Basic Organometallic Chemistry: Types of Reactions

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A fundamental difference between homogeneous and heterogeneous catalysis is that one can provide an acceptable reaction mechanism for the former based on a sequence of well-established reaction steps and isolated or characterized intermediates. To propose an acceptable reaction mechanism for a homogeneously catalyzed chemical reaction that involves transition metal-based catalysts, working knowledge of the different types of reactions possible for an organometallic complex is essential. Unlike reaction mechanisms in classical organic chemistry or transition-metal-ligand chemistry, the presence of metal-carbon σ and π bonds make a significant difference by bringing in new types of reactions that are unique to organometallic compounds. The changes that are possible for both the metal center and carbon-based ligand unit need to be considered, and the standard set of rules governing the use of such reactions needs to be familiarized before detailed reaction mechanisms can be proposed.

Commonly encountered reactions in organometallic chemistry

The following fundamental reactions are commonly encountered in organometallic chemistry. Some of these are also common for classical organic and inorganic reaction mechanisms as well.

1. Oxidative addition

This unique reaction observed for organometallic compounds involves the reaction of a neutral molecule (H_2, Cl_2, Me_3SiH etc.) with a metal complex that is oxidatively unsaturated (such as a square planar complex with a metal ion in a low oxidation state). The reaction results in the addition of two new anionic ligands generated from the neutral molecule onto the metal center. The addition can be *cis* (for homonuclear molecules e.g. Cl_2) or *trans* (for a heteronuclear reactant e.g. MeI). The reaction results in the oxidation state of the metal increasing by two units and the coordination number also increasing by two units. The metal should be in a low coordination number before oxidative addition can occur. Therefore, 18 electron complexes will cleave one or more ligands or undergo a ligand reorganization such as a changeover to a lower hapticity before oxidative addition occurs.

This monograph is a comprehensive update of the material given under the chapter 'Unique reactions in organometallic chemistry' of the text book 'Basic Organometallic Chemistry: Concepts Syntheses and Applications' by B. D. Gupta & A. J. Elias (Universities Press, Hyderabad, India, 2013).
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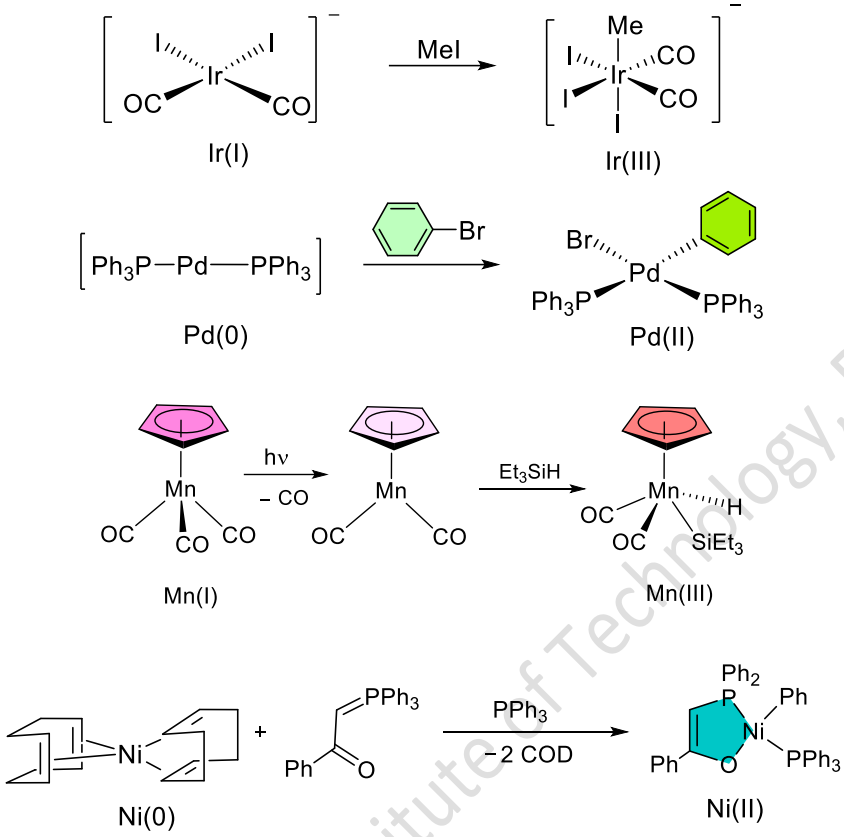


Figure 1. Examples of oxidative addition reactions [1-3]

The reaction can happen by different mechanistic pathways such as concerted, non-concerted (S_N2 type), radical, and ionic [4]. While a concerted mechanism leads to the formation of *cis*-added products, all other mechanisms can lead to both *cis* and *trans* oxidatively added products.

(a) Concerted mechanism

Concerted mechanism, also known as three-centre mechanism involves first an associative step in which a neutral molecule such as H_2 or a σ bond binds to the metal site in a η^2 mode followed by bond breaking and oxidation of the metal unit. For a molecule such as H_2, the initial associative step involves the formation of a three-centre σ complex and during the following oxidative step, metal electrons are transferred to the σ* orbital of H_2.

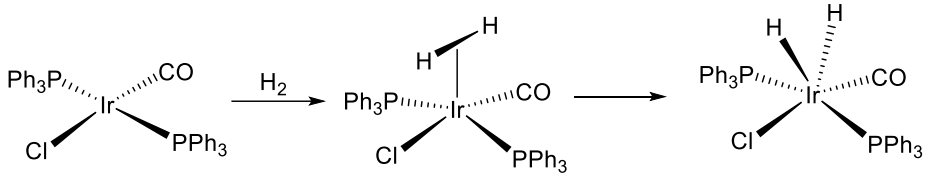


Figure 2. Example of the concerted mechanism of oxidative addition of H_2

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The oxidative addition of aryl halides to palladium metal which is the initial step of many cross-coupling reactions also involves a three-centre concerted step. Computational studies predict that this is more likely when only one phosphine is present on the metal in its transition state.

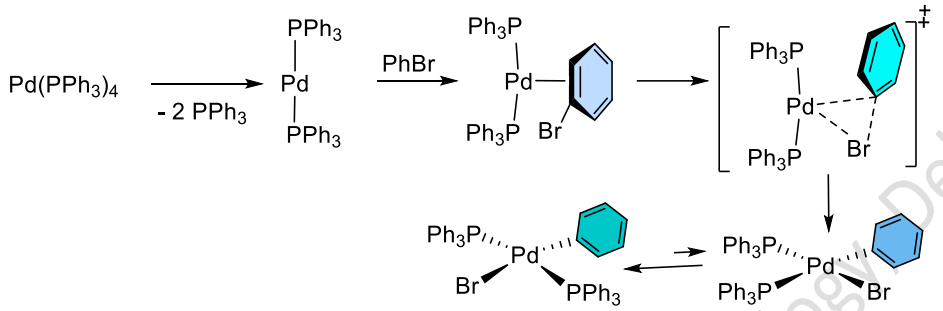


Figure 3. Example of concerted mechanism of oxidative addition of aryl bromide

(b) S_N2 Mechanism (non-concerted)

This mechanism is observed for polarized organic substrates such as MeI and allyl, benzyl and acyl halides with some specific metal complexes. The electron pair from the metal directly attacks the σ* orbital of the molecule AB at the least electronegative atom and forms ML_n^{2+}, A^- and B^-. These type of reactions have a polar-ordered transition state similar to what is observed for conventional organic S_N2 reactions. With suitably substituted organic halides inversion at the carbon was found to happen. The oxidative addition of alkyl halides to $Na_2Fe(CO)_4$ also demonstrates a 2-electron S_N2 mechanism.

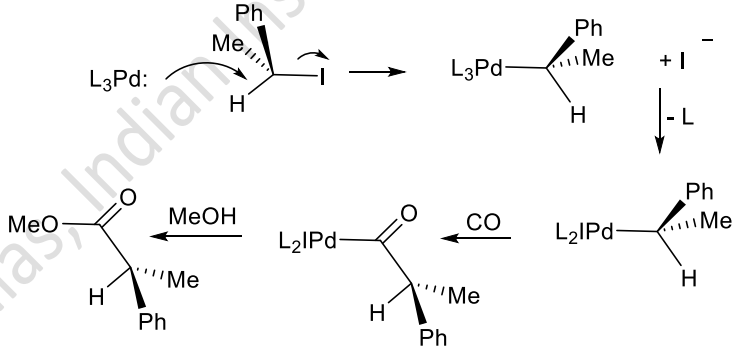


Figure 4. Example of an S_N2 type non-concerted mechanism

(c) Ionic mechanism

Ionic mechanism is shown especially by hydrogen halides which are fully ionized species. The proton and the anion adds to the metal complex in separate steps. In the commonly observed type, the metal complex is basic enough to be protonated and the anion addition follows to give the final product. Protonation is the rate-determining step.

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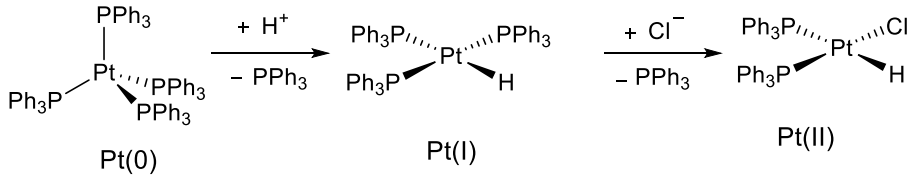


Figure 5. Example of ionic mechanism of oxidative addition of HCl

(d) Radical mechanism

This mechanism is mostly observed in light-induced reactions that are restricted to specific metal complexes and organic substrates such as benzyl halides. The addition of benzyl bromide to $Pt(PPh_3)_3$ is a classic example of a non-chain radical mechanism. The main step of the mechanism is the one-electron transfer from Pt(0) to the $PhCH_2Br$ σ* orbital to form Pt(I) and $[PhCH_2Br]^{\bullet-}$. After the transfer of the bromide to the Pt(I), the $PhCH_2^{\bullet+}$ radical is formed with is added to the metal center forming the Pt(II) complex.

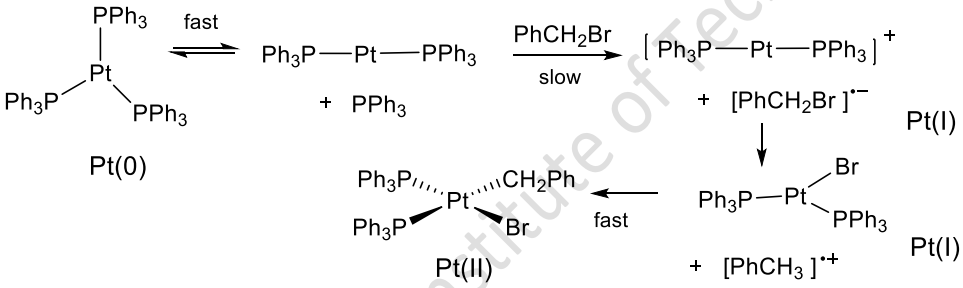


Figure 6. Example of radical mechanism of benzyl bromide oxidative addition

In a closely related radical chain process, such as the reaction between the PMe_3 analog of Vaska's complex and benzyl bromide, a radical initiator sets the reaction forward. A metal centre-based radical then abstracts a halogen radical releasing a chain carrier R• which carries the chain reaction forward.

There are many examples of specialized oxidative additions such as cyclometallations, ortho metalation, turnover cyclometallation, and strained ring oxidative addition which are discussed later in sections 1.2 to 1.6.

1.1 Oxidative coupling

Oxidative coupling is a reaction involving two π bonded alkene units or alkyne units that undergo coupling in the presence of a metal unit to form a cyclic metalla-cyclopentane or metalla-cyclopentadiene. The metal center, which is part of the ring, gets oxidized by two units as two new σ bonds are formed on it. The alkene or alkyne units are coupled to form a metallacyclic species in the process. Interestingly, although the metal gets oxidized, the overall electron count on the metal complex gets reduced by two units as two π bonded ligands are converted to two σ bonded ligands in this reaction. This step is the crucial step in the formation of cyclic compounds from alkenes and/or alkynes such as the trimerization

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of alkynes or alkyne/nitrile combinations to form multi-substituted aryl rings or substituted pyridines.

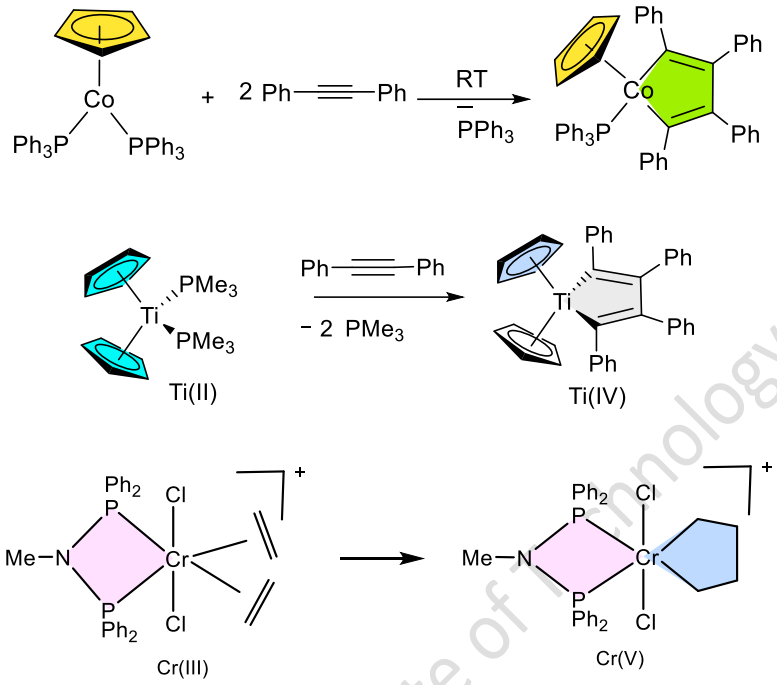


Figure 7. Examples of oxidative coupling reactions [5-7]

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Other Variations of Oxidative Addition Reactions

1.2 Cyclometallation /Orthometallation

Cyclometallation was first reported in 1965 by Arthur C. Cope in the reaction of azobenzene with potassium tetrachloroplatinate where an ortho hydrogen of one of the aryl rings was replaced by a platinum-carbon bond, along with the formation of a five membered ring with one of the azo nitrogen atoms. An analogous palladium (II) cyclometallated compound was also reported along with this compound. However, in both these reactions the oxidation state of the metal did not change from +2 and therefore these reactions do not classify as oxidative addition. 1n 1969, Bennet observed that the red brown colored iridium analogue of the Wilkinsons catalyst, $IrCl(PPh_3)_3$ on simply refluxing in benzene for one hour gives a colorless compound having an Ir-H bond and the reaction of this compound with CO resulted in the formation of Vaska's complex. The colorless compound formed resulted from an orthometallation of one of the aryl groups of a PPh_3 unit and this was an example of an intramolecular oxidative addition of the aryl C-H bond oxidizing the iridium from +1 to +3. Cyclometallation/orthometallation involving oxidative addition of metal centres has been found to observe not only for C-H bonds but also for many other bonds such as C-C, C-F etc. In many cases the reaction does not stop at the cyclometallated state

but continues further with a reductive elimination whereby a small molecule such as CH_4 is released or the strain in a smaller ring formed is released by reverting back to an acyclic compound.

Cyclometallation has also been found to happen as part of σ bond metathesis, especially for complexes having the metal ion in its highest oxidation state.

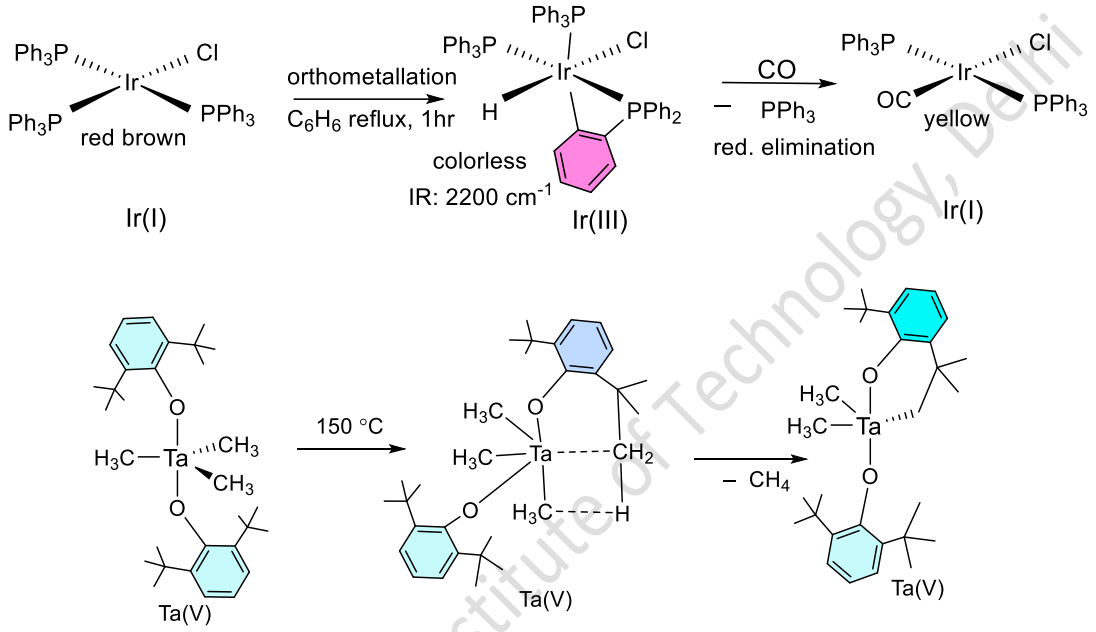
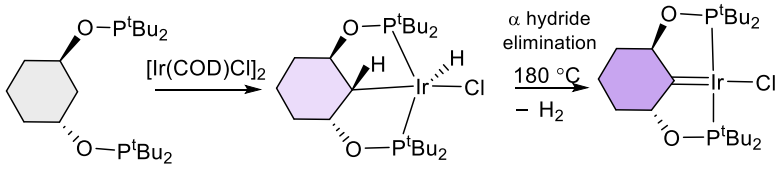


Figure 8. Cyclometallation reactions involving oxidative addition and σ bond metathesis [8, 9]

1.3 α -Hydride elimination, α-hydride abstraction and metal carbene formation

Ways by which a metal-carbene bond can be formed include α-hydride elimination or α-hydride abstraction. In the elimination reaction, a hydrogen atom on the α carbon atom of a σ bonded alkyl ligand such as neopentyl gets transferred to the metal centre and simultaneously a metal carbon double bond is formed. The reaction results in the formal oxidation of the metal by two units; however, this oxidation step is often transient as it will be followed by a reductive elimination. A necessary requirement of this reaction is that the metal ion should not be in the highest oxidation state possible as it has to get oxidized by two units. In the examples of iridium complexes shown (Figure 9), α-hydride elimination is shown. Interestingly, in some cases where reductive elimination does not happen after carbene formation, the reverse reaction can also happen and instead of H, a CH_3 group can get transferred back to the α-carbon.



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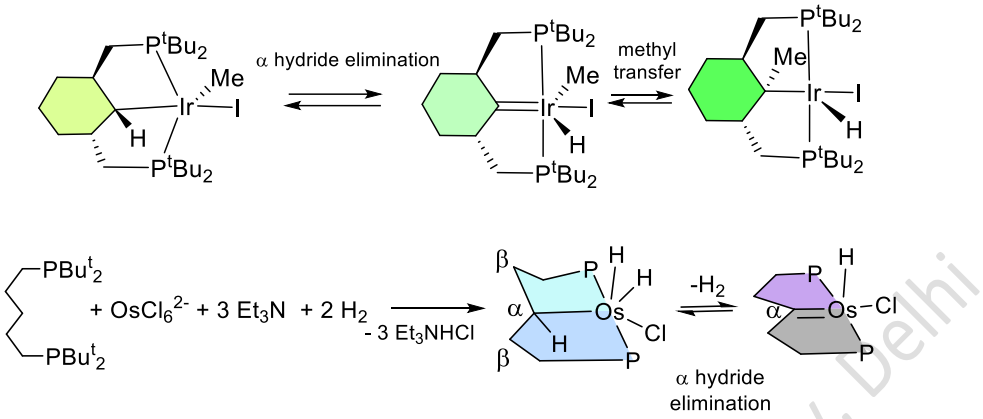


Figure 9. Examples of α hydride elimination reactions [10-12]

The α-hydride abstraction is a similar reaction where the metal ion is already in its highest oxidation state and cannot get oxidized further but a metal-carbene still forms. In this variation, the α hydrogen is not transferred to the metal but to another σ bonded ligand bound to the metal (A step similar to σ bond metathesis) and results in the release of this ligand as a neutral molecule (e.g. neopentane or methane). The metal carbene is formed by the alkyl group which provides the hydrogen. Schrock, who pioneered these two reactions has also mentioned that if there exists a possibility of both α hydride elimination/abstraction and β-H elimination, the latter reaction is often found to occur.

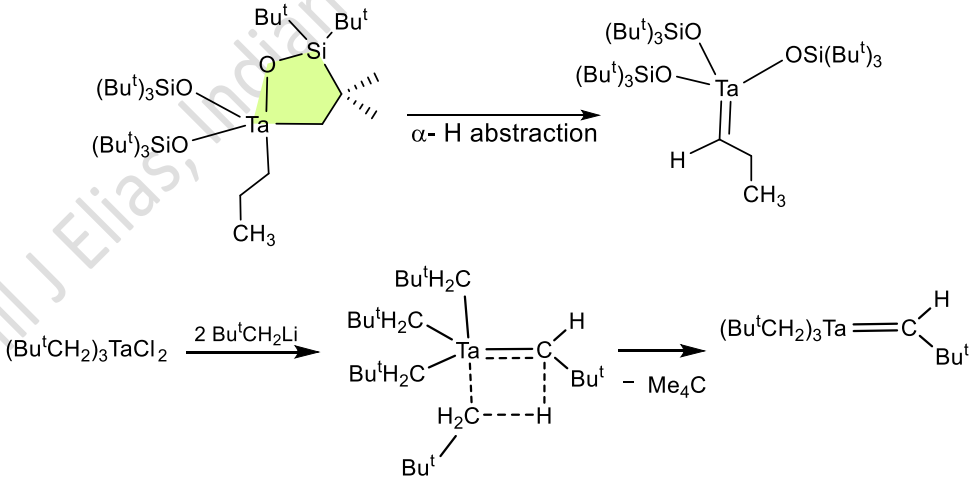


Figure 10. Examples of α hydride abstraction reactions [13-14]

However, Schrock has also shown that in some cases, both α hydrogen abstraction and β hydrogen elimination can occur to the same extent.

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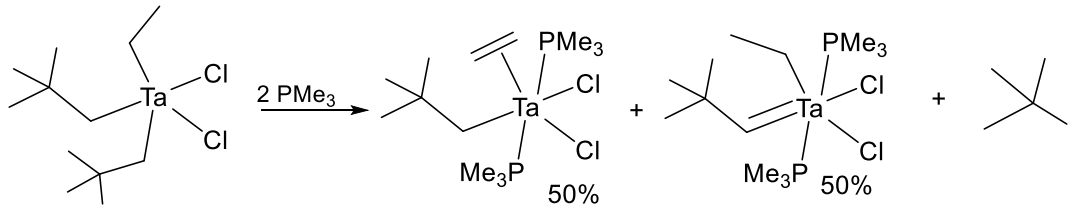


Figure 11. Reaction where both α hydrogen abstraction and β hydrogen elimination occur [5]

1.4 γ, δ and ω hydride abstraction/cyclometallation

Although β-hydride elimination is the most preferred hydride elimination pathway, if there is no β- hydrogen and carbene formation is not facile, γ, δ and ω hydride abstraction can occur if the ligand is flexible enough. Unlike β-hydride elimination where the metal centre is not getting oxidized, in γ, δ and ω hydride abstraction the product formed is a cyclometallated species and in the process the metal ion gets oxidized by two units. Such cyclometallation reactions can also occur on complexes where the process does not involve any change in the oxidation state and reaction proceeds by σ bond metathesis.

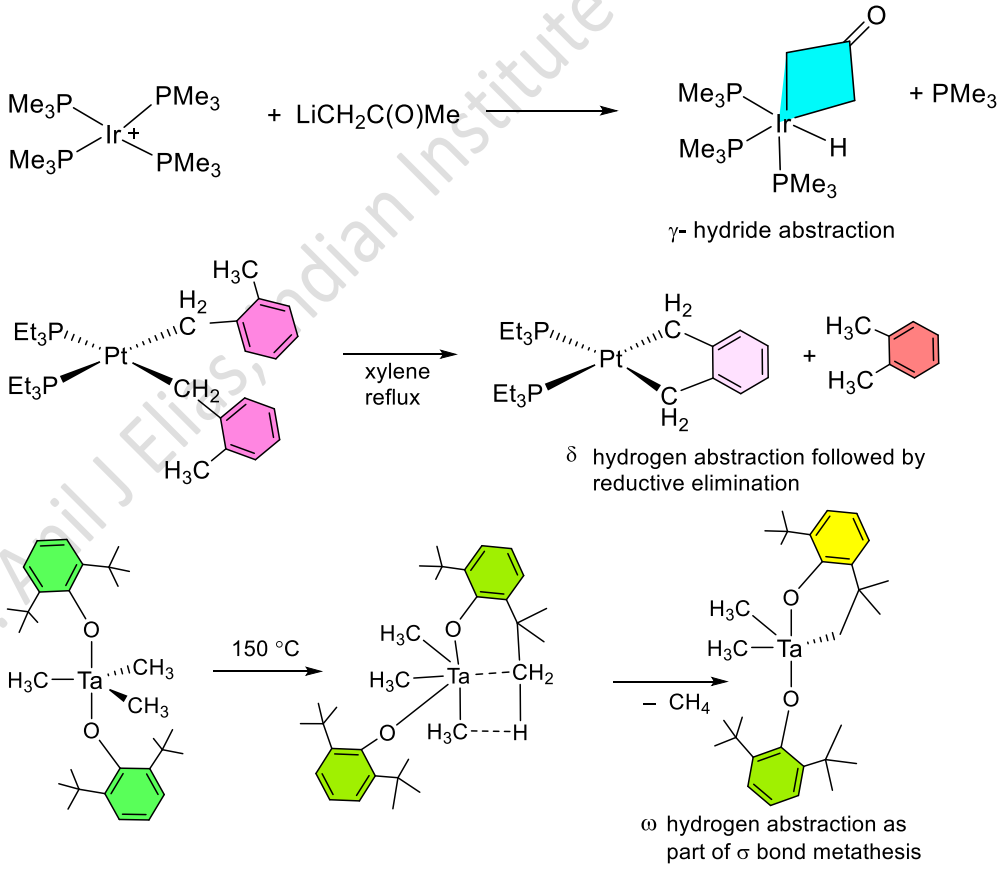


Figure 12. Reactions of γ, δ, and ω hydrogen abstraction [16-18]

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1.5 Rollover cyclometallation

This type of cyclometallation involves chelated heterocyclic multidentate ligands such as bypyridine or terpyridine or their derivatives that change from being a spectator ligand to an actor ligand. During the reaction, the ligand undergoes internal rotation or 'makes a rollover' around a C-C bond, breaking the chelation. A remote C-H bond of a pyridyl unit is activated regioselectively and this C-H bond undergoes oxidative addition on the metal center. A M-N coordinate bond gets replaced by a M-C covalent bond. Quite often this step is followed by a reductive elimination, where the transferred hydrogen along with an alkyl group on the metal center leaves the metal site as a neutral molecule such as CH_4.

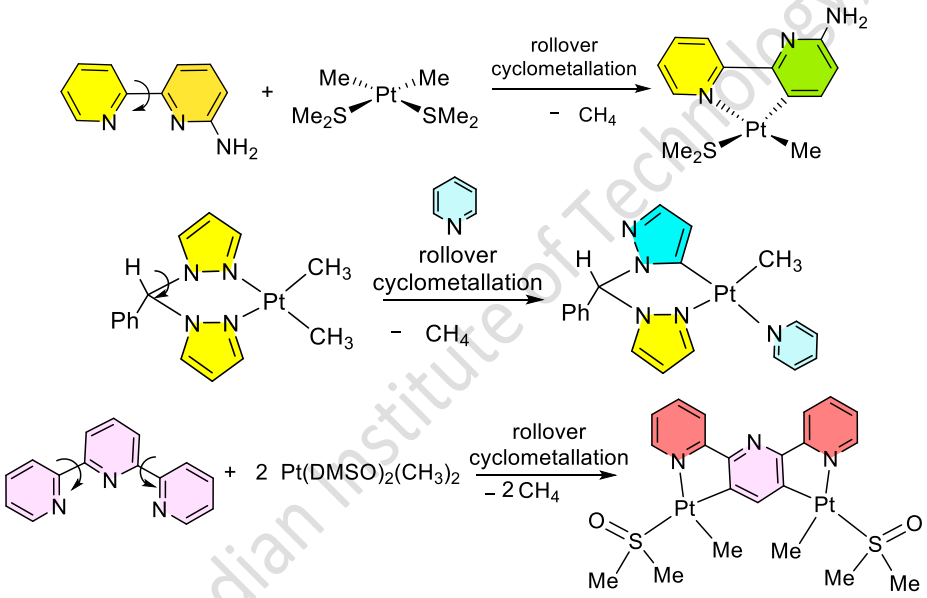
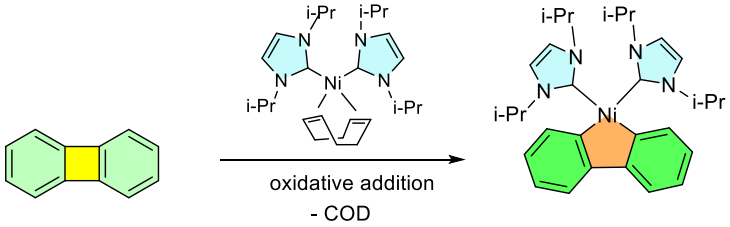


Figure 13. Rollover cyclometallation reactions [19-22]

1.6 Strained ring C-C bond oxidative addition

Three and four membered strained rings which are part of a polyaromatic system (e.g. biphenylene) have been found to undergo oxidative addition with metal complexes where the metal forms a four or five-membered metallacycle. The metal then can take in an alkyne or nitrile unit and expand further, undergo a reductive elimination and convert to a less strained polyaromatic system.



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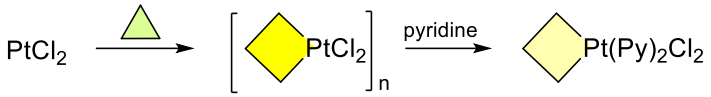


Figure 14. Strained ring C-C bond oxidative addition reactions [23-24]

2. Reductive elimination

Reductive elimination is a unique reaction observed for organometallic compounds which results in the formation of a stable organic molecule and in the process, reduction of the metal ion occurs by two units. A necessary requirement of reductive elimination is that the anionic groups involved in the formation of the expelled neutral molecule from the complex must be oriented *cis* to each other mutually. It is often observed that a competing reaction for reductive elimination is the β-hydride elimination which can happen if the transition metal-based intermediate is not sterically crowded and alkyl groups having β-hydrogen atoms are present on the metal center. Reductive elimination is often the final step of a catalytic cycle as the product molecule of the reaction gets released with this step and the active form of the catalyst is regenerated.

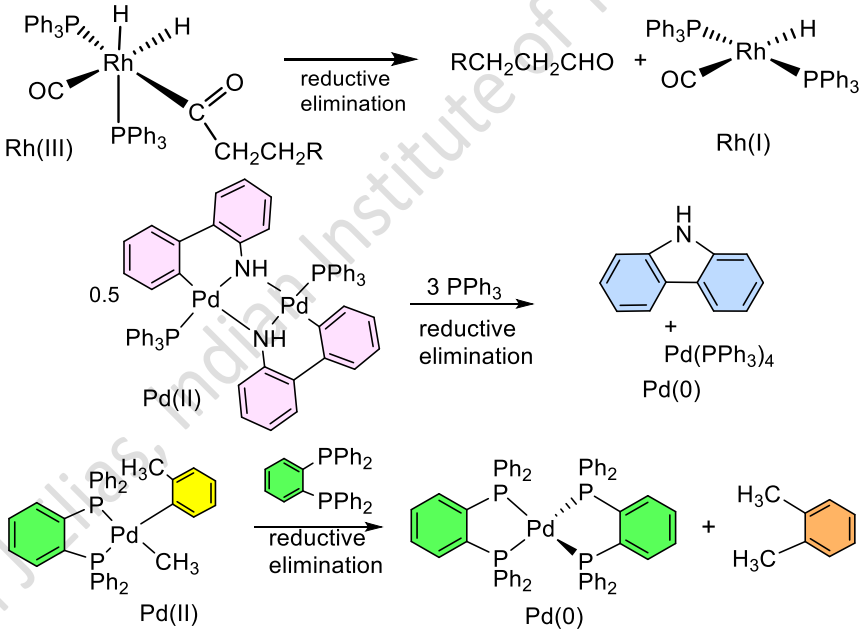


Figure 15. Examples of reductive elimination reactions [1, 25, 26]

3. Migratory Insertions (1, 1 and 1, 2 insertions)

Migratory insertion is a step where a metal-bound actor ligand such as an alkyl group gets transformed into another ligand such as an acyl group. This change happens by the migration of the alkyl group onto a metal-bound CO unit or viewed from a different perspective, the insertion of a metal-bound CO unit into a metal-alkyl bond. Since both activities will result in the same acyl group, the reaction has been called migratory

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insertion. Migratory insertion can also be the ligand transformation of a π bound alkene unit to a σ bound alkyl group by the migration of a metal-bound hydride to the alkene unit. The conversion of the alkyl to the acyl group is an example of 1, 1 migratory insertion (metal and migrating group are bound to the same carbon while the conversion of alkene to an alkyl is a 1, 2- migratory insertion since the metal and the migrating group gets bound to different carbon atoms.

The distinct feature of a migratory insertion is that the oxidation state of the metal does not change during this step. Also, this reaction is entropy-prohibited but enthalpy facilitated as the number of molecules formed after the step is less than before the reaction. Since there is no change in the oxidation state of the metal, this reaction is not restricted to transition metal complexes alone.

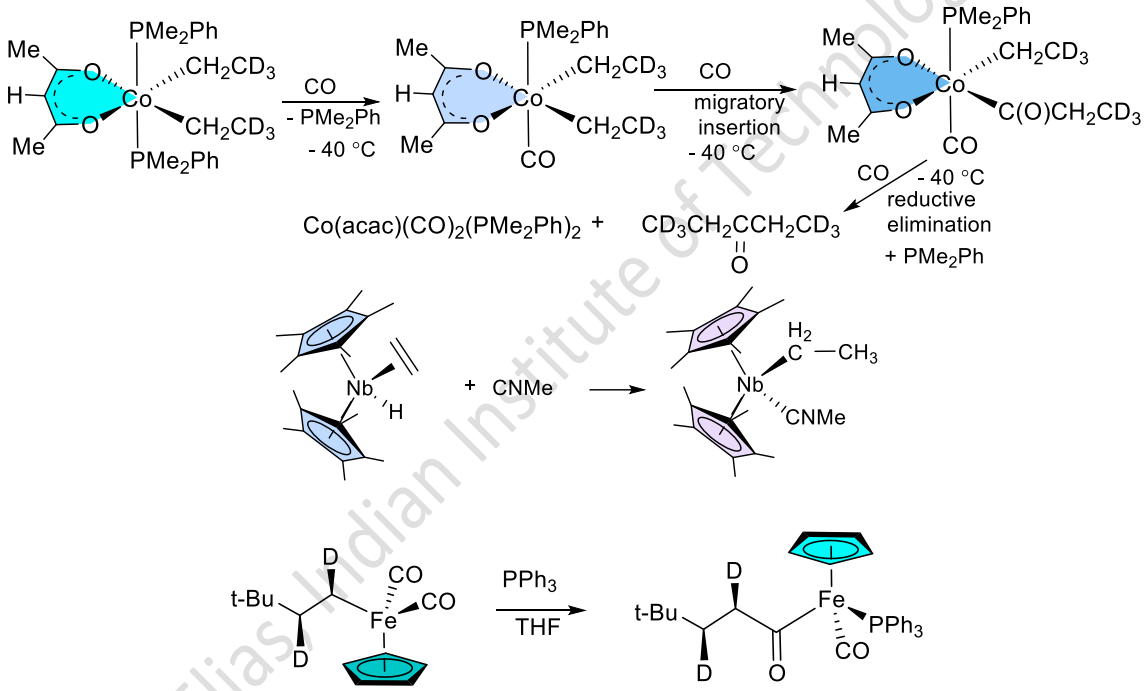


Figure 16. Examples of migratory insertion reactions [27-29]

4. β - Hydride elimination

In simple terms, β-hydride elimination can be considered as the exact reverse of a 1, 2-migratory insertion. Typically, during a β-hydride elimination, the hydrogen atom bound at the β- position of an alkyl group forms a 4-membered intermediate with the metal atom followed by the transfer of the hydride to the metal center and the alkyl group converts to an alkene which remains bound to the metal center in a η^2- mode. β-hydride elimination also does not involve a change in the oxidation state of the metal center. However, during the reaction the electron count of the metal increases by two units as a σ bonded ligand gets converted to a σ bonded H and a π bonded alkene unit. Therefore, sufficient space

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should be available on the metal center to accommodate an extra π-bonded ligand and for this reaction to happen.

β-Hydride elimination can be prevented by increasing the steric crowding on the metal centre. This reaction is not restricted to alkyl units but happens with other ligands such as alkoxy and amido groups if there is β-hydrogen available with such ligands and the 4 membered intermediate with the metal unit can be formed. This reaction is not restricted to transition metal complexes and has been found to occur with main group compounds as well. The formation of DIBAL-H from $(i\text{-}Bu)_3Al$ is a well-known example for β-hydride elimination in aluminum compounds. The reaction does not happen if there is no β-hydrogen available on the σ bonded ligand, or the orientation of the β-hydrogen on the alkyl chain does not allow the formation of the 4 membered intermediate such as that of an alkyne unit or a metallacycle formed by the ligand. For example, products of Mizoroki–Heck coupling or Shell higher olefin (SHOP) process are released via β-hydride elimination, while C–C coupling of alkyl fragments and linear polymerization of ethylene often suffer from the occurrence of undesirable β-hydride elimination.

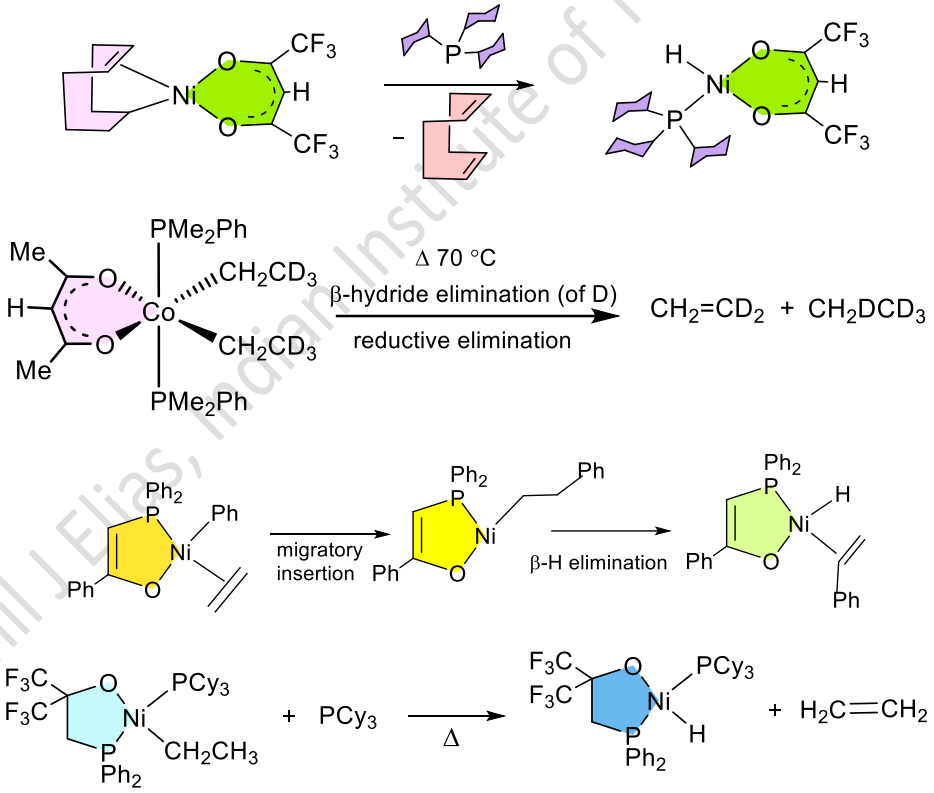


Figure 17. Examples of β-hydride elimination reactions [3, 27, 30-31]

5. σ Bond metathesis

For organometallic complexes having σ bonded ligands where the metal ion is already in its highest oxidation state, oxidative addition with another neutral molecule becomes

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impossible as the metal ion cannot be oxidized further. However, such complexes may still undergo a reaction with some neutral molecules where a metathesis happens between the σ bond of the complex (M-C, M-H, etc.) and the σ bond of a neutral molecule (C-H, C-C etc.) resulting in the release of a stable molecule such as H_2, methane or benzene and formation of a new metal -ligand σ bond and the reaction does not affect the oxidation state of the metal. σ Bond metathesis was first observed for early transition metal complexes such as those of scandium and lutetium in their highest oxidation states. However, it is not restricted to these metals. It has been observed to happen in situations where the oxidative addition may force the metal to go to an unusually higher oxidation state or for main group and lanthanide metal compounds where oxidative addition/reductive elimination cycles are not practically feasible but metathesis is a possibility. The unique step of the reaction mechanism is the formation of a four membered cyclic transition state with the metal forming part of the ring. In such reactions, adherence to the 18-electron rule is seldom observed.

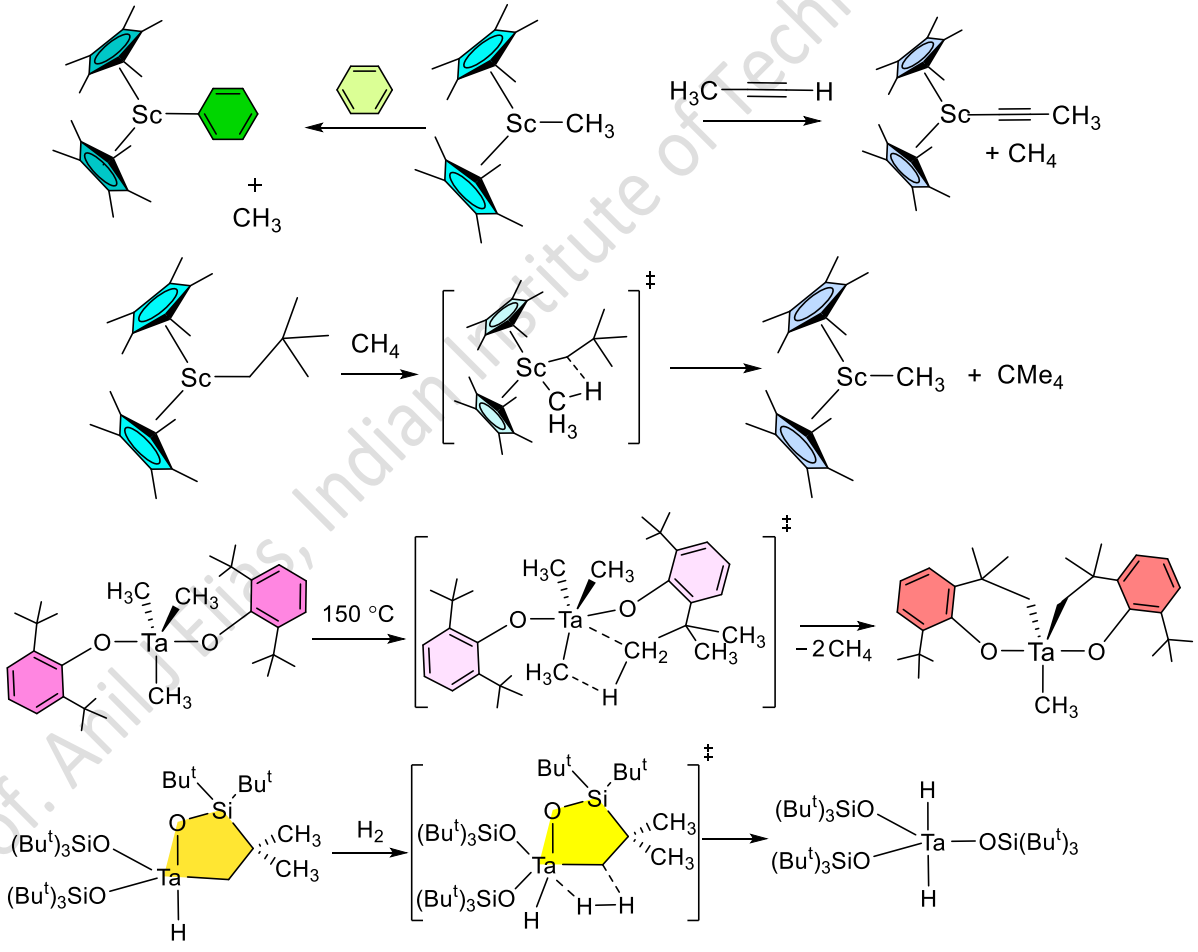


Figure 18. Examples of σ bond metathesis reactions [13, 18, 32]

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6. π Bond metathesis

Olefin and alkyne metathesis reactions come under the classification of π- bond metathesis where π- bonds (of alkenes/alkynes and carbenes/carbynes) undergo a 2+2 cycloaddition reaction to form a four-membered metallacyclobutane intermediate (from an alkenes and a carbene) or a metalla-cyclobutadiene intermediate (from an alkyne and a carbyne). These cyclic intermediates have been isolated in some cases. A cyclo-reversion follows resulting in the formation of a new alkene or alkyne which is removed from the reaction. This reaction also does not involve any change in the oxidation state of the metal ion and has a very good scope in pharmaceutical and industrial synthesis, especially for making large cyclic organic compounds having unsaturation or unsaturated polymers. The discoverers of the olefin metathesis reaction received the Nobel prize in 2005. This reaction makes use of metal-carbenes or metal-carbynes as catalysts (Figure 19).

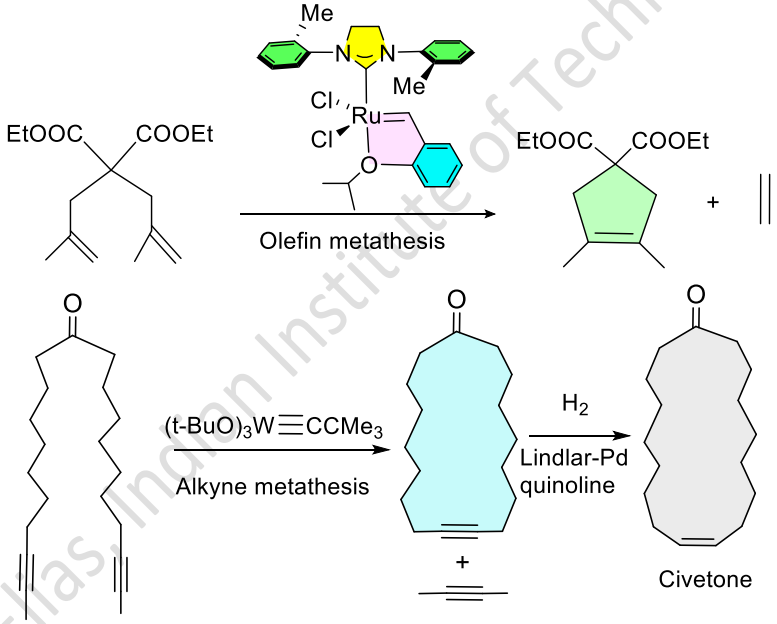


Figure 19. Examples of π bond metathesis reactions [33, 34]

7. Ligand association and dissociation

During a reaction involving an organometallic complex, ligands such as phosphines, carbon monoxide, or pyridines often dissociate from the metal center. This is observed frequently for the generation of the active form of a catalyst from a stable pre-catalyst (especially for an 18-electron species where ligand dissociation or ligand reorganization such as hapticity change becomes imminent before the metal can accept a new ligand or undergo a reaction that will result in an increase in electron count) In cases where it is applicable, the dissociation may also occur by the *trans* effect initiated by a stronger ligand positioned *trans* to the ligand undergoing dissociation. Actor ligands such as CO can also dissociate from the metal center either by ligand cleavage initiated by UV radiation or by

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its oxidation to CO_2 by reagents such as Me_3NO. In the absence of another ligand, dimerization or oligomerization of the species formed also may happen. Alkenes such as ethylene or cyclooctadiene (COD) have been observed to readily dissociate from a metal center paving way for the association of a stronger ligand. Ligand dissociation of an anionic ligand to generate a cationic complex stabilized by an anionic counter ion is also a well known type of reaction which is discussed in section 10.

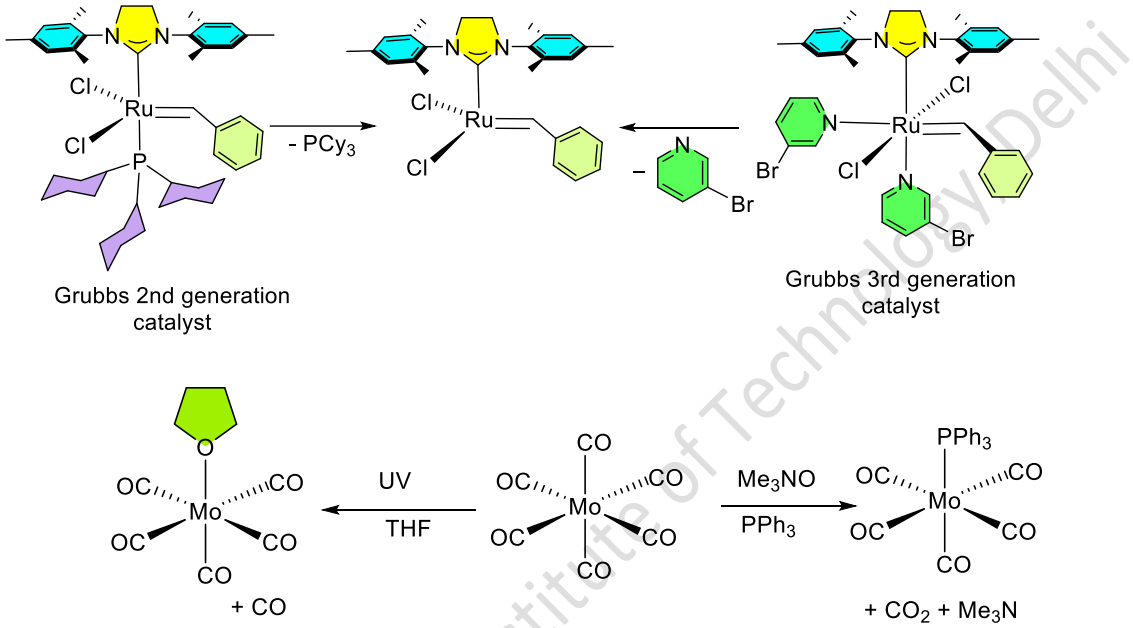


Figure 20. Examples of ligand dissociation reactions [33, 35]

Ligand association step is described as the binding of a neutral substrate molecule such as an alkene or CO to the metal site before it undergoes further reactions. It can also be the re-association of a previously dissociated molecule from the metal center to regenerate the catalyst. The necessary requirement is that the association should not result in a species that has more than 18 electrons. In addition, sufficient space should also be available on the metal center for accommodating such a ligand. It may be noted that during ligand association or dissociation, the oxidation state of the metal does not change but the electron count changes.

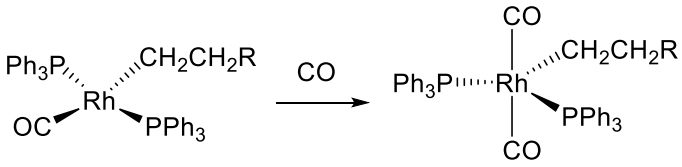


Figure 21. Example of a ligand association step [1]

8. Ligand substitution

During ligand substitution of neutral and anionic ligands of an organometallic complex by analogous ligands, no change in electron count is observed. Substitution can also occur on a 18 electron species. A well-known example of anionic ligand substitution is the

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introduction of alkyl groups by a Grignard or organolithium reagent substituting a metal-bound halide. The preparation of Grubbs first generation catalyst and its conversion to the second generation catalyst are examples of neutral ligand substitution where a phosphine gets substituted by another phosphine or a N- heterocyclic carbene. The feasibility of this reaction is decided by the leaving group ability of the ligand already present on the complex as well as the strength of the incoming ligand. During ligand substitution, neither there is change in the oxidation state nor there is change in the electron count of the complex.

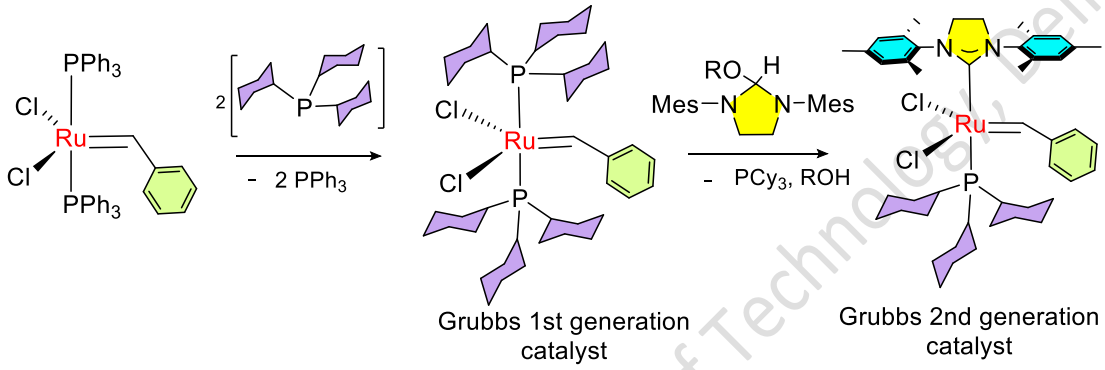


Figure 22. Examples of ligand substitution in the synthesis of Grubbs catalysts [33]

9. Ligand modification

A metal-bound carbonyl can get modified to a metal-bound carbene by reaction with a strong base such as nBuLi (Fischer carbene synthesis). A π bonded alkene can get modified to a σ bonded alkyl group and a σ bonded alkyl unit can get modified to a σ bonded acyl group. These reactions are discussed under migratory insertion reactions.

10. Interconversions of neutral, cationic, and anionic complexes.

An organometallic compounds can be neutral, anionic, or cationic. There are reagents which can be used specifically to convert a neutral complex to a charged complex by the addition or the removal of hydrides or protons. For example, HBF_4 is used to provide H^+ to a complex while $NaBH_4$ is used to provide H^- to a complex. A strong base such a n-BuLi is used to remove an H^+ from a complex while Ph_3CBF_4 can be used to remove an H^- from a complex. The reaction of salts such as KPF_6, $NaSbF_6$ $NaCF_3SO_3$ with metal halogen bonds results in removal of the halide as sodium or potassium salts and formation of cationic complexes. Other specialized reagents include superacids such as HF/PF_5 which has been used to protonate the iron centre of ferrocene. Boron and aluminium based Lewis acids such as $B(C_6F_5)_3$ or methylalumoxane $(MeAlO)_n$ have been effectively used for converting neutral half-sandwich compounds such as zirconocene dihalides and dialkyls to the corresponding cationic complexes.

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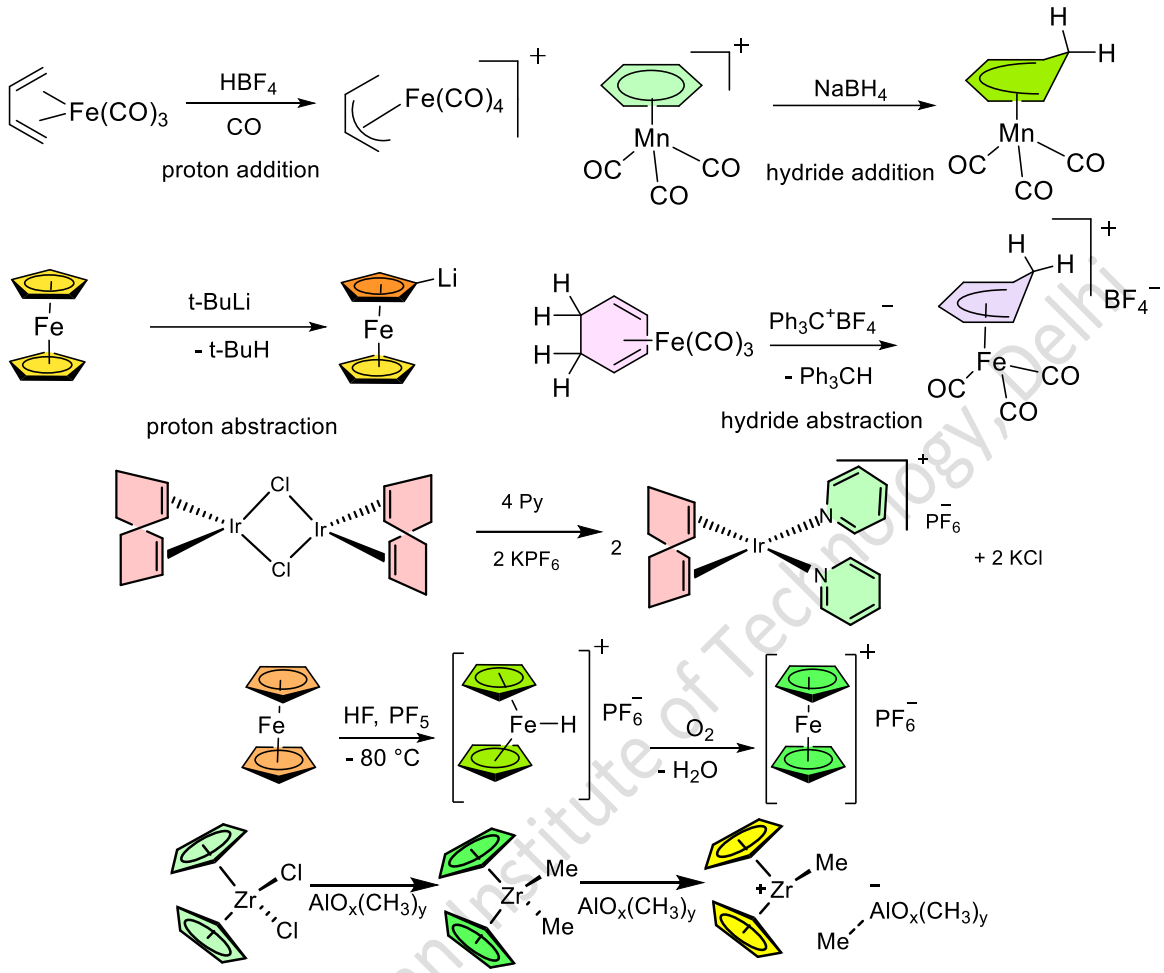


Figure 23. Interconversions between neutral and cationic complexes [1, 36-42]

Reactions of neutral complexes such as $Fe(CO)_5$ with sodium metal results in the formation of anionic complexes.

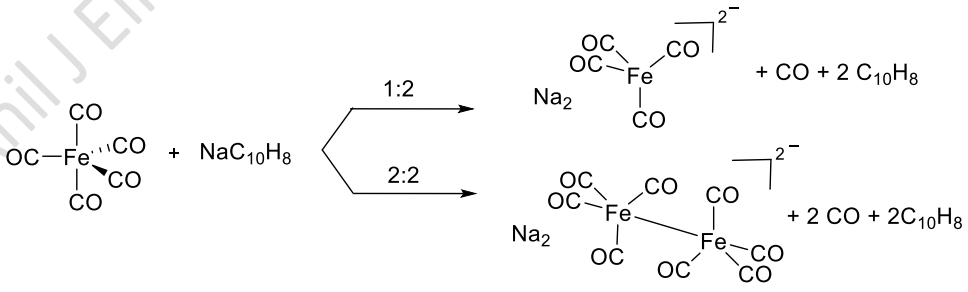


Figure 24. Interconversion between neutral and anionic complexes [43]

11. Redox reactions

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Oxidation of the metal ions of an organometallic compound can be carried out by reagents such as $AgBF_4$ and $NOBF_4$. These reagents can also be used for replacing halide ions from organometallic complexes and generating cationic complexes with tetrafluoroborate as counter ion. In addition, synthesis of many low valent complexes useful as catalysts from metal salts involve redox reactions with the ligand such as ethylene undergoing oxidation.

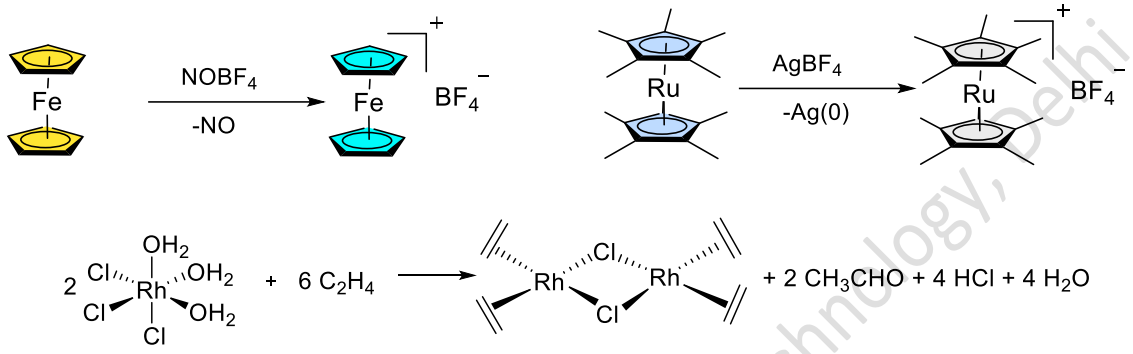


Figure 25. Redox reactions in the synthesis and modification of organometallic compounds [44]

12. Transmetallation

Transmetallation is a type of reaction where an alkyl or aryl group bound to a main group-based reagent is transferred to a transition metal ion in exchange for a halogen or hydroxyl group. It is observed to take place, especially in palladium-catalyzed cross-coupling reactions. In general, a transmetallation can involve the exchange of groups such as alkyl, aryl alkynyl, allyl, halogen or pseudohalogen group. The reaction can also be considered as an alkyl or aryl substitution step happening on a reaction intermediate during a reaction. This reaction does not involve any change in the oxidation state of the metal centers involved in the reaction. There are two schools of thought on the generation of the pre-transmetallation palladium intermediate in Suzuki cross coupling reactions namely through a boronate pathway (which is widely accepted) or indirectly through an oxopalladium pathway.

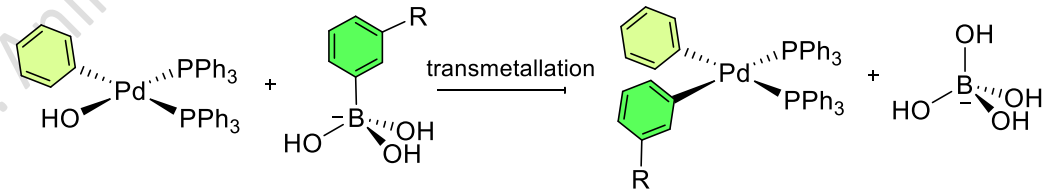


Figure 26. Transmetallation step in the Suzuki coupling reaction [45]

13. Competing reactions observed in organometallic reaction mechanisms

13.1 Reductive elimination versus β-hydride elimination

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A commonly observed competing reaction in homogeneous catalysis involving organometallic catalysts is between reductive elimination and β-hydride elimination. When a σ bonded alkyl group is present on a metal site which is already in a high oxidation state and if there is another σ bonded unit available *cis* to this group, then reductive elimination is the preferred reaction. However, if the metal is not sterically crowded with other ligands and there is sufficient space to accommodate an additional alkene unit, then β-hydride elimination can also happen as a competing reaction. In such a situation also, if the metal is in its highest oxidation state possible reductive elimination is found to happen compared to an identical situation where metal is in a relatively lower oxidation state.

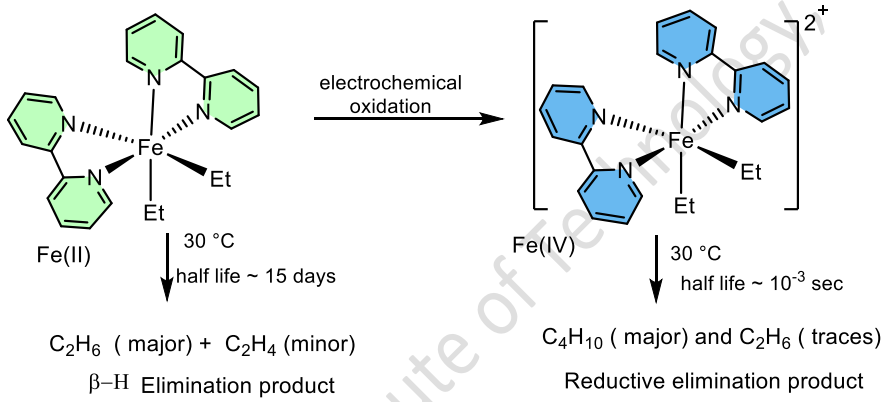


Figure 27. Effect of oxidation state on reductive elimination versus β-hydride elimination reaction [46]

13.2 σ Bond metathesis versus oxidative addition/reductive elimination

Since σ bond metathesis does not involve any change in the oxidation state of the metal centre, it is brought in to explain reactions involving the activation of σ bonds of neutral molecules in the presence of metal ions in their highest oxidation state. For the same reason σ bond metathesis is applied more universally as it is applicable to reactions involving main group and lanthanide compounds as well. However, when a metal is in a low oxidation state and there is an easily accessible higher oxidation state available for this metal separated by two units, the oxidative addition step followed by reductive elimination becomes more facile and is often invoked.

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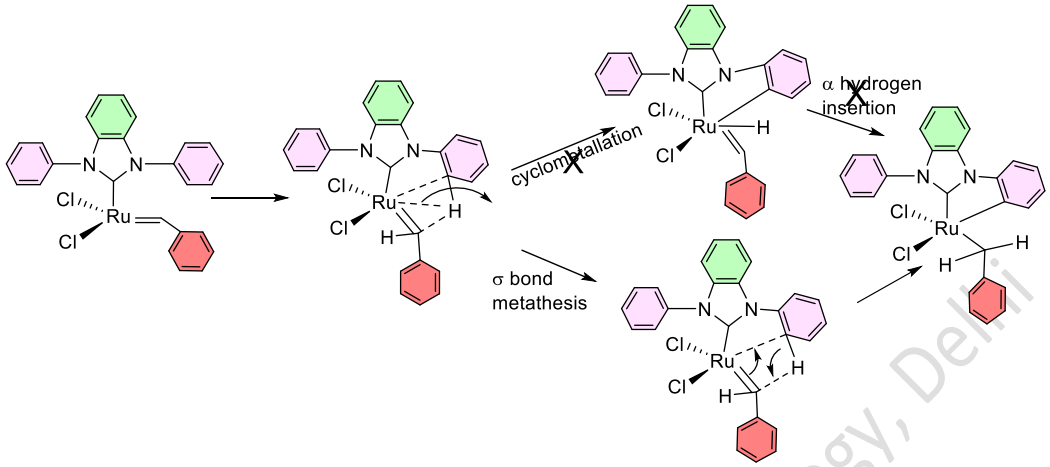


Figure 28. Oxidative addition/reductive elimination versus σ bond metathesis [47-48]

Energy calculations carried out on many mechanisms have shown that if the oxidative addition is involving an intermediate where the metal ion is in an accessible yet unusually high oxidation state, σ bond metathesis becomes a more likely step.

13.3 Cyclometallation of small rings versus large rings

In many reactions where cyclometallation followed by removal of a small molecule such as CH_4 is a likely step, there may be the possibility of the formation of metallacycles with ring sizes varying from 3-7. When you have more than one possibility of cyclometallation, the formation of strained rings with ring sizes 3 and 4 are less likely. Larger ring formation also may depend upon the overall flexibility of the chain unit involved as well as firmness and stability of the overall structure formed after the reaction

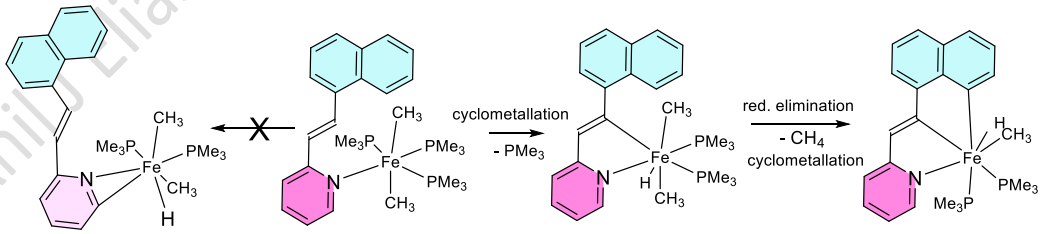


Figure 29. Cyclometallation of small rings versus large rings [49]

13.4 α-Hydride abstraction versus β-hydride elimination

Under normal circumstances when there is the possibility of both α-hydride abstraction and β-hydride elimination, the latter gets a preference over the former.

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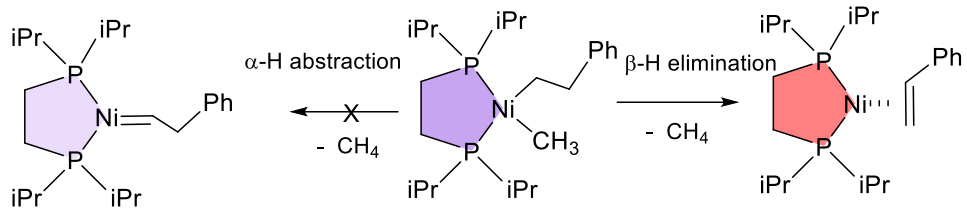


Figure 30. Reaction showing a preference for β-hydride elimination [50]

However, under sterically hindered conditions, it is observed that α-hydride abstraction leading to the formation of a metal-carbene complex gets preference. Formation of Schrock carbenes by α-hydride abstraction happens readily with neopentyl ligand, $-CH_2CMe_3$ and not with $-CH_2SiMe_3$. This has been ascribed to the fact that unlike the former, the latter does not produce a crowded environment due to a longer C-Si bond.

Tris pyrazolylborate complexes of iridium have been found to cleave the α-CH bonds of some ethers and primary amines with the formation of Fischer type carbene complexes as shown. In the final step of this reaction although β- hydrogen atoms are present, α-hydrogen elimination takes place from the alkyl intermediate.

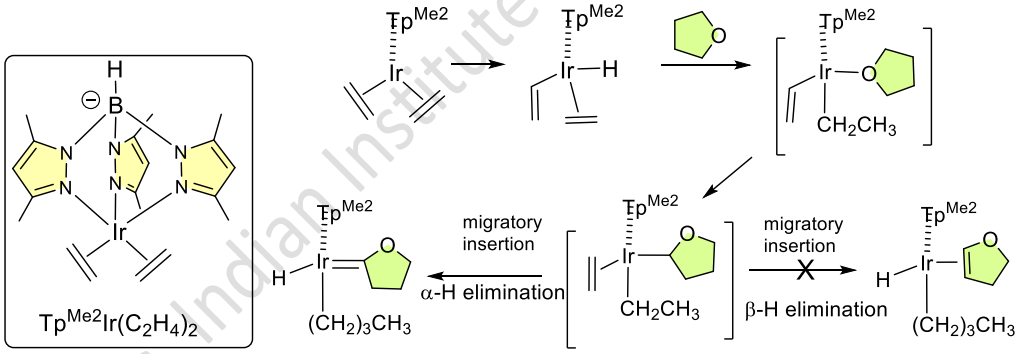


Figure 31. Reaction showing a preference for α-hydride elimination [51]

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