

● Reductive elimination :-

• Reductive elimination is exactly reverse of oxidative addition reaction, i.e;

- i) Decrease in co-ordination number by two units.
- ii) ~~Decrease~~ Increase in oxidation state by two units.

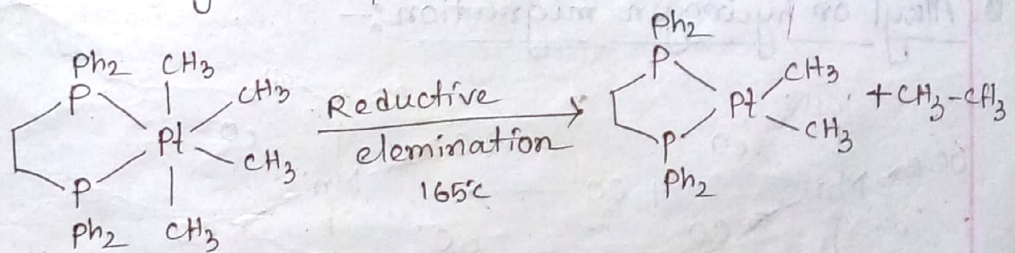
● Requirements for reductive elimination reaction :-

Essential :

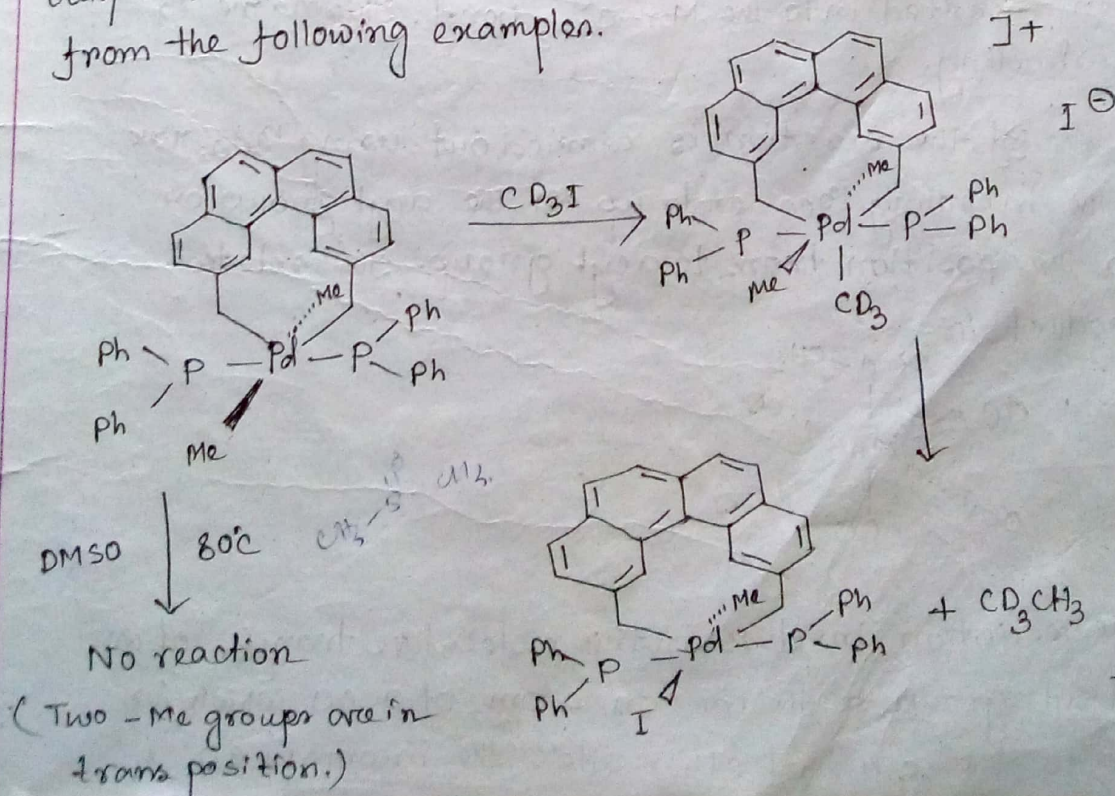
The eliminating groups must be adjacent (cis) to each other.

Other requirements :-

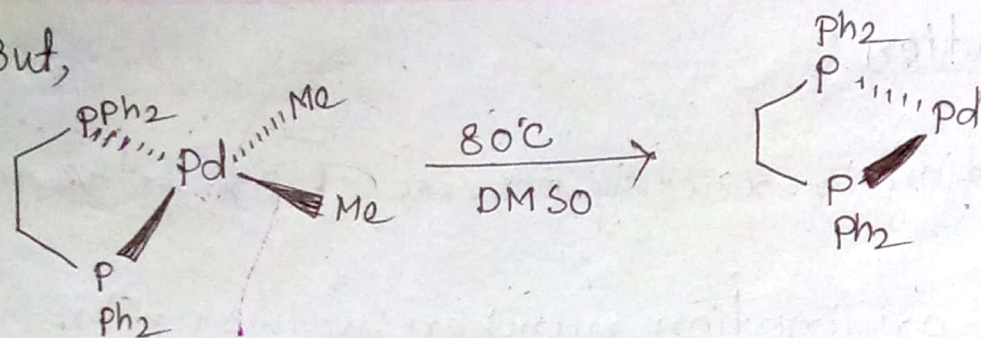
- A high formal (+)ve charge on the metal.
- The presence of bulky group on the metal.
- An electronically stable product.



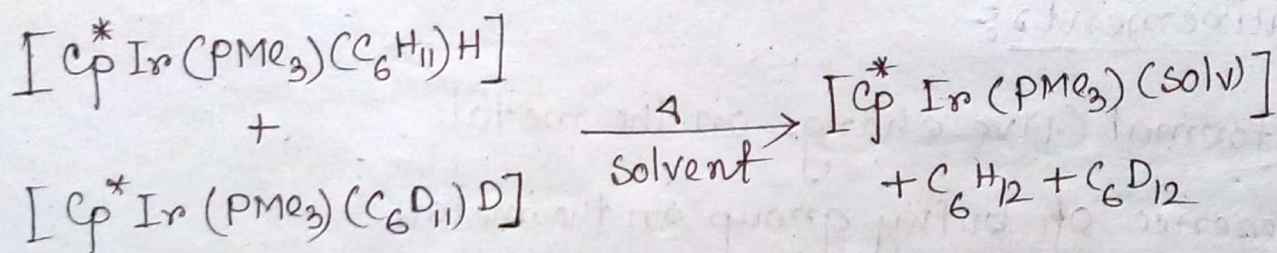
The significance of having two eliminating group in the cis disposition, the reductive elimination to occur can be inferred from the following examples.



But,



Reductive elimination reactions are intramolecular and this can be seen from the following reaction where no cross product is formed when the reaction is carried out with a mixture of deuteriated and non deuteriated cyclohexane complexes.

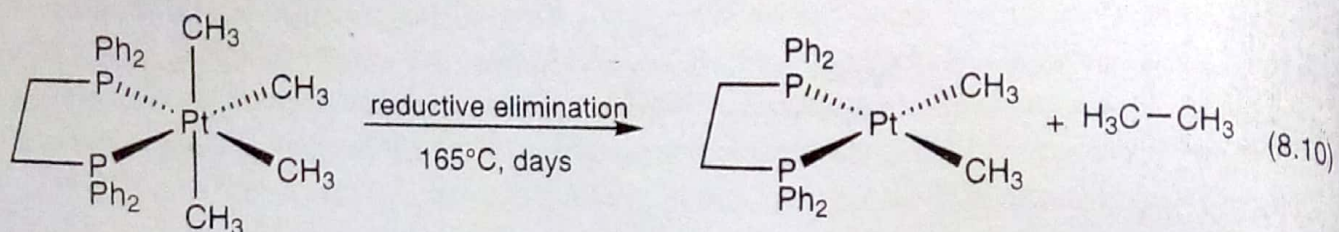


8.2 REDUCTIVE ELIMINATION

Reductive elimination is almost exactly the reverse of oxidative addition and it decreases both the coordination number as well as the oxidation state of the metal by two units.

The key requirement for reductive elimination to occur is that the eliminating groups must be adjacent (*cis*) to each other. Other factors that facilitate an easy reductive elimination are,

- a high formal positive charge on the metal,
- the presence of bulky groups on the metal, and
- an electronically stable organic product.

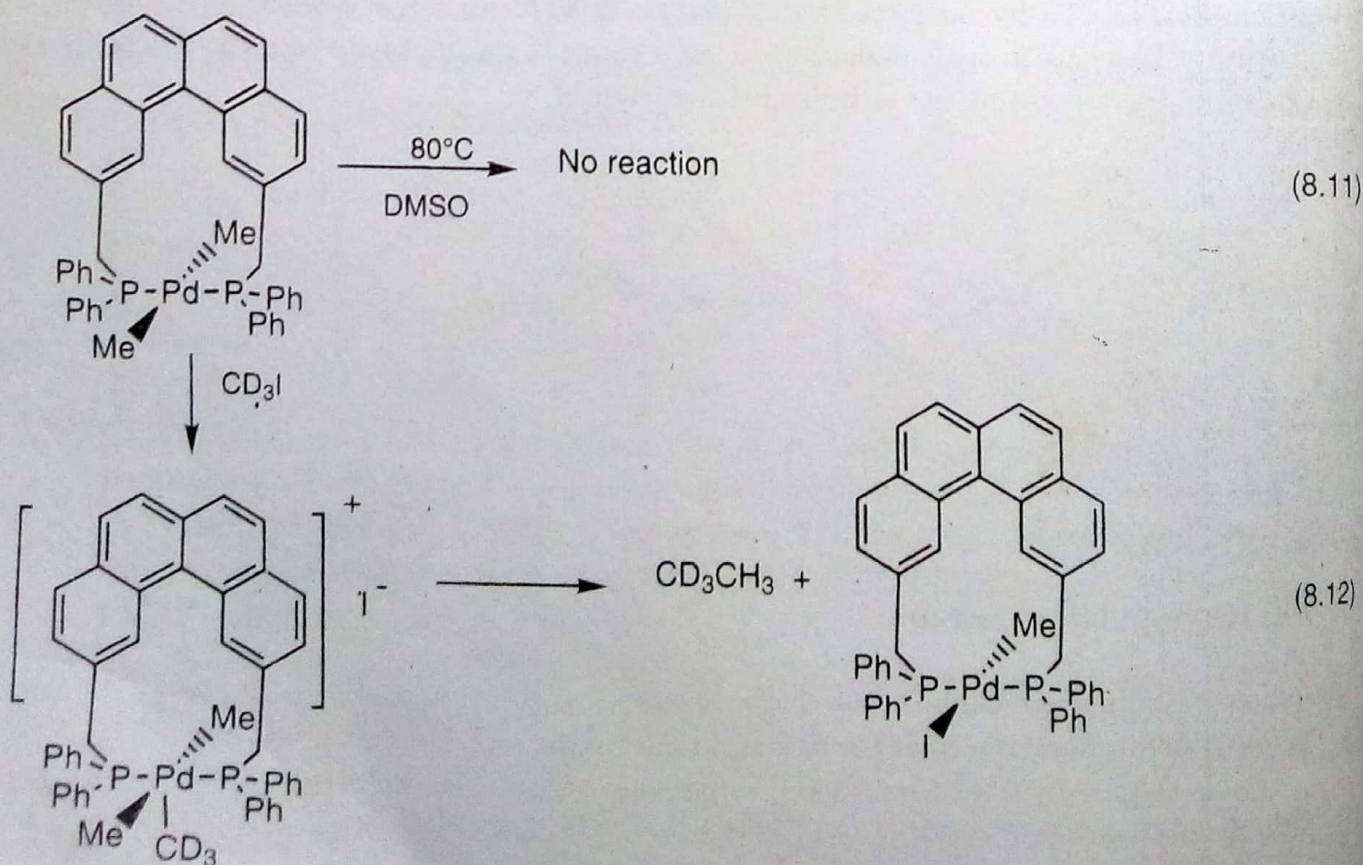


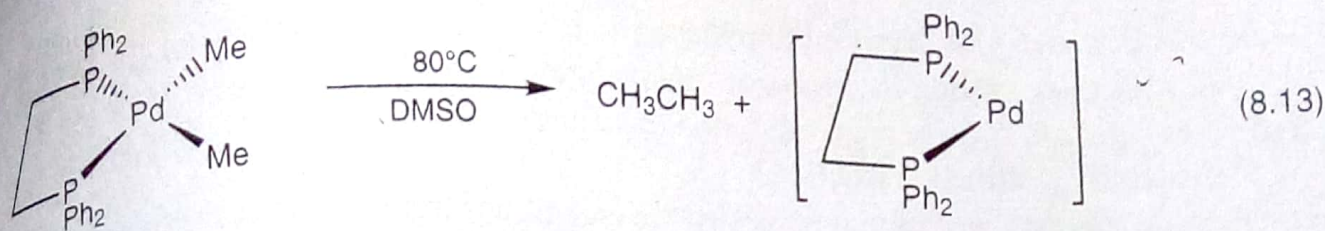
Other observations related to reductive elimination are:

- The rate of reductive elimination follows the trend $\text{H}-\text{C} > \text{H}-\text{H} > \text{C}-\text{C}$. This is slightly different from the change in free energies.
- The low valent ML_n complex formed after reductive elimination must be stable.
- π -accepting ligands on the metal generally accelerate reductive elimination.

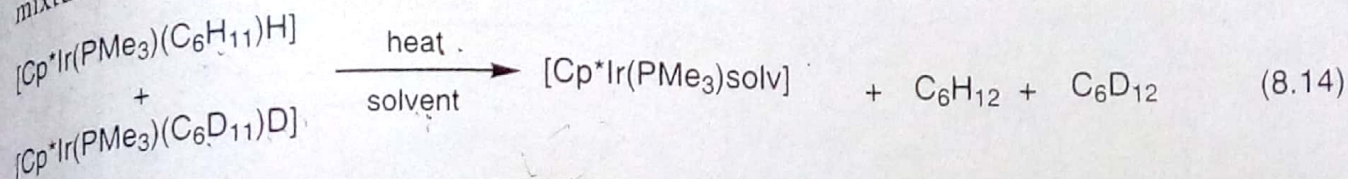
8.2.1 Mononuclear Systems

The significance of having two eliminating groups in the *cis* disposition, for reductive elimination to occur, can be inferred from the following examples.





Reductive elimination reactions are intramolecular and this can be seen from the following example (Eq. 8.14) where no cross product is formed when the reaction is carried out with a mixture of deuteriated and non-deuteriated cyclohexane complexes.



As oxidative addition and reductive elimination are microscopic reverse reactions of each other, the position of the equilibrium depends on the thermodynamics of the process. For example, many metal complexes will oxidatively add on MeI, but only few will reductively eliminate MeI. Similarly, oxidative addition of $\text{RCH}_2\text{-H}$ is less common while reductive elimination of alkanes from $\text{M}(\text{H})\text{CH}_2\text{R}$ is very often observed. These points are well illustrated from the thermochemical studies specific to iridium(I) complexes (Table 8.1). Notably, oxidative addition with CH_3I and H-H is feasible as per this analysis while it is thermodynamically unfavourable with $\text{CH}_3\text{-H}$ and $\text{CH}_3\text{-CH}_3$. This is indeed so because only CH_3I and H-H oxidative addition is known with Vaska's complex.

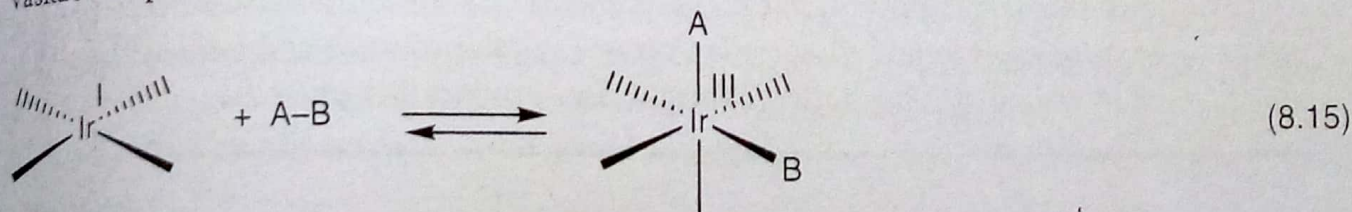


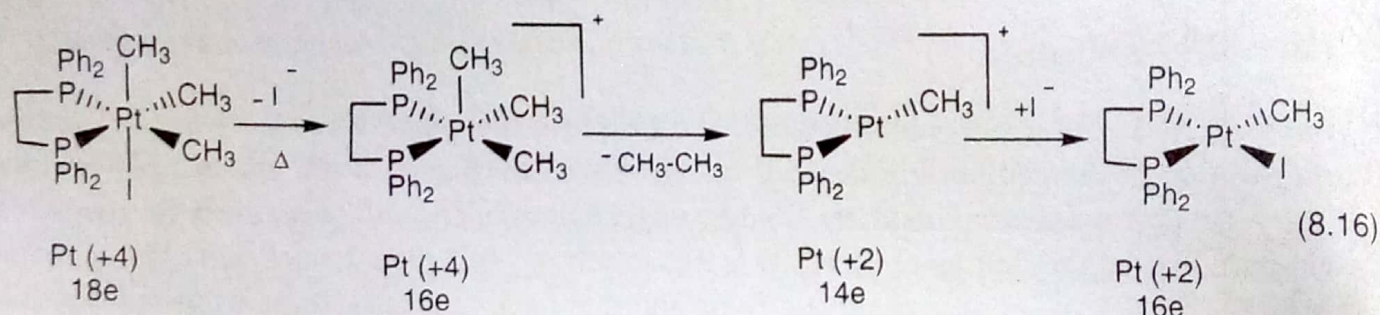
Table 8.1 Thermochemical data and bond dissociation energies of iridium complexes

A-B	Bond dissociation energy of A-B (kcal/mol)	Bond dissociation energy of Ir-A (kcal/mol)	Bond dissociation energy of Ir-B (kcal/mol)	ΔH (kcal/mol)	ΔG (kcal/mol)
H-H	104	Ir-H : 60	Ir-H : 60	-16	-6
$\text{CH}_3\text{-H}$	104	Ir- CH_3 : 46	Ir-H : 60	-2	+8
$\text{CH}_3\text{-CH}_3$	88	Ir- CH_3 : 46	Ir- CH_3 : 46	-4	+6
$\text{CH}_3\text{-I}$	56	Ir- CH_3 : 46	Ir-I : 45	-35	-25

Since an *electron rich* metal favours oxidative addition, the reverse is true for reductive elimination. As the latter involves pushing a pair of electrons back onto the metal centre from two anionic ligands which are usually more electronegative than the metal centre, it is best if the metal centre

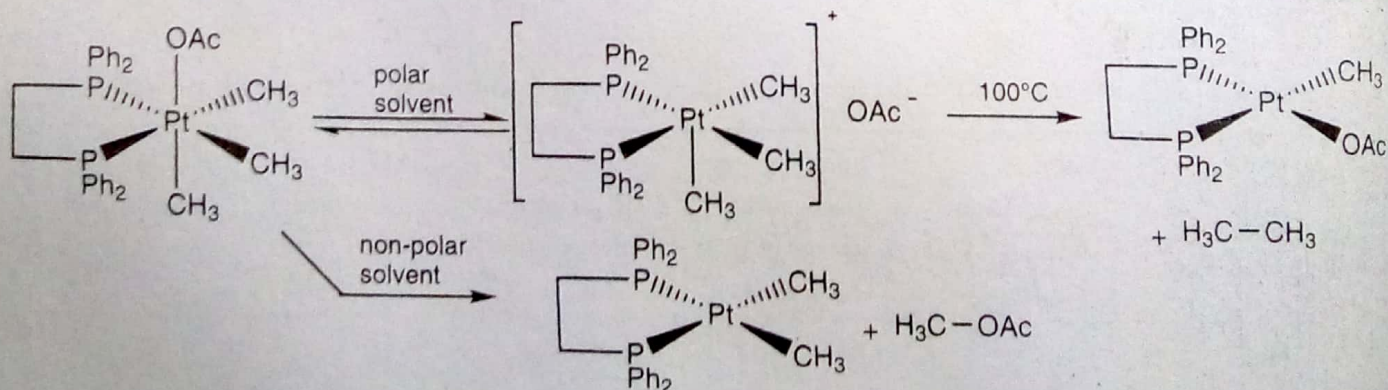
is *electron deficient*. This can be accomplished by having electron withdrawing ligands like CO, cationic charge(s), and/or coordination unsaturation (sub-18 electron counts). The following examples highlight the role of coordination unsaturation and the cationic nature of the complex in the reductive elimination reactions.

Generally, reductive elimination of two *cisoidal* groups from saturated 18e complexes occurs without difficulty. However, it has been shown that the rates of such reactions can be promoted by a ligand dissociation which generates an unsaturated and more electron deficient metal centre. In the following reaction, the reductive elimination of ethane from the cation, formed by the iodide dissociation, occurs much more rapidly compared to the direct elimination from the initial 18e complex.



Oxidation, therefore, can be used to induce reductive elimination when the reaction would not occur otherwise. The classical case of $\text{Et}_2\text{Fe}(\text{bipy})_2$ which involves oxidation has been discussed later in this chapter (Section 8.3.5).

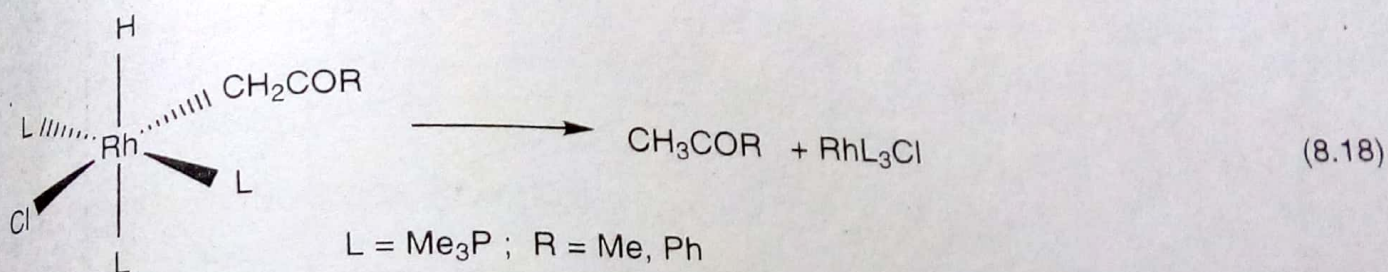
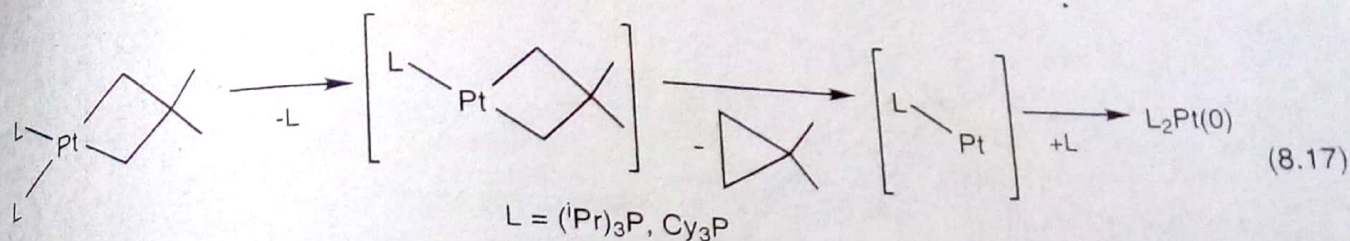
The solvent plays an important role in the following reaction and leads to different elimination products because prior ligand dissociation occurs in polar solvents and forms a coordinatively unsaturated intermediate which then forms the final product (Scheme 8.2).



Scheme 8.2 Effect of solvents on reductive elimination reactions

There are many more examples where ligand dissociation is essential before elimination. In the following reaction, the dissociation of one phosphine ligand prior to reductive elimination of 1, 1-dimethylcyclopropane is mandatory.

Some reactions which form a C-H bond also require prior dissociation of the ligand. For example, in Eq. 8.18, reductive elimination occurs by a dissociative mechanism. The loss of PMe_3 prior to this step is the rate determining step and this has been confirmed by kinetics studies.



Though coordinative unsaturation is a general feature of reductive elimination reactions, it may so happen that other factors may dominate in some reactions. For example, some reductive elimination reactions that form C-H bonds are so facile that they do not require prior dissociation of any ligand. The elimination of methane from *cis*-PtL₂(H)CH₃ and the elimination of dihydrogen from *cis*-(Me₃P)PtH₂ occur without prior phosphine dissociation.

Considerable effort has been devoted by theoreticians to understand the entire phenomenon. It is generally agreed that the reductive elimination of *cis* ligands from 4-coordinate *d*⁸ square planar complexes is possible, but the reaction in the corresponding 3 and 5 coordinate complexes is easier. Some unusual facile reductive elimination such as those forming C-H bonds can occur in planar complexes without prior ligand dissociation, as mentioned above. Similarly, although reductive elimination of *cis* ligands from an octahedral complex is possible, it is much easier after the dissociation of a ligand leads to a 5-coordinate species.