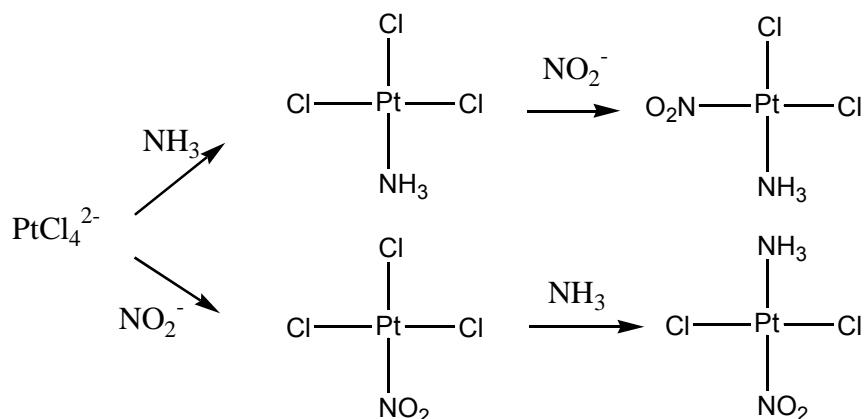


Inorganic Chemistry 2 (033021) - Inorganic Reaction Mechanisms

Problem sheet - model answers

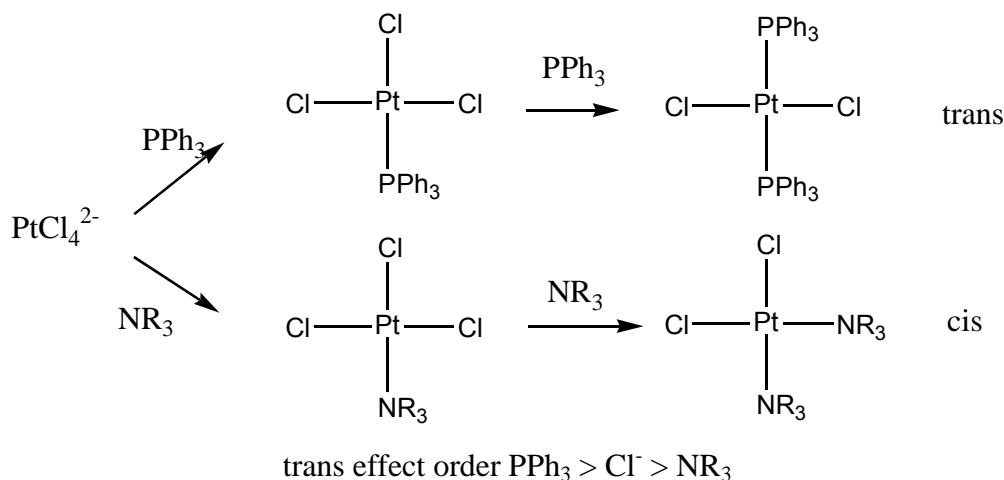
- (a) Using either $[\text{PtCl}_4]^{2-}$ or $[\text{Pt}(\text{NH}_3)_4]^{2+}$ as metal containing starting materials, outline the synthesis of *cis* and *trans* isomers of $[\text{Pt}(\text{NH}_3)(\text{NO}_2)\text{Cl}_2]^-$, given that the substituent *trans* effects are in the order $\text{NO}_2^- > \text{Cl}^- > \text{NH}_3$.



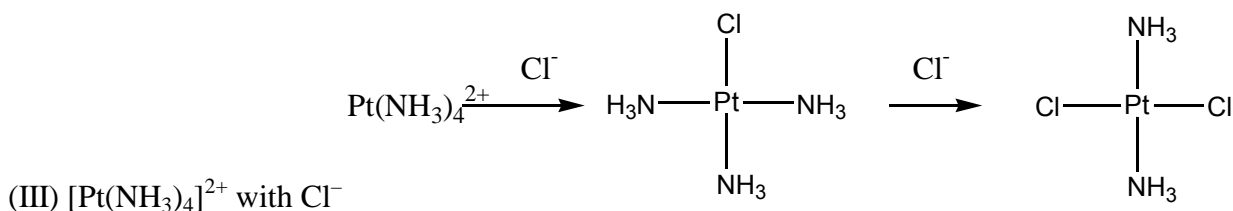
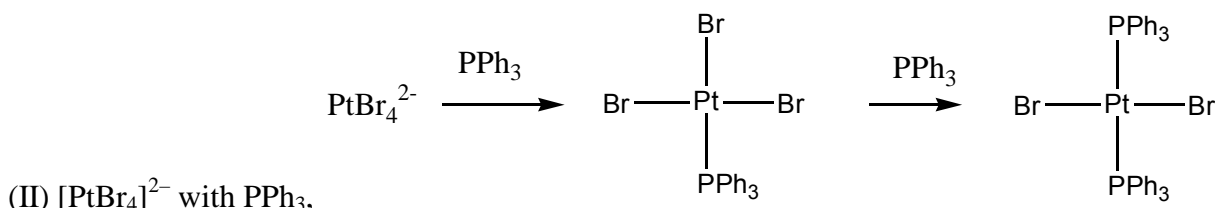
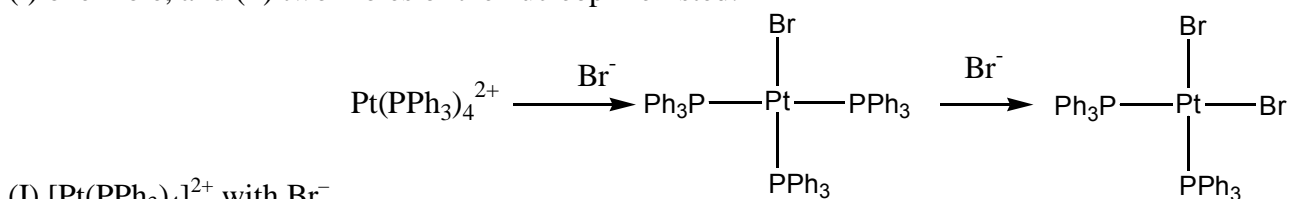
Note that ionic charges have been omitted in this diagram and some of the others which follow.

- (b) Why do phosphine ligands show such a high *trans* effect? (Hint: recall the molecular orbital basis for the *trans* effect, and consider the orbital interactions when a phosphine bonds to a metal centre.)
 What are the products of the reaction of K_2PtCl_4 with
- two moles of R_3P , and
 - two moles of R_3N ?

Phosphines are σ donors and π -acceptors. The π -acceptor character means that a phosphine removes electron density from the metal, and thus stabilises the electron-rich 5 coordinate transition state

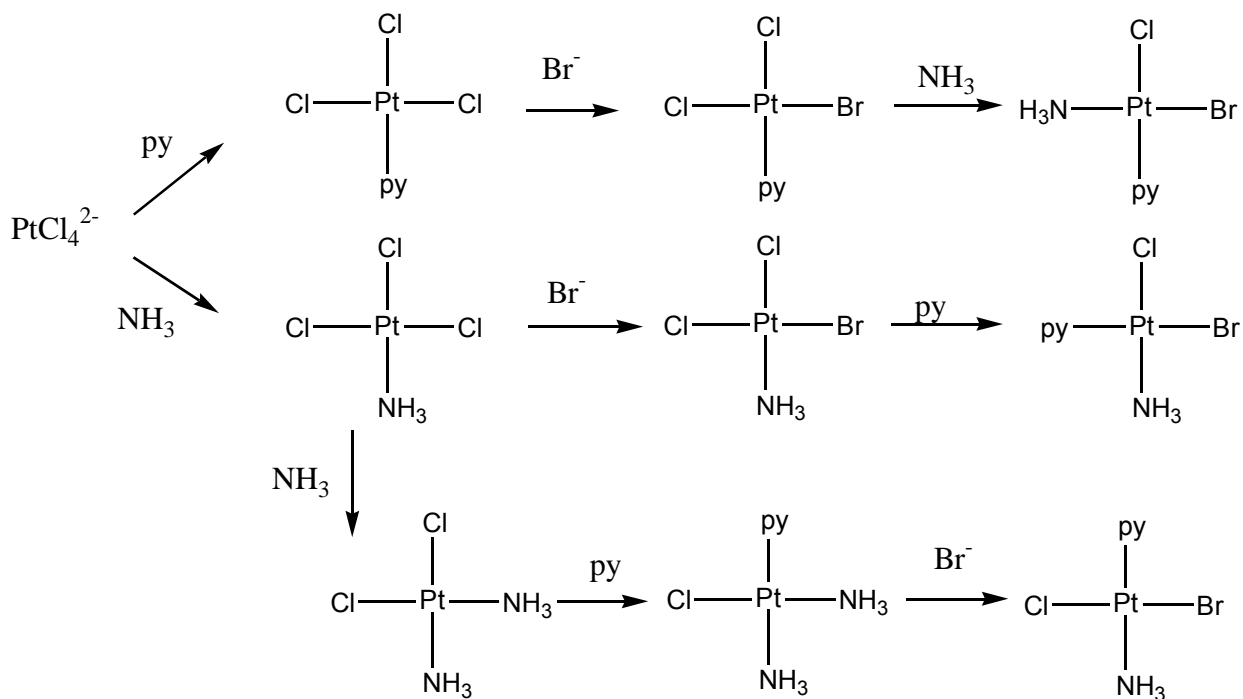


- (c) Predict the products of the reaction of each of the following metal complexes with (i) one mole, and (ii) two moles of the nucleophile listed:



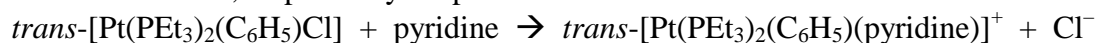
- (d) Using the reagents PPh_3 , NH_3 and $[\text{PtCl}_4]^{2-}$, propose efficient routes to all the possible isomers of $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$. (Shriver, Atkins and Langford, 1st edition, p474)

There are three isomers. If the metal were tetrahedral rather than square planar then there would be only two isomers (enantiomers). Historically, this fact forms part of the proof that Pt(II) is square planar. The trans effect series is $\text{Br}^- > \text{Cl}^- > \text{py} \approx \text{NH}_3$



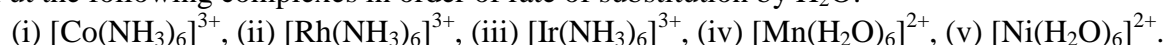
The third isomer is the more difficult to see an obvious synthesis of and there is more than one way to do the final step of the synthesis of this isomer.

- (e) For the reaction below, the second-order rate constants, in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, for $M = \text{Ni}, \text{Pd}, \text{Pt}$ are 33, 0.58 and 6.7×10^{-6} , respectively. Explain.



Nickel is faster than Pd than Pt. The reason is that there is a large Crystal Field contribution to the activation energy. The value of Dq is larger for Pt than for Ni, and so the activation energy is greater for Pt.

- (f) Put the following complexes in order of rate of substitution by H_2O :



This question comes from Shriver and Atkins, who give the answer:

$\text{Ir(III)} < \text{Rh(III)} < \text{Co(III)} < \text{Ni(II)} < \text{Mn(II)}$.

Mn(II) is d^5 and high spin, so no CFSE. Ni(II) is d^8 and there is a large loss of CFSE on going to any 5 coordinate geometry, so there is a significant CFAE. The other 3 are all d^6 low spin and hence SLOW. Shriver and Atkins argue that the M-L bonds are stronger for 5d than 3d metals. An alternative argument based on charge/size ratio would provide the opposite sequence.

- (g) For the reactions: $[\text{M}(\text{H}_2\text{O})_6]^{2+} + \text{H}_2^{17}\text{O} \rightarrow [\text{M}(\text{H}_2\text{O})_5(\text{H}_2^{17}\text{O})]^{2+} + \text{H}_2\text{O}$, the volumes of activation (ΔV^\ddagger in $\text{cm}^3 \text{mol}^{-1}$) are found to be $\text{V}^{2+} -10.1$, $\text{Mn}^{2+} -4.1$, $\text{Fe}^{2+} +3.8$, $\text{Co}^{2+} +6.1$, and $\text{Ni}^{2+} +7.2$.

Discuss these data in terms of the mechanism of these reactions.

$\Delta V^\ddagger / V(\text{H}_2\text{O})$ will be +1 for D and -1 for A mechanisms, with values in between for I_d , I and I_a mechanisms. The data indicate a change from I_a to I_d across the series.

- (h) Why does $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ exchange coordinated water molecules faster than $[\text{Al}(\text{H}_2\text{O})]^{3+}$? How would $[\text{Tl}(\text{H}_2\text{O})_6]^{3+}$ compare? What about $[\text{Tl}(\text{H}_2\text{O})_n]^{+}$?

Charge/size ratio provides the reason here. Ga^{3+} will be faster than Al^{3+} . Tl^{3+} will be faster still. The 1+ ion will be even faster.

- (i) The reaction of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ with H_2O is 10^3 times faster than the reaction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. By considering how the charge on a complex affects bond strengths, discuss briefly whether this data is consistent with a I_d or I_a mechanism.

Increasing the +ve charge on a complex increases the strength of M-L bonds and so will hinder a dissociative process. Hence conclude I_d .

- (j) Why is the hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in the presence of base much faster than that of $[\text{Co}(\text{py})_5\text{Cl}]^{2+}$?

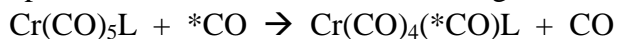
Conjugate base mechanism. Requires amine ligands with protons which can be removed by the base, giving $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ as an intermediate or transition state. Not possible with pyridine ligands.

- (k) The reactions of Rh(III) complexes proceed via I_d mechanisms. State the effect of the following on the rate of such reactions:

- (i) an increase in the positive charge on the complex;
- (ii) changing the leaving group from NO_3^- to Cl^- ;
- (iii) changing the entering group from Cl^- to I^- ;
- (iv) changing the *cis* ligands from NH_3 to H_2O .

- (i) Increasing +ve charge increases M-L bond strength and so will decrease an I_d rate
- (ii) NO_3^- is a better leaving group, so rate is slower - look at LFER plot in notes
- (iii) Little effect, since an I_d reaction is not sensitive to the nucleophile
- (iv) NH_3 is a better σ donor and so increases electron density at the metal. H_2O gives lower electron density at the metal, and the leaving group X binds more strongly in the H_2O complex, which will react more slowly.

- (l) Explain the trends in the rate constants given in the table below for the following reaction:



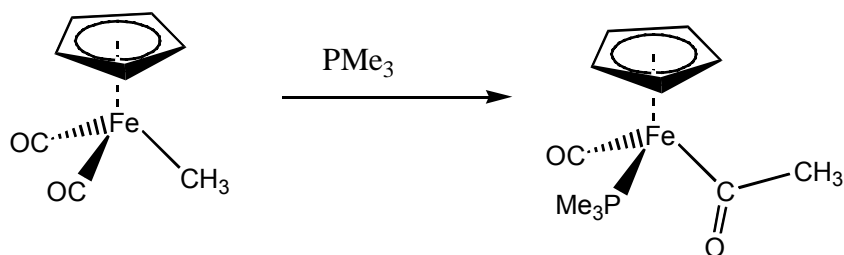
L	CO	PMe_2Ph	PPh_3	Br^-	Cl^-
k (s^{-1} , 30°C)	1.0×10^{-12}	1.5×10^{-10}	3.0×10^{-10}	2.0×10^{-5}	1.5×10^{-4}

This is a dissociative (D) substitution reaction, and the rate will be enhanced by ligands which stabilise the 5 coordinate transition state/intermediate. Hence good σ -donor ligands are required, and the trend essentially reflect σ -donor ability.

- (m) Indicate whether the following complexes would undergo substitution by PPh_3 by associative or dissociative pathways:

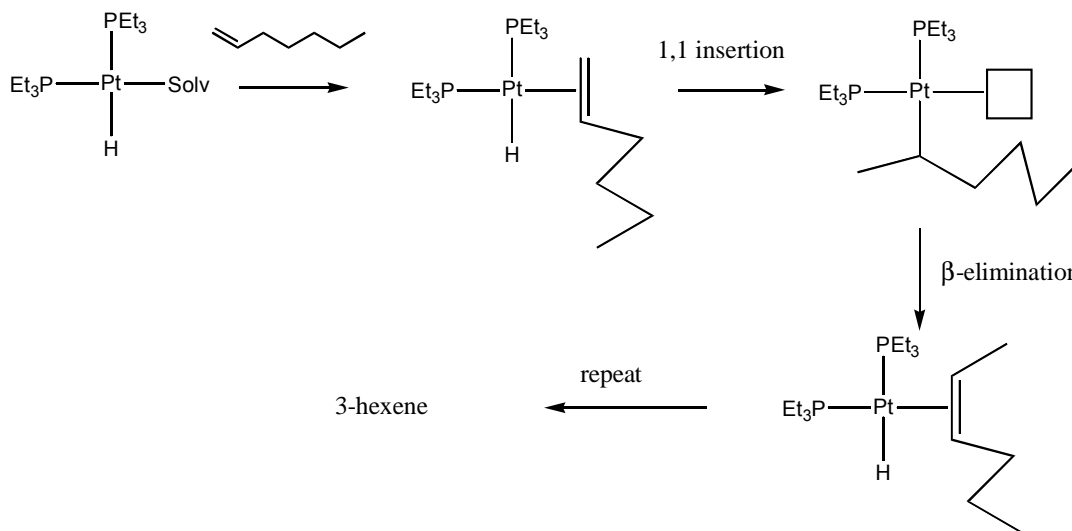
$\text{Mo}(\text{CO})_6$,	dissociative
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})$,	associative 3e-1e NO
$\text{V}(\text{CO})_6$,	associative - 17 electron not 18
PtCl_4^{2-} ,	associative
$\text{Co}(\eta^5\text{-indenyl})(\text{CO})_2$.	associative η^5 to η^3 ring slip

- (n) The complex $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CH}_3)$ reacts with PMe_3 to give $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{COCH}_3)(\text{PMe}_3)$, in a reaction that is first order in both starting materials. Explain.

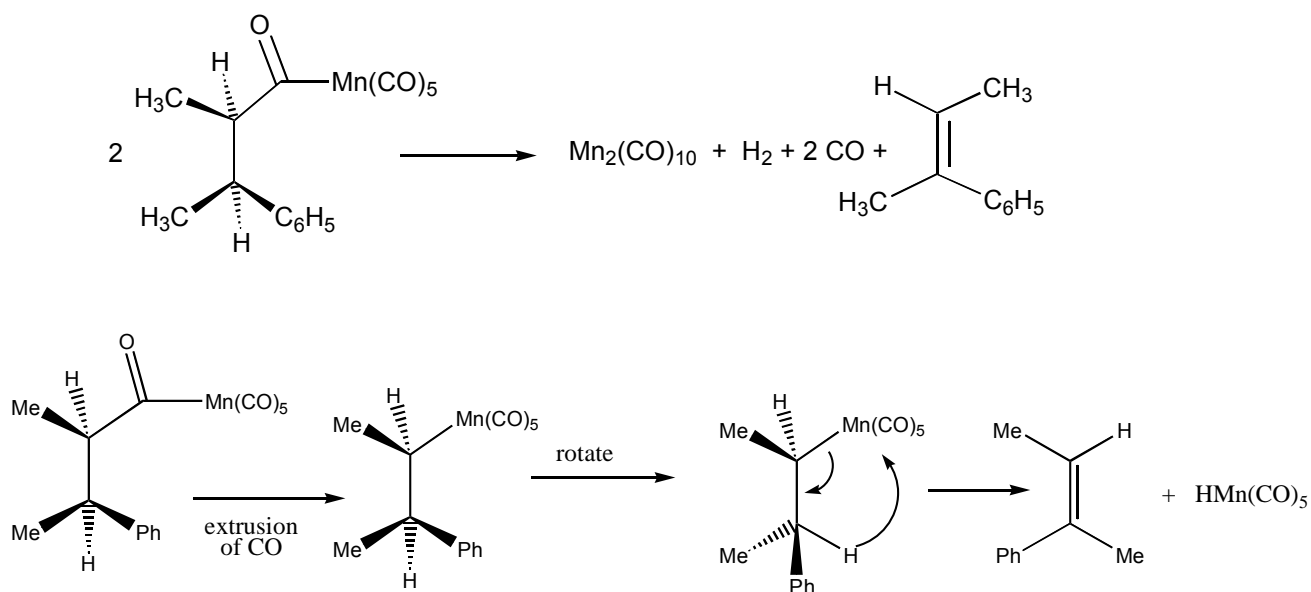


Migratory insertion. both reagents are involved in the rds, hence 1st order in both.

- (o) The complex $[\text{cis-Pt}(\text{PEt}_3)_2\text{H}(\text{solv})]^+$ ($\text{solv} = \text{methanol or acetone}$) isomerises 1-hexene to a mixture of 2-hexene and 3-hexene. Suggest a mechanism for this process.



- (p) Account for the stereochemistry of the following reaction:



(q) The reaction of $V(CO)_5(NO)$ with PMe_3 to give $V(CO)_4(NO)(PMe_3)$ obeys the rate law:

$$\frac{-d[V(CO)_5(NO)]}{dt} = k_1[V(CO)_5(NO)] + k_2[PMe_3][V(CO)_5(NO)]$$

Suggest a mechanism for this reaction consistent with the rate law and the 18-electron rule.

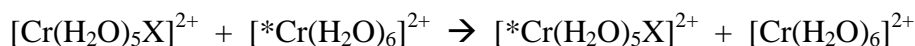
Two pathways in operation. The first is rate limiting dissociation of CO followed by attack of phosphine. The second is bend 3e NO to 1e NO, coordinate PMe_3 and then lose CO in a rate limiting step that now contains both substrate and nucleophile in it.

(r) In the reaction of $[Co(NCS)(NH_3)_5]^{2+}$ with $[Fe(H_2O)_6]^{2+}$ in water as solvent, it is possible to identify $[Fe(NCS)(H_2O)_5]^{2+}$ as an intermediate. Explain. What are the final products of this reaction?

This is an inner sphere electron transfer reaction, and will proceed via the species:

$[(NH_3)_5Co---NCS--Fe(H_2O)_5]^{4+}$ which will transfer an electron between the two metals, giving labile Co(II) and inert Fe(III). Water will substitute all the Co(II) ligands, giving $[Co(H_2O)_6]^{2+}$ as product.

(s) The rate constants for the exchange reaction:

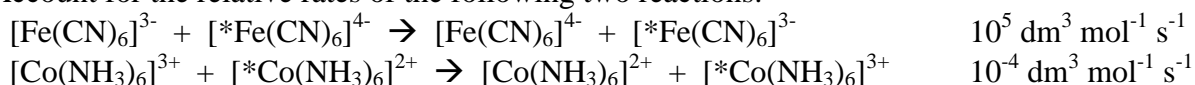


where $*Cr$ is ^{51}Cr , a radioactive nuclide and X is a mono-anionic ligand, are given in the table. Outline the likely mechanism and explain the difference in the rate constants.

X	F ⁻	Cl ⁻	Br ⁻	N ₃ ⁻
k (mol ⁻¹ dm ³ s ⁻¹)	1.2 x 10 ⁻³	11	60	>1.2

This is an inner sphere electron transfer reaction, and the rates reflect the ability of the X group to act as a bridging ligand. Fluoride is not a good bridging ligand.

(t) Account for the relative rates of the following two reactions:



The first reaction involves Fe(III) d^5 , t_{2g}^5 and Fe(II) d^6 , t_{2g}^6 ; so the electron is transferred between t_{2g} levels of the two iron species. The two species are not greatly different in their size, so there is a relatively small contribution to the activation energy from the need to generate vibrationally excited states of the same radius.

The second reaction involves Co(III), d^6 , t_{2g}^6 and Co(II) d^7 $t_{2g}^5 e_g^2$; so the electron is transferred from t_{2g} on one metal ion to e_g on the other. Since e_g electrons are M-L σ -antibonding, the two species will have markedly different radii, so there will be a large contribution to the activation energy from the need to produce a vibrational state with the two ions of the same radius.