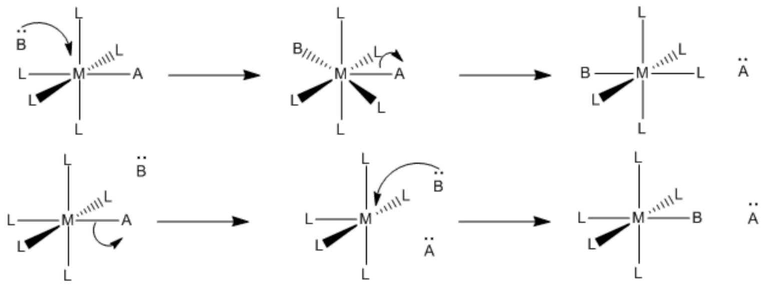
3.2: Mechanistic Possibilities

There are two basic steps in ligand substitution: association and dissociation. Association, in this case, refers to the binding of a ligand to the metal. The ligand donates an electron pair to the metal and the two molecules come together to form a new bond. Dissociation, in this case, refers to the release of a ligand from a metal. The metal-ligand bond breaks and the ligand leaves with its electron pair.

Two mechanistic possibilities seem pretty obvious. Either the new ligand binds first and then the old one leaves, or the old ligand leaves first and then the new one binds.



- Associative mechanism is association first. The new ligand binds and then the old one leaves.
- Dissociative mechanism is dissociation first. The old ligand leaves and then the new one binds.

Knowing the mechanism is important because the mechanism has an impact on what factors affect the reaction. For example, if the reaction is associative, adding lots more new ligand may speed up the reaction, because then it becomes more likely that the new ligand will find the metal complex and bind with it. However, if the old ligand is supposed to leave before the new ligand arrives, then it doesn't matter how much new ligand is around. It has to wait for the old ligand to leave before it can bind, anyway, so adding a lot more new ligand won't speed things up.

Exercise 3.2.1

a) Which kind of step costs more energy: bond-making or bond-breaking?

b) What would be the rate-determining step in the associative mechanism?

c) What would be the rate-determining step in the dissociative mechanism?

d) What would be the rate law for the associative mechanism?

e) What would be the rate law for the dissociative mechanism?

Answer a

Energy is released when bonds are formed. Energy must be added to break bonds. In general, bond-breaking costs more energy than bond-making.

Answer b

On the basis of question (a), we would assume that the second, bond-breaking step is the rate determining step in association mechanisms.

Answer c

The first, dissociative step would be the rate-determining step, on the basis of question (a).

Answer d

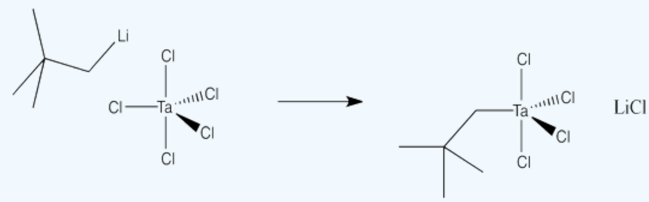
The rate law would include steps prior t the rate determining step. $Rate = k[MLn][X]$ if MLn is the complex and X is the new ligand.

Answer e

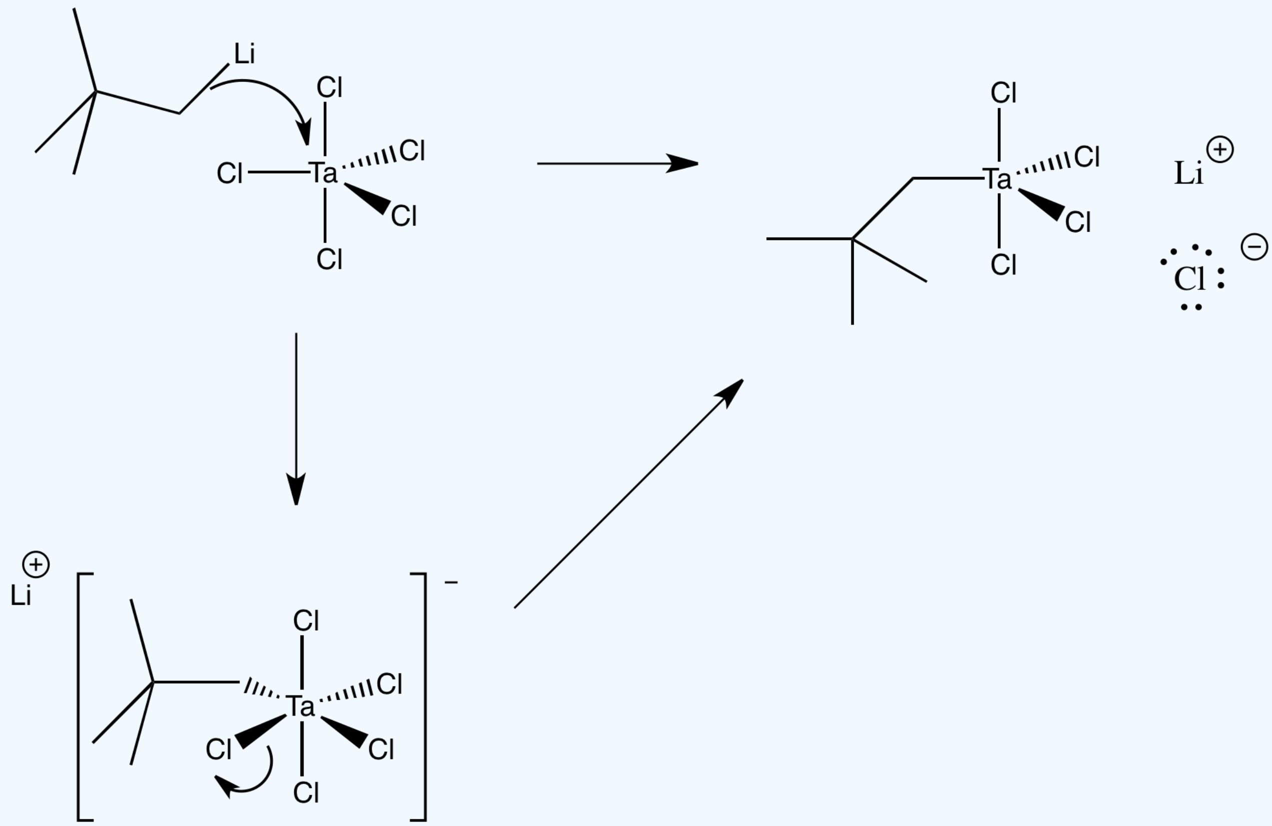
$$Rate = k[MLn]$$

Exercise 3.2.2

Draw a mechanism, with arrows, for the following substitution. Assume an associative mechanism.

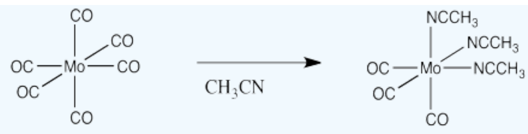


Answer

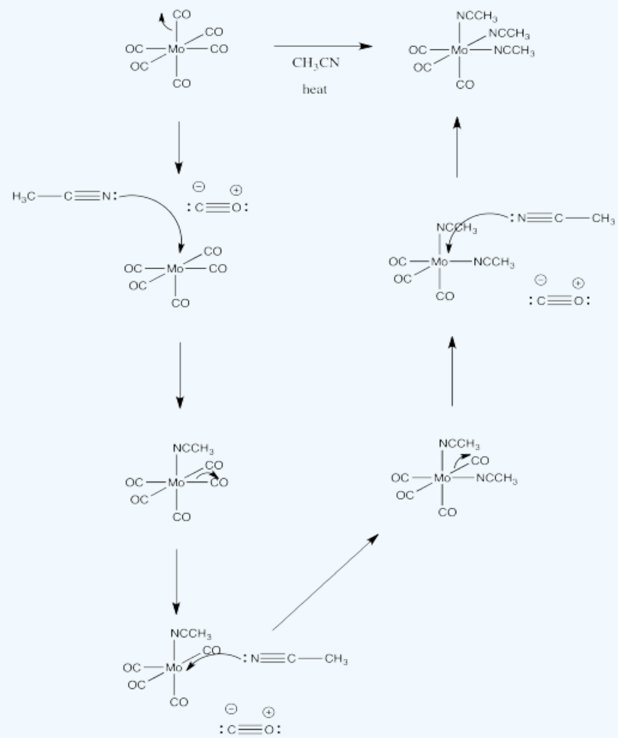


Exercise 3.2.3

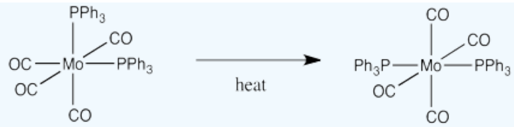
Draw a mechanism, with arrows, for the following substitution. Assume a dissociative mechanism.



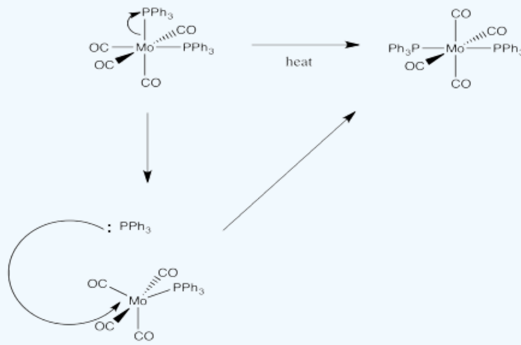
Answer



Draw a mechanism, with arrows, for the following isomerization.



Answer



Exercise 3.2.5

The ability to substitute for a ligand depends partly on its ability to leave. Rank the following ligands, from the easiest to replace to the hardest to replace:

CO Cl^- PPh NH_3 NO_3^- H_2O

Answer

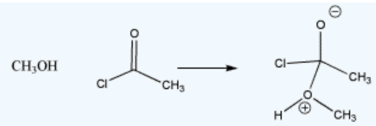
This problem is answered through consideration of the spectrochemical series.

from easiest to hardest to replace: NO_3^- Cl^- H_2O NH_3 PPh_3 CO

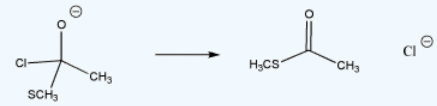
Exercise 3.2.6

Draw curved arrows for the following steps. Classify each step as associative or dissociative.

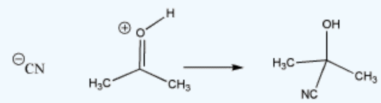
a)



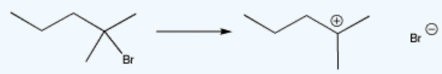
b)



c)



d)



Answer

a)

b)

c)

d)