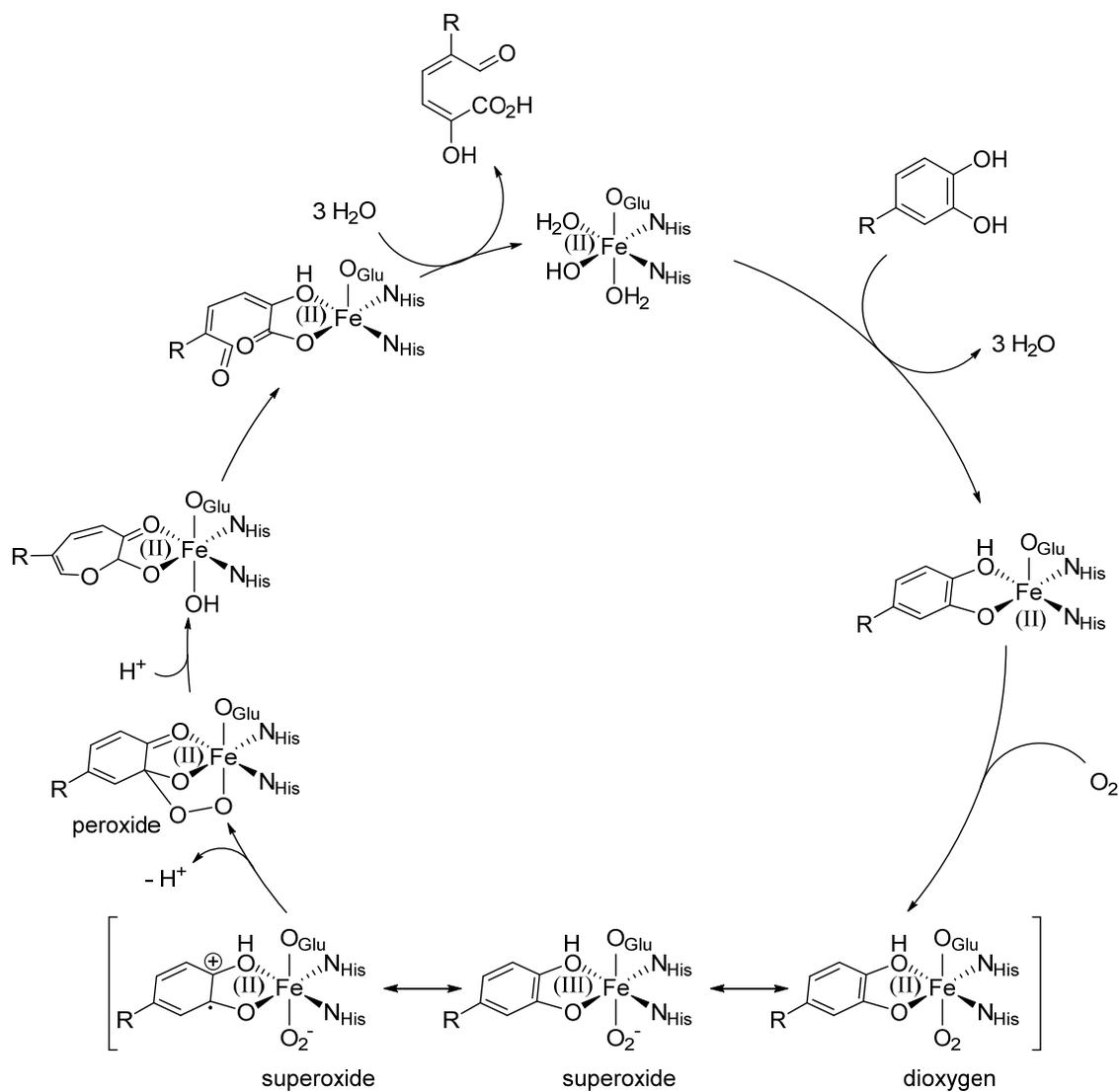W(VI), d⁰, 12 e⁻
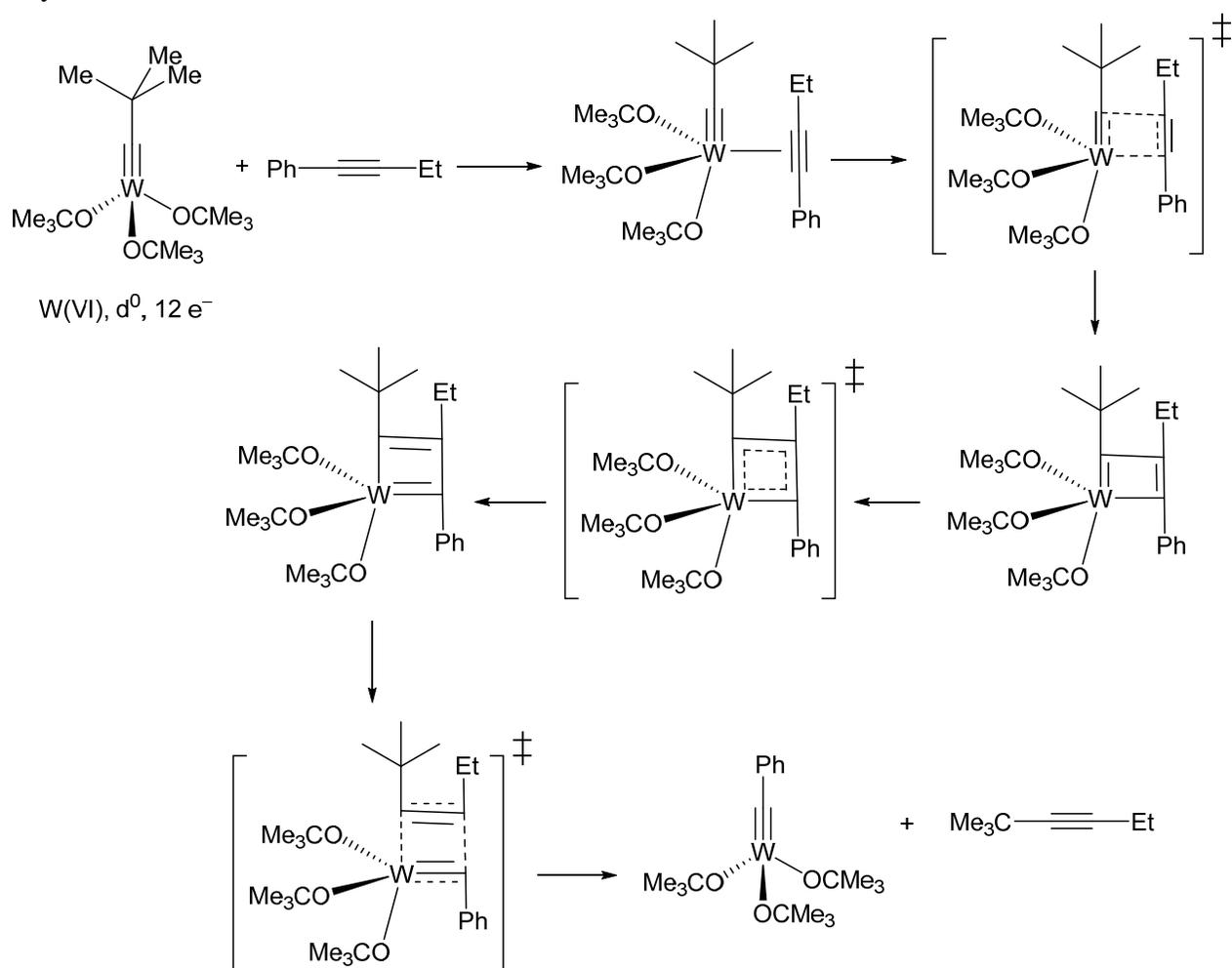
c) alkene insertion

Rh(II), d^7, 13 e$^-$

Problem 4 (3 points)

Part I
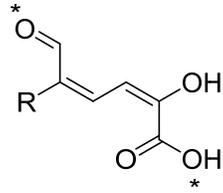
a)

b,c)
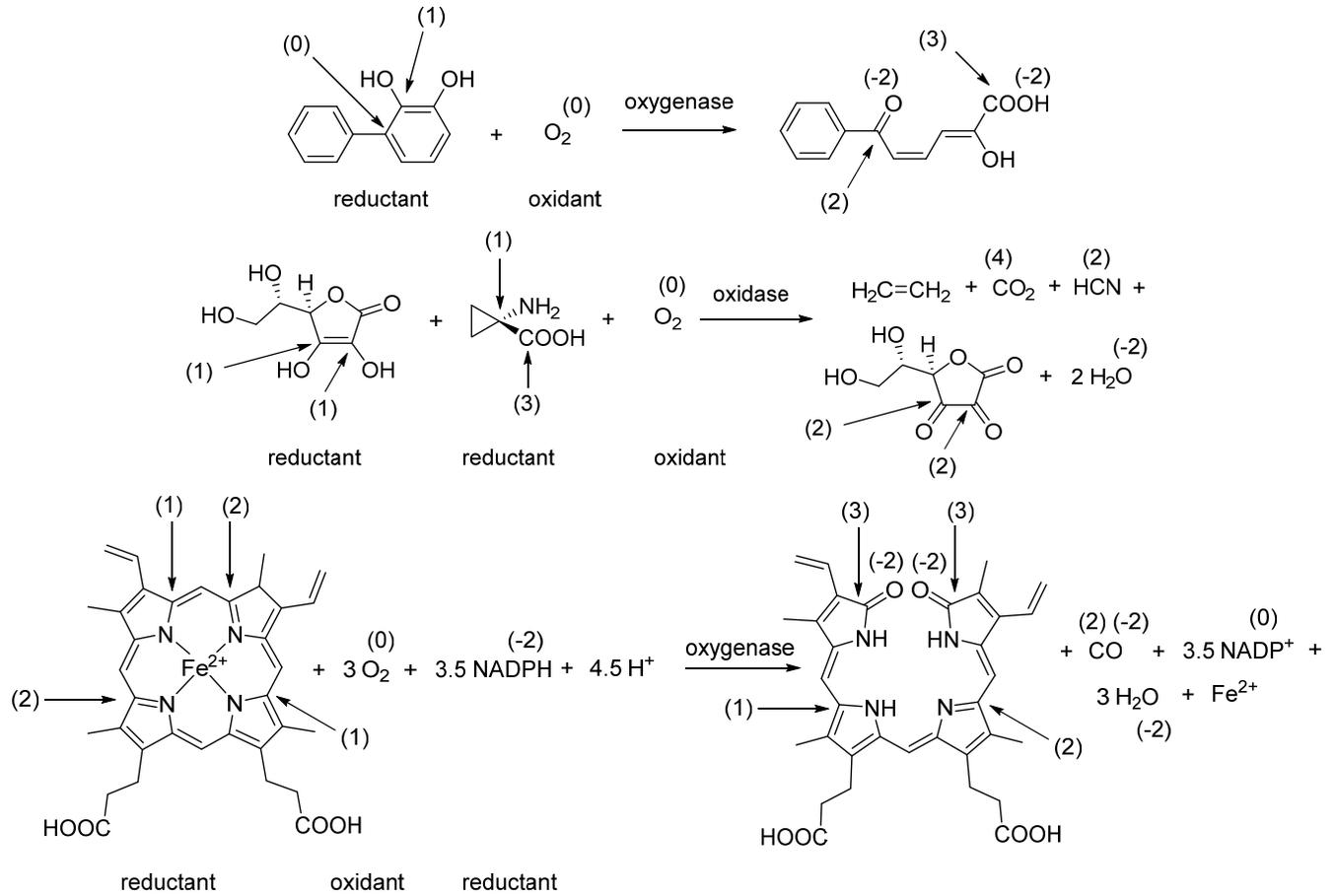
d)

e) Oxygenase

Part II

(0) O_2 oxygenase

reductant   oxidant

(1) HO OH (0) (-2) COOH (3) (-2) OH (2)

$H_2C{=}CH_2$ + CO_2 + HCN + (4) (2)

(0) O_2 oxidase

reductant   reductant   oxidant

+ 2 H_2O (-2)

Fe^{2+} + 3 O_2 + 3.5 NADPH + 4.5 H^+ oxygenase

reductant   oxidant   reductant

+ CO + 3.5 $NADP^+$ + 3 H_2O + Fe^{2+}
(2) (-2) (0) (-2)

HOOC   COOH

Part III

a) $2 O_2^- + 2 H^+ \rightarrow H_2O_2 + O_2$
    $H_2O_2 + 2 e^- + 2 H^+ \rightarrow 2 H_2O$
    $2 H_2O_2 \rightarrow 2 H_2O + O_2$

b)

Also accepted:

c)