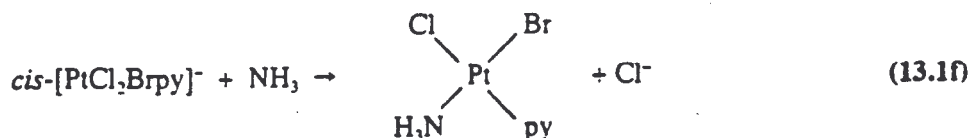
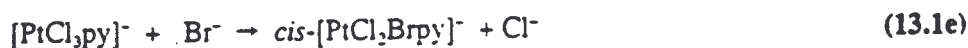
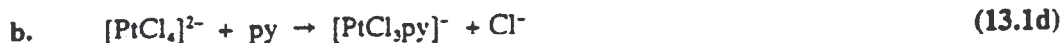
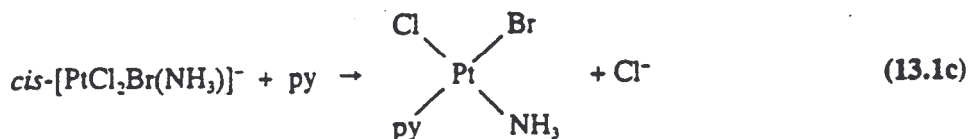


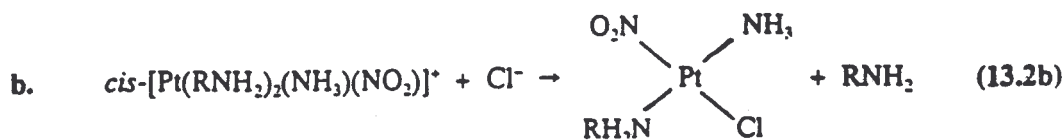
13

Coordination Chemistry: Reactions, Kinetics, and Mechanisms

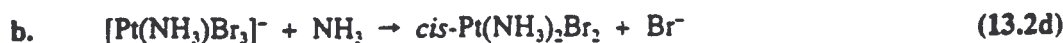
13.1



13.2

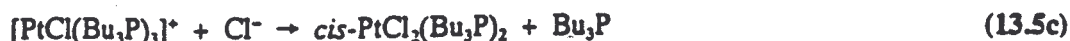


13.3



13.4 Isomerization of *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$ is catalyzed by the presence of PPh_3 . The *cis* isomer is

much less soluble than the trans isomer and as a result it precipitates from solution. Precipitation upsets the position of equilibrium inducing more cis isomer to form. The reaction is driven by the insolubility of the cis isomer.



13.6 Substitution in square planar complexes proceeds by an associative mechanism that involves formation of a five-coordinate activated complex. Five-coordinate complexes of nickel are more stable than those of platinum. Stabilization of the transition state means a smaller energy of activation and thus a faster reaction rate.

13.7 Use equation 13.12 of the text: $k_{\text{obs}} = k_1 + k_2[\text{Y}]$. Plot k_{obs} versus $[\text{Y}]$. The intercept and slope of the best straight line will be k_1 and k_2 , respectively. The intercept is found at 4.3×10^{-3} and the slope is 1.7. The correlation coefficient is 0.9997 and the standard deviation is 6.1×10^{-3} .

13.8 a. If the solvent pathway is insignificant, k_1 (the intercept) will be zero.

b. If the solvent pathway is exclusive, then the slope, k_2 , will be zero.

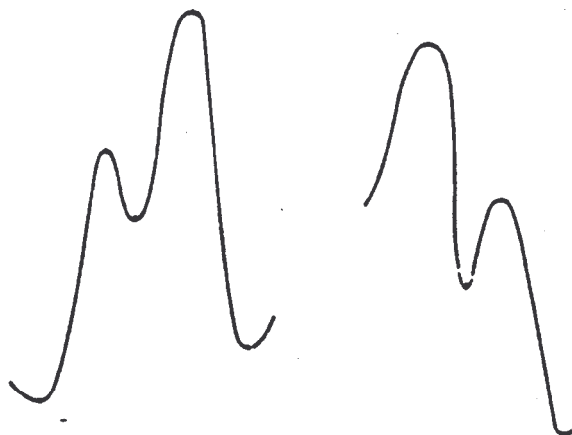
13.9 The metal-X bond is broken in the transition state. Ligands that are good trans directors are also strongly bonded to the metal, and as a result are poor leaving groups. Thus the reaction that involves breaking the M-CN bond is slower than the one that involves breaking the M-OH₂ bond.

13.10 The hydroxide ion has a greater affinity for hydrogen ions (a hard acid) than ammonia, but not for square planar Pt(II) complexes (a soft acid). Nucleophilicity is better correlated with the polarizability than with basicity. Ammonia is somewhat more polarizable than hydroxide ion and therefore reacts faster.

13.11 The reaction proceeds by an associative mechanism. This mechanism requires that the coordination number of the central metal increase. As the steric requirements of L become larger, an increase in coordination number becomes less favorable, and the rate of the reaction decreases.

13.12 See Sketch 13.1.

13.13 The Pt(I) complex is analogous



Sketch 13.1 Reaction profiles for substitution in which (a) bond breaking is more important or (b) bond making is more important. [Modified from Langford, C.; Gray, H. B. *Ligand Substitution Processes*, Benjamin: New York, 1965. Reproduced with permission.]

to the Pt(II) complexes in that both have a square-planar 16-electron configuration. The much faster rate of substitution for the Pt(I) complex would suggest that the Pt-Pt bond exhibits a powerful trans effect.

13.14 Deuterium has a higher trans influence than H because the average internuclear Pt-D separation is shorter than the average Pt-H separation. This results because of different zero point energies and because of anharmonicity of the Pt-H potential well. Thus D spends more of its time near the metal atom than does H. The smaller Pt-C coupling constant for the structure in which CO is trans to D results because the Pt-C bond is somewhat weaker (longer) as a result of the trans influence of D.

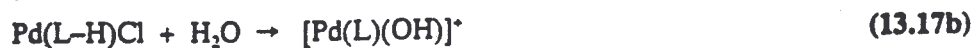
13.15 The dication, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, is kinetically and thermodynamically very stable. Furthermore, ammonia is not a good trans directing ligand. Also, neutral ligands are not good leaving groups in polar solvents. The dianion, $[\text{PtCl}_4]^{2-}$, is not as kinetically stable, the chloride group is a better trans directing ligand, and anions are good leaving groups in polar solvents.

13.16 The silver ion functions as a Lewis acid and pulls off the chloride ligands producing silver chloride precipitate and generating vacant coordination sites on platinum.

13.17 Not all of the data found in the table were collected under the same experimental conditions (see *Inorg. Chem.* 1984, 23, 1865-1869). The volumes of activation were recorded at 50 bars but the k_1 and k_2 values were obtained at room pressure. Even so the same general conclusions can be drawn from the data.

(a) The k_2 values for the 1,4,7-Me₃dien complexes are much larger than the k_1 values for both OH⁻ and I⁻. From this we conclude that direct associative substitution (as measured by k_2) is more important than the solvolysis pathway (as measured by k_1). For 1,4,7-Me₃dien complexes it is also noted that I⁻ is more nucleophilic than OH⁻, but the opposite is true for the 1,1,7,7-Me₄dien complexes. This suggests that different mechanisms may be operative (see part b). The k_1 and k_2 values for both ligands are significantly reduced for the 1,1,7,7-Me₄dien complex compared with those of the 1,4,7-dien complex. This is because of the increased steric interaction caused by the additional methyl groups.

(b) The significantly negative values of the solvolysis process and the reaction of I⁻ with the 1,4,7-Me₃dien complex strongly support an associative process. The direct reaction of OH⁻ with both complexes, however, is accompanied by a significantly positive volume of activation. At first glance this would suggest some kind of dissociative process. It has been concluded, however, that the reaction proceeds by a conjugate base mechanism.



13.18 See Sketch 13.1. The sketches for Problem may be derived from that sketch, sometimes with modifications:

a. If no intermediate is formed, there will be only a single energy maximum at the transition state.

b. If bond breaking and bond making are equally important, the reaction profile will have both activation energies equal.

c. Sketch 13.1a.

d. Sketch 13.1b.

13.19 The +3 ions will exchange more slowly than the +2 ions. The order is:



13.20 a. The high charge of the cation is consistent with slow exchange. Furthermore, loss of a water molecule to give a square pyramidal complex is accompanied by a $-0.20 \Delta_o$ LFSE loss.

b. The existence of seven-coordinate molybdenum(III) complexes requires one to consider an associative process for a substitution reaction involving a six-coordinate molybdenum(III) complex. The large negative volume of activation is consistent with an associative process. Furthermore substitution of water with an anionic ligand on a highly charged ligand leads to a large reduction in solvent electrostriction as a result of charge neutralization. If this were not the case the measured volume of activation would be expected to be even larger and even more indicative of an associative process.

13.21 One could argue that aquation of the chromium complexes proceeds by an associative interchange mechanism while aquation of the cobalt complexes proceeds by interchange dissociative mechanism. The results for the chromium complexes would then be explained on the basis of steric retardation. It has been found, however, that the Cr-Cl bond in the ammine complex is 3 pm longer than in the methylamine complex (see reference in the problem). In view of these data, the faster rate for aquation of the ammine complex could be interpreted to result from an interchange dissociative mechanism in which a weaker Cr-Cl bond is broken. The Co-Cl bond lengths are the same, so the rates of aquation of the two cobalt complexes cannot be based on differences in Co-Cl bond strengths. The methylamine complex is believed to be aquated faster than the ammine complex because greater relief of steric strain results when the Co-Cl bond is broken in the former.

13.22 In acid solution, when one end of the carbonato group dissociates it becomes protonated, preventing re-formation of the chelated complex. When the other end dissociates it also becomes protonated. The two Lewis acids, Co^{3+} and H^+ compete for the carbonato Lewis base. Vacant coordination sites become available for H_2O on Co^{3+} as H^+ ions tie up the carbonato ligand. In neutral solution the high effective concentration of the dangling end of the partially dissociated carbonato ligand makes it highly likely that it will reassociate to form the chelated complex (chelate effect).

13.23 The larger radius of Cd^{2+} (109 pm) in comparison to Zn^{2+} (88) makes it much more likely that substitution of the cadmium complex will go by an associative interchange mechanism. Substitution in the Cd^{2+} complex proceeds with large negative entropy and volume of activation, consistent with an associative interchange mechanism. For the Zn^{2+} complex, substitution proceeds with a small negative entropy and a positive volume of activation supporting a dissociative interchange mechanism.

13.24 Radii decrease going across the periodic table. The smaller the ionic radius of the central metal ion, the less available will be coordination sites, and the less likely an associative reaction will take place. Also the smaller the ionic radius the more steric interaction

between attached ligands and the more likely a dissociative reaction will take place.

13.25 Account for this difference by giving an evaluation of the relative importance of the factors contributing to the energetics of activation. Oxidation of $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ to $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ is accompanied by a significant decrease in the Ru-O bond distance (9 pm). The analogous reaction for oxidation of $[\text{Ru}(\text{NH}_3)_6]^{2+}$ gives a Ru-N bond distance change of only 4 pm. The more modest change in the Ru-N bond distance upon oxidation would suggest that the reorganizational energy is less, leading to a lower energy of activation for the process, and thus a faster reaction.

13.26 In order for an inner sphere mechanism to be operative, ligand dissociation must occur that would create a vacant coordination site that would allow a ligand to bridge the two metal centers. Since electron transfer is faster than ligand dissociation, this process cannot occur.

13.27 The cross-reaction rate constant, k_{12} , can be obtained from the equation, $k_{12} = (k_1 k_2 K_{12} f_{12})^{1/2}$. The value of f_{12} is found from the following equation:

$$\log f_{12} = (\log K_{12})^2 / 4 \log (k_1 k_2 / Z^2) \quad (13.27a)$$

First finding f_{12} :

$$\log f_{12} = (\log 2.1 \times 10^{11})^2 / 4 \log [4.2 \times 4.0 \times 10^3 / 10^{11}] \quad (13.27b)$$

$$= -1.803 \text{ and } f_{12} = 0.015 \quad (13.27c)$$

$$k_{12} = (4.2 \times 4.0 \times 10^3 \times 2.1 \times 10^{11} \times 0.015)^{1/2} \quad (13.27d)$$

$$= 7.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \quad (13.27e)$$

This value of k_{12} is in reasonable agreement with the observed value ($3.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), reported in Table 13.8 of the text. The Marcus equation is not expected to give very good agreement for reactions with large equilibrium constants. See Meyer, T. J.; Taube, H. *Inorg. Chem.* 1968, 7, 2369-2379.

13.28 It suggests that the exchange reaction does not proceed by an outer sphere reaction. An inner sphere mechanism involving a water-bridged pathway has been proposed. See Endicott, J. F.; Durham, B.; Kumar, K. *Inorg. Chem.* 1982, 21, 2437-2444.

13.29 The chromium reactant is quite labile as expected for a d^4 complex and the hydroxide group is a good bridging ligand. An inner sphere mechanism is consistent with these facts. Water is a poorer bridging ligand than the hydroxyl group, and as a result electron transfer takes place much slower. The larger the concentration of the hydrogen ion, the lower the concentration of the hydroxyl group, and the slower the reaction.

13.30 The presence of two reaction mechanisms, one involving remote and more involving adjacent attack gives two intermediates with N- and S-bonding and two linkage isomers as products.

13.31 The two reactants are $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_5]^{2-}$ and the two products are $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Co}(\text{CN})_5]^{2-}$. It would appear that the Co-N bond breaks more readily than the Fe-C bond. Iron(II) is more stabilized by six CN^- ligands than is cobalt(II).

13.32 The fact that Cr(III) is found attached to the remote end of the isonicotinamide ligand does