CHAPTER IV

ACTIVATION OF C–H BONDS BY LOW-VALENT METAL COMPLEXES ("THE ORGANOMETALLIC CHEMISTRY")

In the end of the 1960s the leading specialist in homogeneous catalysis Jack Halpern wrote [1]: "to develop a successful approach for activation of C–H bonds, particularly saturated hydrocarbons, this problem being at present one of the most important and challenging in the entire field of homogeneous catalysis". By that time, a large quantity of data had accumulated, indicating the possibility of activating alkanes by transition metal complexes, where the alkane molecule reacts directly with the metal center by entering into the coordination sphere of metal complexes to form intermediately alkyl derivatives.

Indeed, it had been known, that

(i) a large number of complexes react with various compounds, containing carbon–hydrogen bonds, particularly with aromatic hydrocarbons, with rupture of the C–H bond and the formation of a metal-carbon fragment;

(ii) an aliphatic carbon-hydrogen bond can be activated if it is present in a ligand attached to a metal center in the complex;

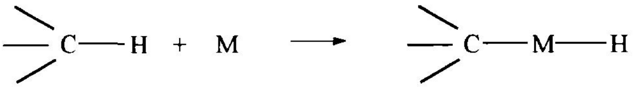
(iii) reactions of alkanes on the surface of metals or their compounds, which undoubtedly involve the C–H bond cleavage in an alkane molecule, also indicate the possibility of such reactions with metal complexes in homogeneous solutions, at least for polynuclear cluster complexes containing several metal atoms;

(iv) the reactions of alkanes in homogeneous solutions with electrophilic oxidizing agents containing metal in a high oxidation state sometimes suggest the possibility of direct participation of the metal ion in the reaction with the alkane to form a metal-carbon bond.

Starting from analogies with the activation of other compounds that do not contain any **π-bonds**, in particular dihydrogen:

$$H{-}H + M \longrightarrow H{-}M{-}H$$

it was possible to assume that the initial alkane reaction with compounds of transition metals in a low oxidation state would be an oxidative addition of the C-H bond to a metal center, M, according to the general equation:



Numerous processes of such type affording organyl hydride metal complexes became known in the end of 1970s and in 1980s. Many processes discovered at that time occur via intermediate formation of organyl hydrides. In **σ-organyl** hydride complexes of formula **σ-R–M–H**, the organyl group R can be alkyl, aryl, acyl, vinyl etc. Oxidative addition of simple alkanes gives rise to the formation of alkyl hydride complexes **(R = alkyl)**

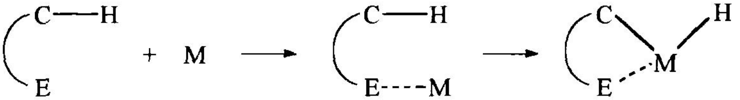
The reactions between C–H compounds and metal complexes in a low oxidation state, which produce organometallic derivatives (i.e., compounds containing direct carbon–metal bonds) will be considered in this chapter. In some cases the intermediate **σ-organyl** and organyl hydride complexes can not be isolated, although the evidence for their formation is obtained. Reactions of such type (often-catalytic processes) will be considered in this chapter.

IV.1. FORMATION OF σ-ORGANYL HYDRIDE COMPLEXES

In reactions between a C–H compound, RH, and a metal complex, M, to produce R–M–H, the oxidation state of a metal ion is changed and it is two units higher in the organyl hydride than it was in the initial metal compound. Alkanes, arenes, alkenes and monosubstituted acetylenes enter into such processes. The reactions frequently occur in solution at room temperature, but sometimes heating is required. Certain reactions are stimulated by irradiation. An increase in temperature or light is essential for the abstraction of several ligands from the initial complex and the formation of a coordinatively unsaturated species capable of effecting the oxidative addition of the C–H compound to itself.

IV.1.A. CYCLOMETALATION

Due to the chelate effect, the *intra*molecular cleavage of the C–H bond occurs much more readily than *inter*molecular activation and gives rise to a more stable σ-organyl hydride complex. The general schematic equation of this cyclometalation is depicted as follows:

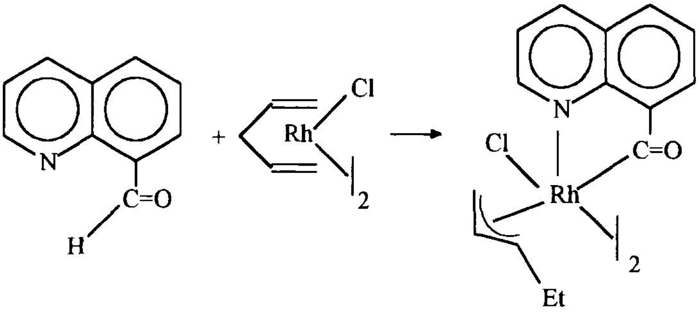


Here E is a donor atom, e.g., N, P, As etc.

A book [2] and reviews [3] have been devoted to the cyclometalation reaction with participation of metal complexes in a low oxidation state. Many examples of cyclometalation into *ortho*-position of monosubstituted aromatic ring are known, some of them are presented in Scheme IV. 1 [4]. Sometimes the cyclometalation can occur with splitting either at an aryl or methyl group in the same molecule of a ligand. Thus the reaction of 6-R-2,2'-bipyridine (R = CH_2Ph, CHMePh, CMe_2Ph, CH_2Me, CMe_3, CH_2CMe_3) with $HAuCl_4$ gives the cyclometalated species which arise from direct activation of a C–H bond either of a phenyl or a methyl substituent [5], Cyclometalation reactions of heterocyclic aromatic ligands are shown in Scheme IV.2 [6]. Not all of the cyclometalation reactions shown in these schemes proceed via oxidative addition mechanism.

The most interesting (from the point of view of alkane activation) cyclometalation reactions of sp^3-C–H bonds are demonstrated in Scheme IV.3 [7] (in addition to references [7] depicted in this scheme, see also [8]). Scheme IV.4 gives some examples of the cyclometalation of vinylic C–H bonds, occurring with the splitting of bonds between carbon and some elements, and other special cases [9]. For cyclometalation of the C–H bonds at the C=C bonds, see also [10a,b].

The activation of the aldehyde C–H bond gives an acyl complex [10c]:

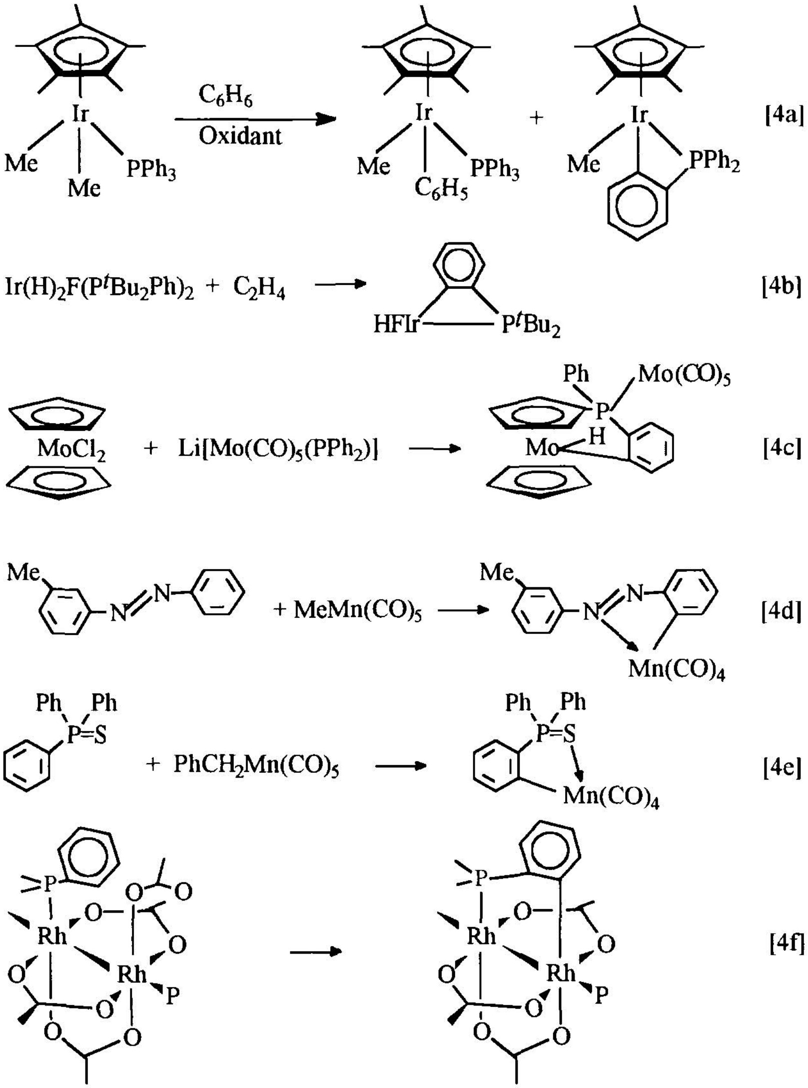


In some cases, the functionalization of C–H compounds involves the cyclometalation stage. For example, **$CoH_3(PPh_3)_3$** catalyzes the regiospecific double and monoinsertion of tolan into the *ortho-C–H* bonds of 1,2-diarylazenes (Scheme IV.5) [11a] and **L_3RhCl** catalyzes the alkylation of 2-vinylpyridines with alkenes (Scheme FV.6) [lib]. Carefully investigated cyclopalladation (orthopalladation) reactions which proceed most likely as electrophilic substitution, as well as cyclometalation with complexes of metals in a high oxidation state will be considered in Chapter VIII.

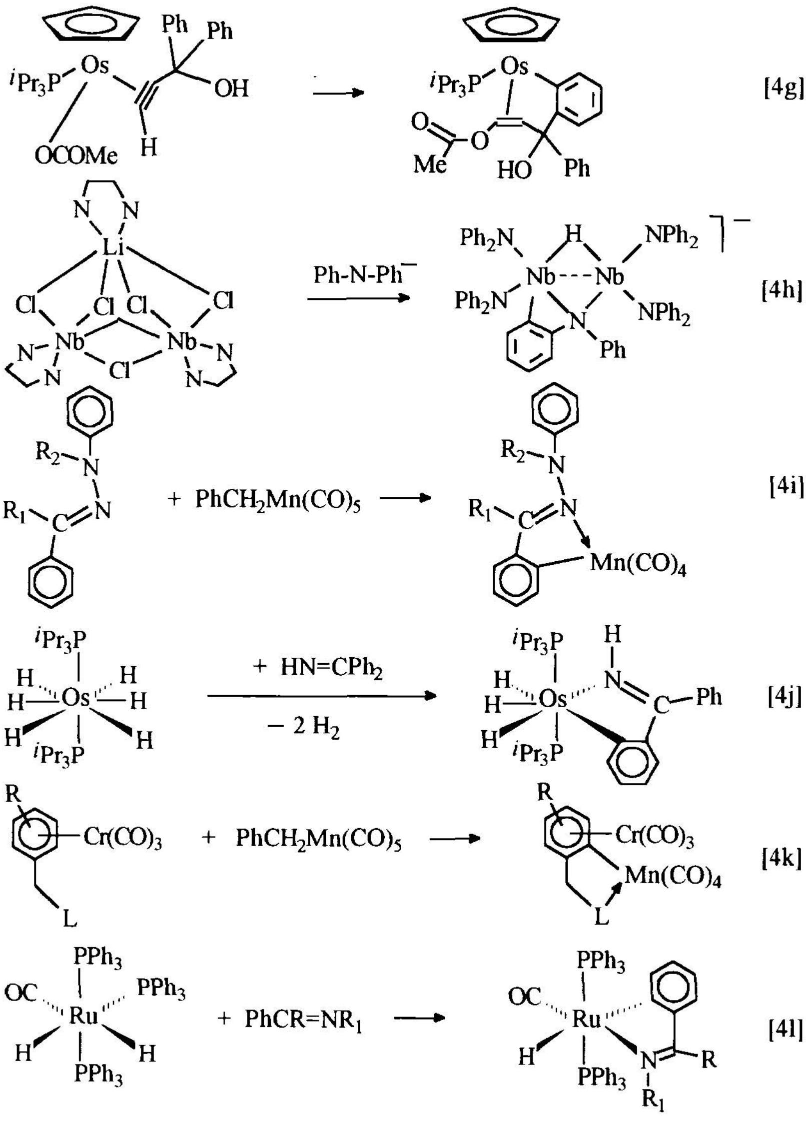
IV. 1.B. INTERMOLECULAR OXIDATIVE ADDITION

The **σ-organyl** complexes formed in oxidative addition [12] of alkanes, arenes as well as alkenes and monosubstituted acetylenes can be fairly stable and in many cases have been isolated. Thus, upon heating or photolysis, the complexes **Cp_2WH_2**, **Cp_2WCO**, and **Cp_2WHCH_3** give rise to a coordinatively unsaturated tungstocene species **Cp_2W**, which readily combines with aromatic or alkylaromatic hydrocarbons [13].

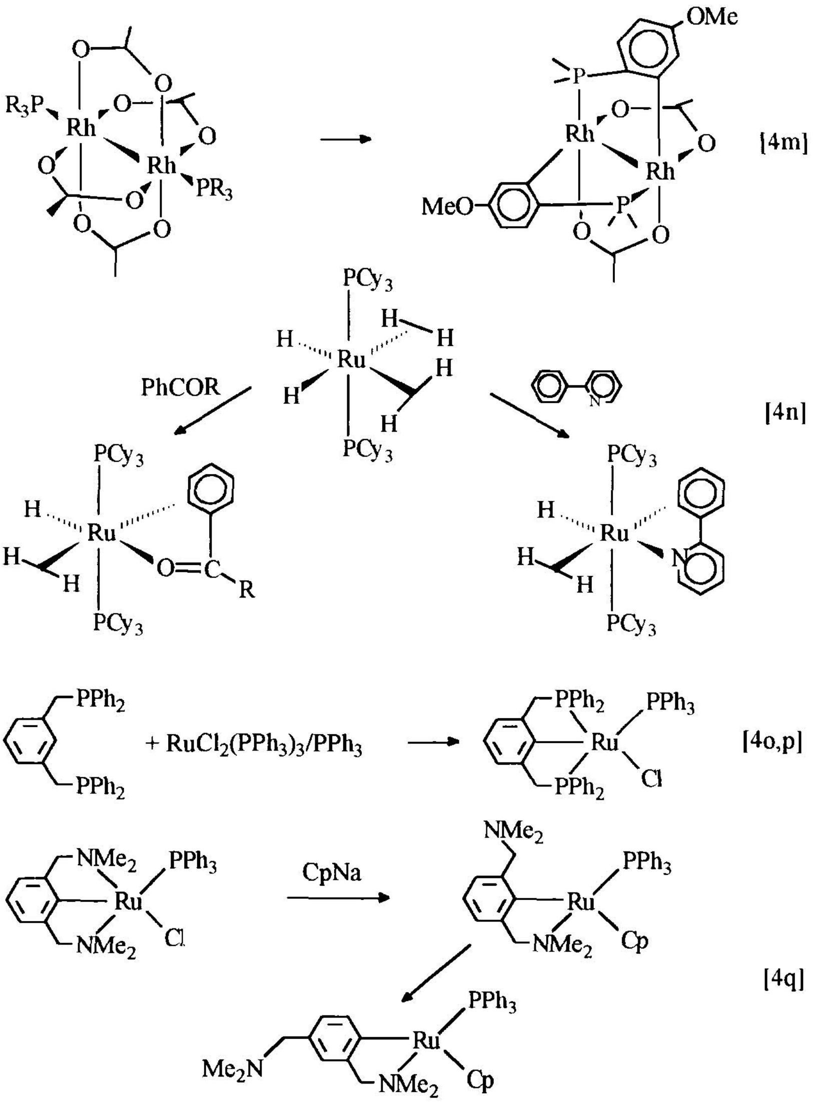
In the reaction with toluene, the products are **$Cp_2W(H)C_6H_4CH_3$** and **$Cp_2W(CH_2Ph)C_6H_4CH_3$**, i.e., tungsten is inserted both in a C–H bond in the aromatic ring and in a C–H bond at sp^3**-hybridized** carbon atom. However, cyclohexane and neopentane do not give rise to insertion products in this instance.



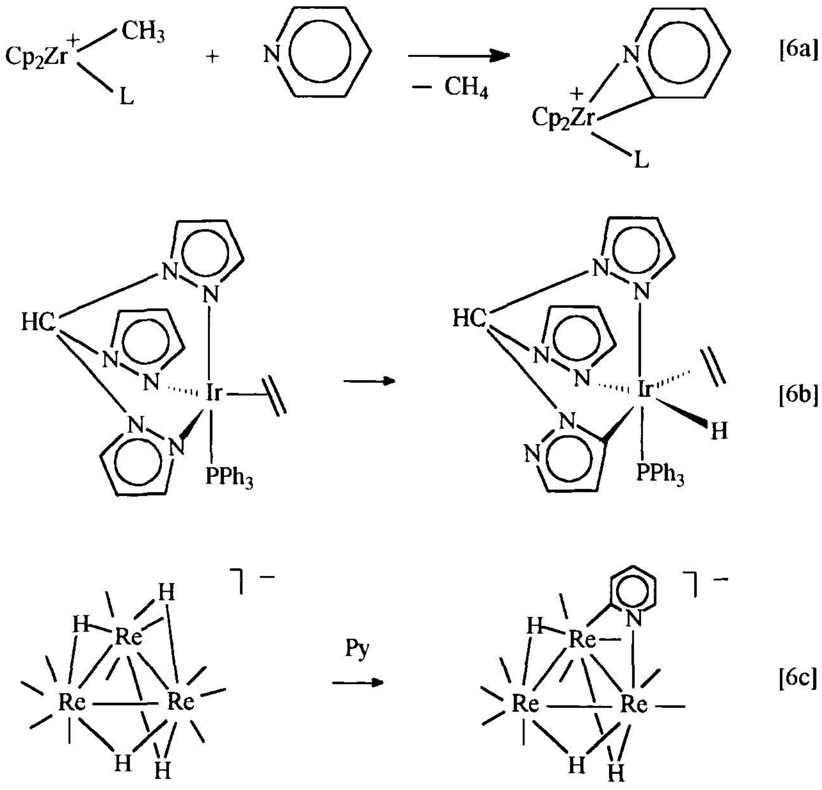
Scheme IV.1 (part 1). Examples of the cyclometalation of aromatic compounds by metal complexes in a low oxidation state. Reference numbers are in brackets.



Scheme IV.1 (part 2). Examples of the cyclometalation of aromatic compounds by metal complexes in a low oxidation state. Reference numbers are in brackets.

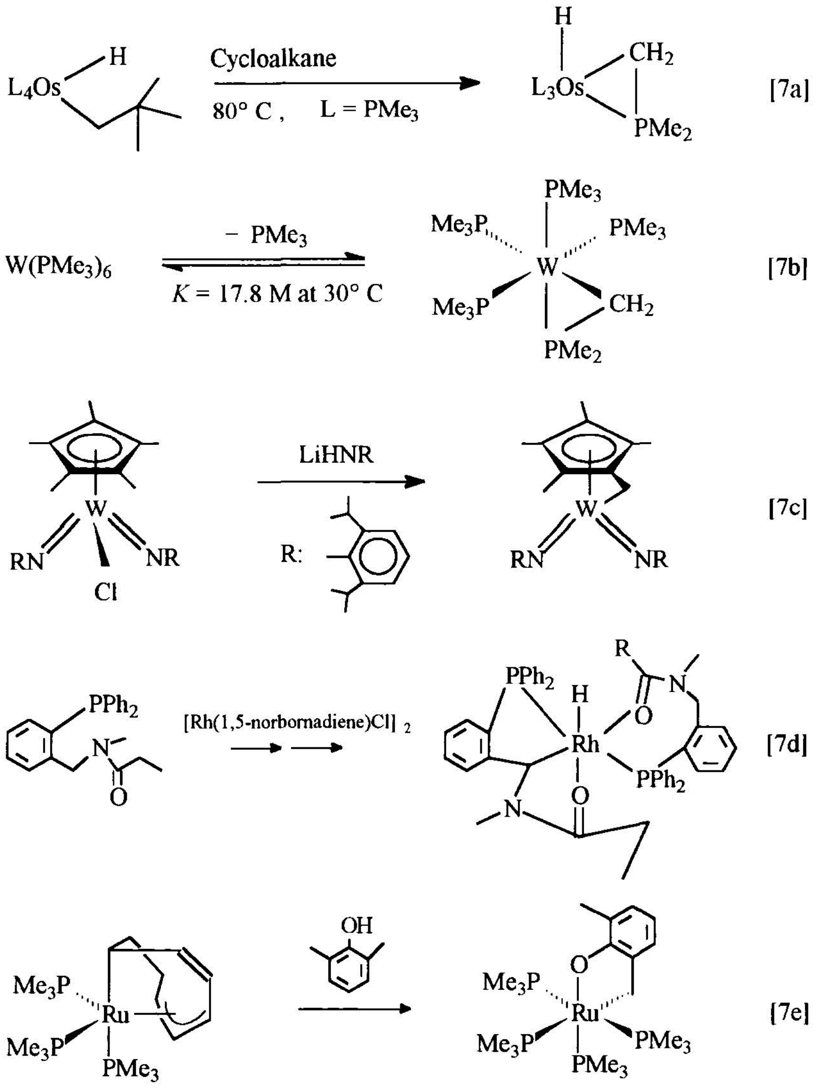


Scheme IV.1 (part 3). Examples of the cyclometalation of aromatic compounds by metal complexes in a low oxidation state. Reference numbers are in brackets.

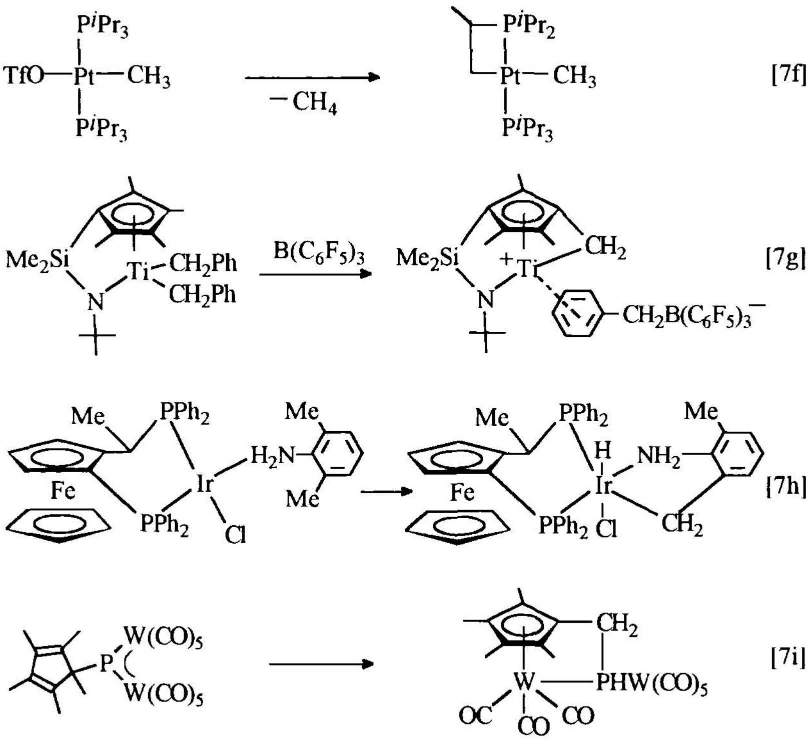


Scheme IV.2. Examples of the cyclometalation of aromatic heterocycles by metal complexes in a low oxidation state. Reference numbers are in brackets.

The oxidative addition of alkanes with formation of alkyl hydride complexes was first demonstrated directly in studies using indium complexes [14]. Thus the iridium dihydride derivative $Cp^*Ir(H)_2PMe_3$ (Cp^* = pentamethylcyclopentadienyl) after irradiation in solution in cyclohexane or neopentane, produces the complexes $Cp^*(PMe_3)Ir(H)(C_6H_{11})$ and $Cp^*(PMe_3)Ir(H)CH_2CMe_3$ in a satisfactory yield. Other saturated hydrocarbons and benzene also readily add to an iridium complex.



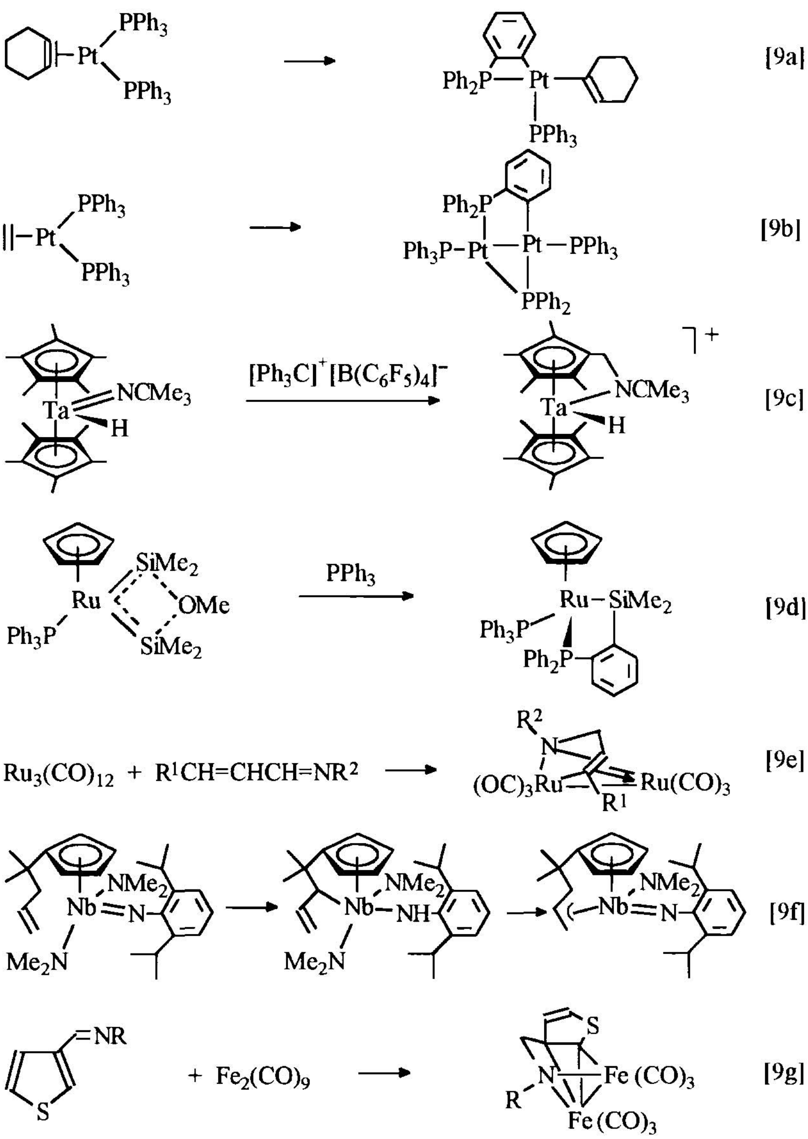
Scheme IV.3 (part 1). Examples of the cyclometalation reactions between metal complexes in a low oxidation state and aliphatic C–H bonds. Reference numbers are in brackets.



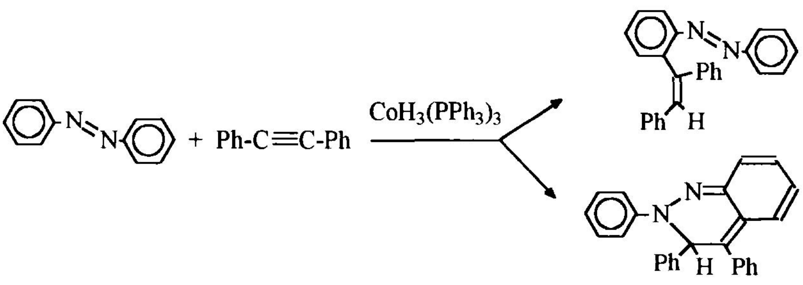
Scheme IV.3 (part 2). Examples of the cyclometalation reactions between metal complexes in a low oxidation state and aliphatic C–H bonds. Reference numbers are in brackets.

By treatment with $CHBr_3$ at −60 °C, alkyl hydride complexes were converted into the more stable derivatives Cp*(PMe$_3$)Ir(Br)R. Irradiation of Cp*Ir(H)$_2$PMe$_3$ in CMe$_4$+C$_6$D$_{12}$ mixture led to the formation of Cp*(PMe$_3$)-Ir(H)CH$_2$CMe$_3$ and Cp*(PMe$_3$)Ir(D)C$_6$D$_{11}$ with very small admixtures of cross-addition products.

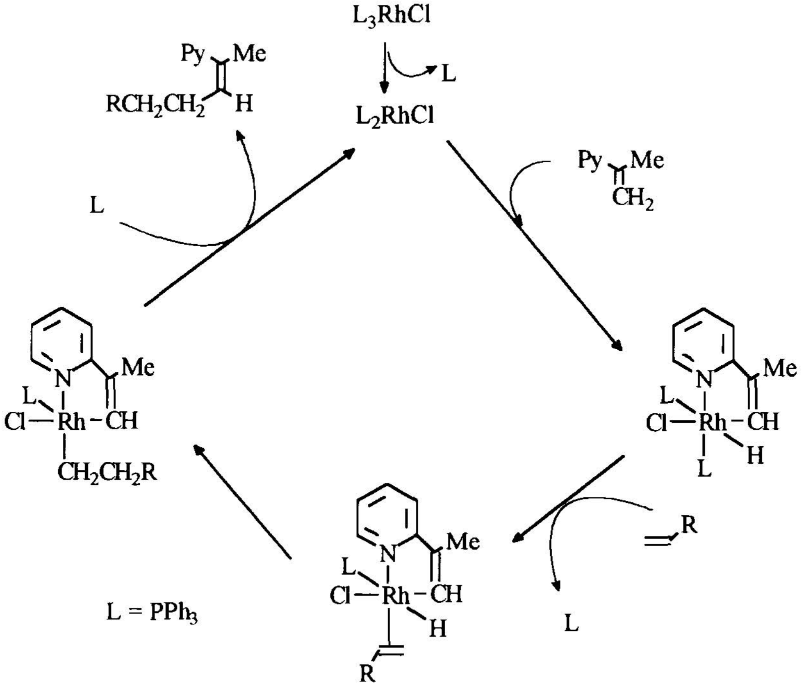
The reaction of alkanes with the complex Cp*Rh(H)$_2$PMe$_3$ takes place analogously under irradiation at a temperature below −30 °C [14b]. The selectivity (both substrate and positional selectivity) proved to be much higher for the rhodium complex than for the iridium one.



Scheme IV.4. Some other examples of the cyclometalation reactions. Reference numbers are in brackets.



Scheme IV.5. The insertion of tolan into the *ortho*-C–H bonds of 1,2-diarylazenes.



Scheme IV.6. The alkylation of 2-vinylpyridines with alkenes.

When the cyclohexyliridium hydride complex **IV-1** or the n-pentyliridium hydride derivative **IV-2** was heated for 50 h at 140 °C in a mixture of 91.5 % of cyclohexane and 8.5 % of *n*-pentane, the following equilibrium was established:

$$\underset{\textbf{IV-1}}{\mathrm{Cp^*(PMe_3)Ir(H)C_6H_{11}}} + \mathrm{CH_3(CH_2)_3CH_3} \overset{K}{\rightleftharpoons}$$

$$\rightleftharpoons \underset{\textbf{IV-2}}{\mathrm{Cp^*(PMe_3)Ir(H)(CH_2)_4CH_3}} + \mathrm{C_6H_{12}} \qquad \text{(IV.1)}$$

The ratio **IV-2** : **IV-1** was 1.0 ± 0.1. Hence the constant

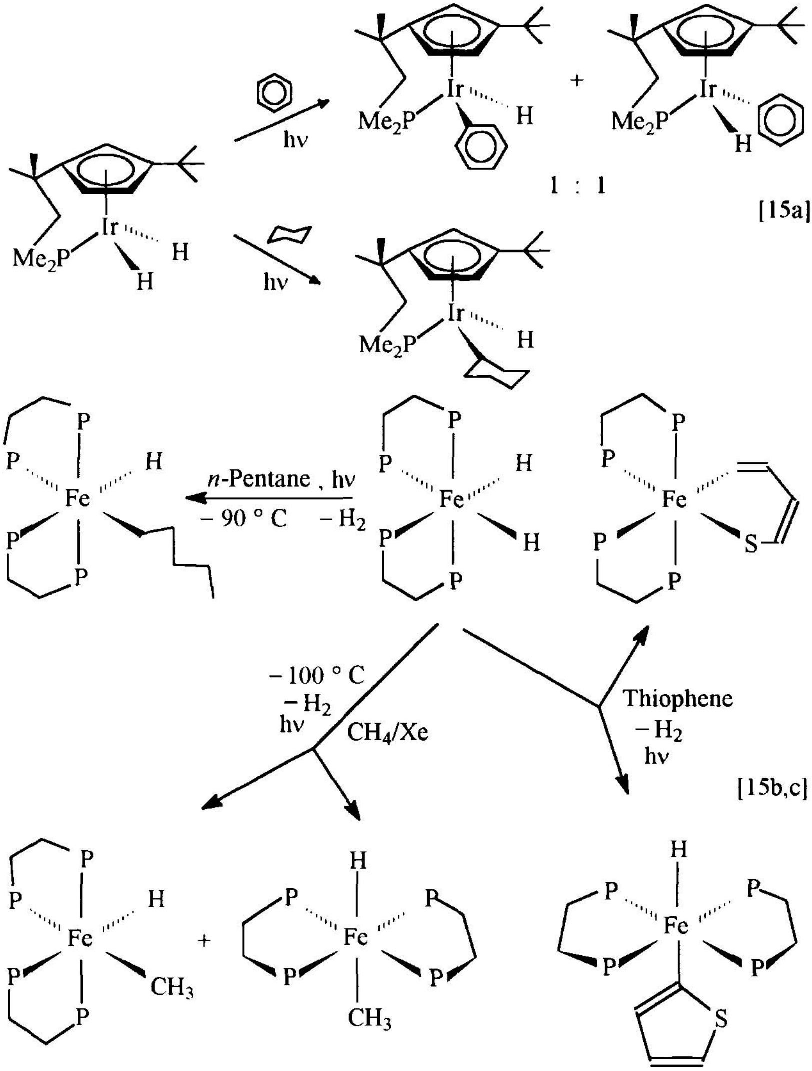
$$K = [\textbf{IV-2}][\mathrm{C_6H_{12}}]/[\textbf{IV-1}][n\text{-}\mathrm{C_5H_{12}}] = 10.6,$$

which corresponds to $\Delta G^\circ = -2.0$ kcal/mol. It has been suggested that the entropy changes in the reaction are small and, assuming that the CH_2 and CH_3 bond energies in cyclohexane and *n*-pentane are 94.5 and 98 kcal mol^{-1} respectively, we can find that the energy of the M-C bond in the complex **IV-2** is higher by 5.5 kcal mol^{-1} than in the complex **IV-1**. It follows from the estimates that the methyliridium hydride complex $Cp^*(PMe_3)Ir(H)CH_3$ should also be very thermodinamically stable. It was obtained in 58% yield on heating a solution of the complex **IV-1** in cyclooctane in the presence of methane [14b].

A large number of reactions are known in which, as in reactions just discussed, a coordinatively unsaturated species is formed by elimination of molecular hydrogen or a molecule RH (R = alkyl, aryl etc.). Examples of reactions that occur according to equation (IV.2) [15, 16] are demonstrated in Scheme IV.7.

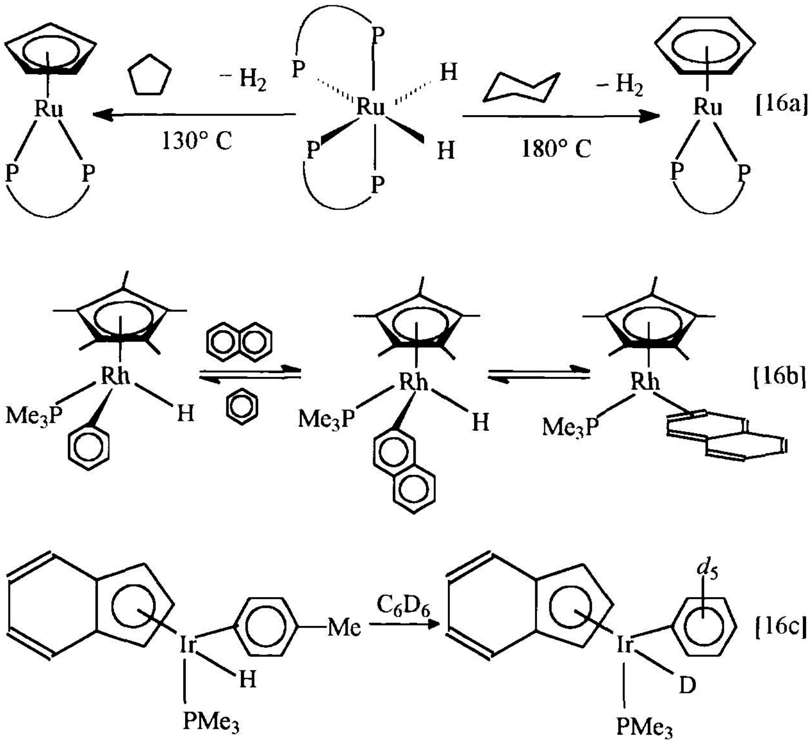
$$\mathrm{R{-}M{-}H} \xrightarrow{-\mathrm{RH}} \mathrm{M} \xrightarrow{+\mathrm{R'H}} \mathrm{R'{-}M{-}H} \qquad \text{(IV.2)}$$

Here both R and R' are H, alkyl, aryl etc.

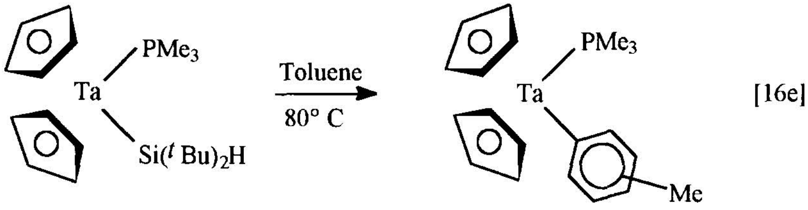


Ligand = $Me_2PCH_2CH_2PMe_2$

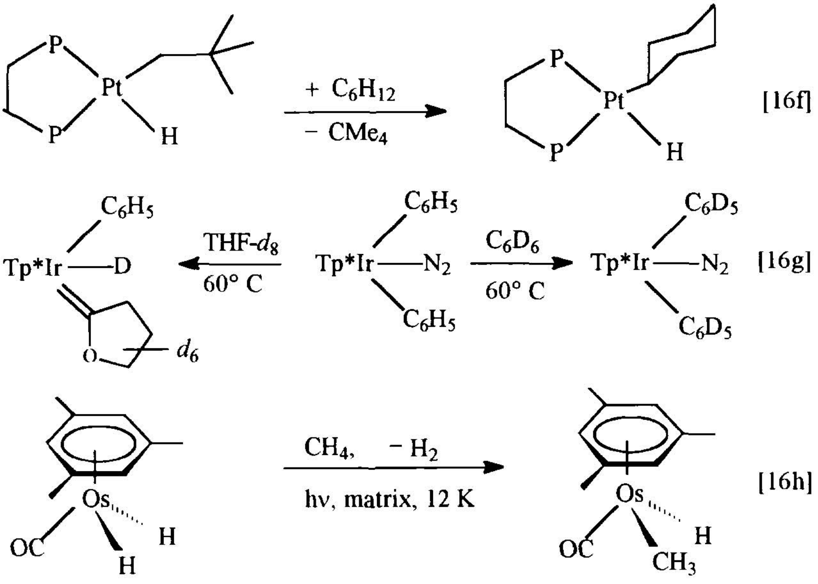
Scheme IV.7 (part 1). Reductive elimination of H–H or R–H from metal complexes followed by oxidative addition of C–H compounds. Reference numbers are in brackets.



$(Me_3P)RhMe + C_6H_5Me \longrightarrow (Me_3P)RhC_6H_4Me + MeH$ [16d]



Scheme IV.7 (part 2). Reductive elimination of H–H or R–H from metal complexes followed by oxidative addition of C–H compounds. Reference numbers are in brackets.

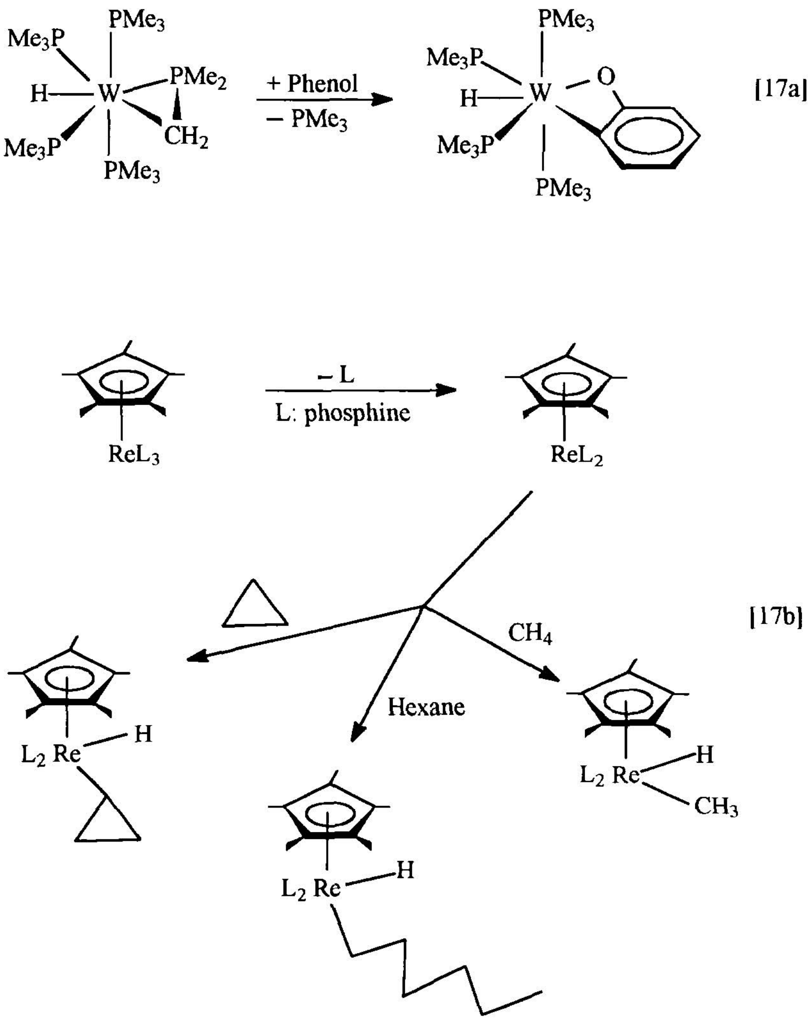


Scheme IV.7 (part 3). Reductive elimination of H–H or R–H from metal complexes followed by oxidative addition of C–H compounds. Reference numbers are in brackets.

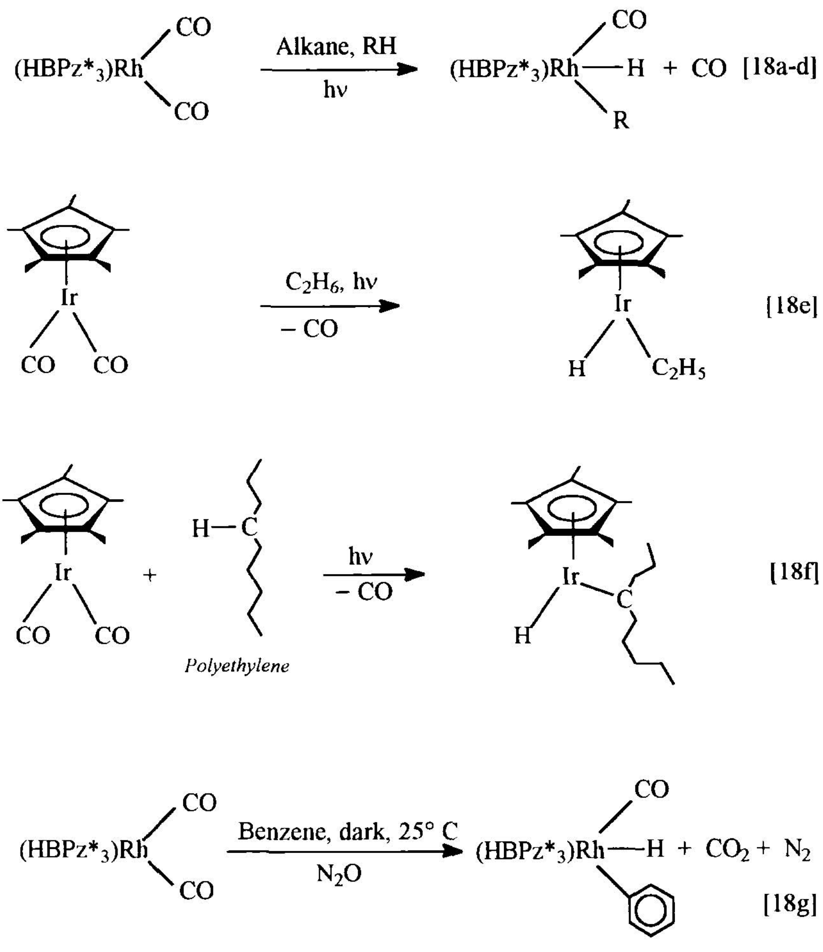
A coordinatively unsaturated species capable of adding RH can also be generated by extrusion from such neutral ligands as phosphine (Scheme IV.8) [17], carbon monoxide (Scheme IV.9) [18], olefin and, as well as, some other ligands (Scheme IV.10) [19].

IV.1.C. FORMATION OF SOME OTHER PRODUCTS

Examples of oxidative addition coupled with some other transformations were mentioned in previous sections. Here we discuss other reactions of oxidative addition, which are rather complicated and do not lead to the formation of organyl hydrides.

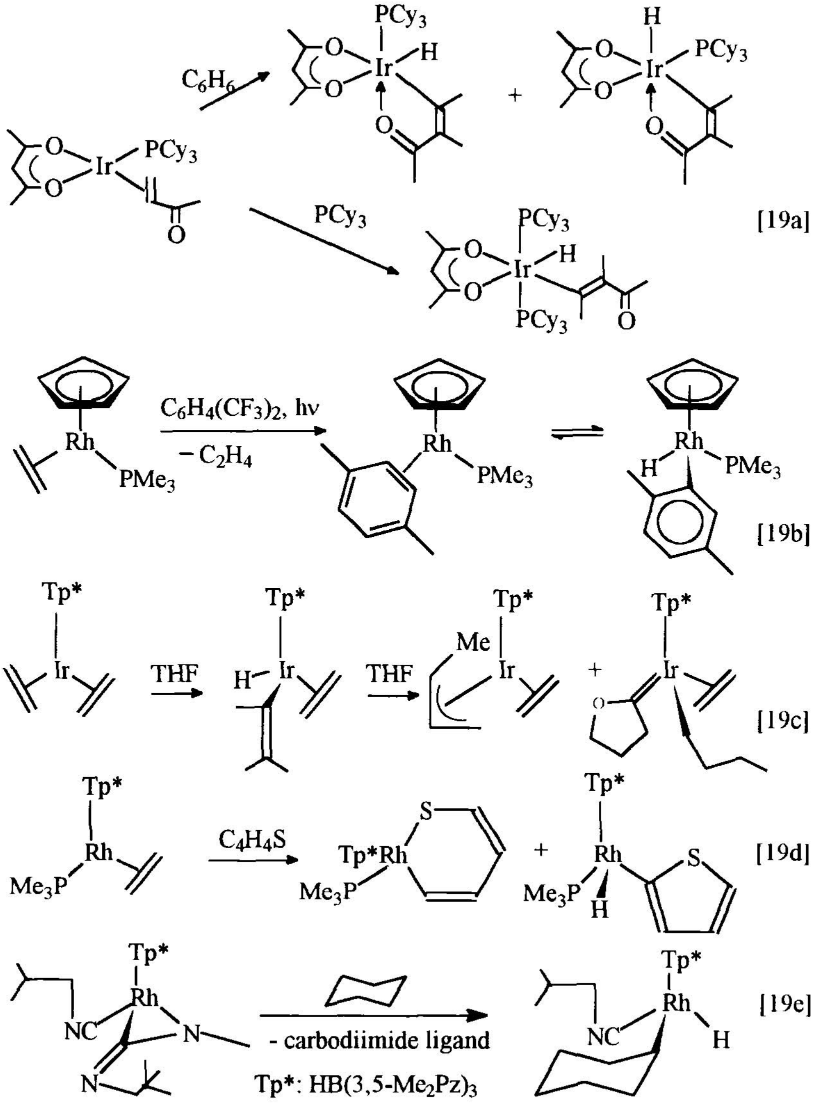


Scheme IV.8. Oxidative addition of C–H compounds to coordinatively unsaturated species generated by extrusion of phosphines. Reference numbers are in brackets.

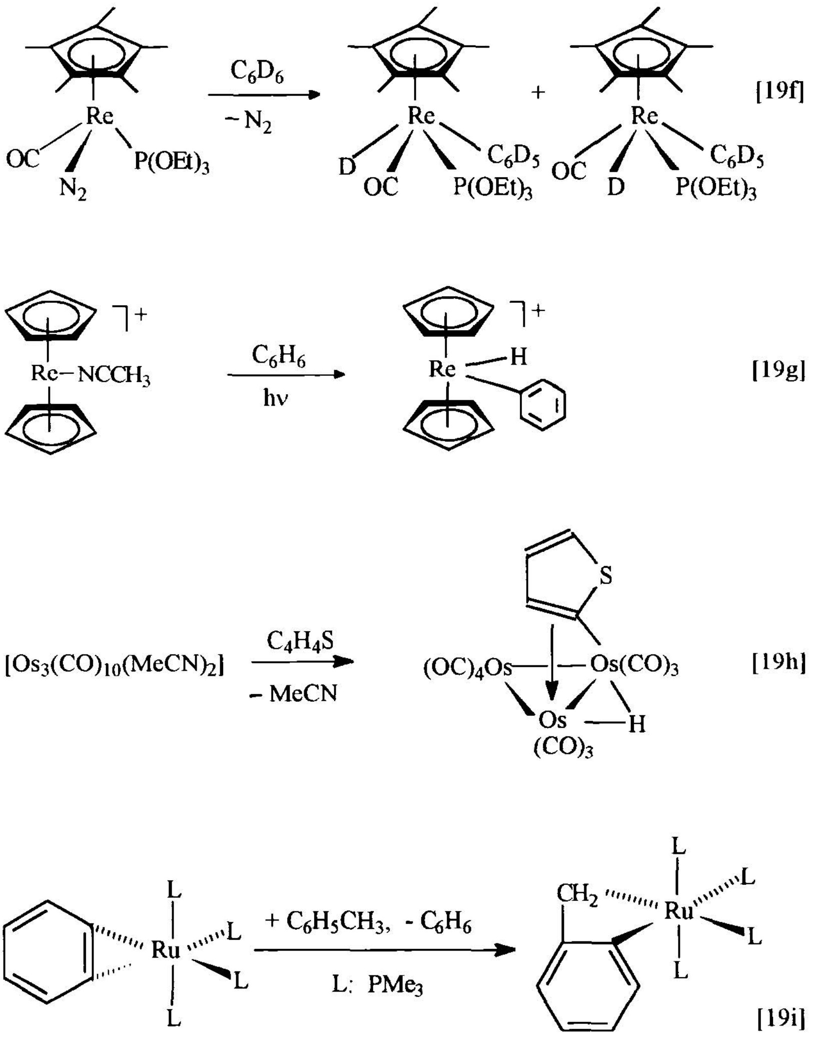


$$\textit{trans}\text{-RhCl(CO)(PMe}_3)_2 + C_6H_6 \xrightarrow{h\nu} \text{(Ph)(H)RhCl(CO)(PMe}_3)_2 \text{ [18h]}$$

Scheme IV.9. Oxidative addition of C–H compounds to coordinatively unsaturated species generated by extrusion of CO. Reference numbers are in brackets.



Scheme IV.10 (part 1). Oxidative addition of C–H compounds to coordinatively unsaturated species generated by extrusion of olefins and some other ligands. Reference numbers are in brackets.

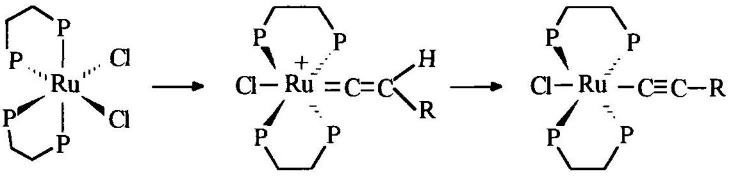


Scheme IV.10 (part 2). Oxidative addition of C–H compounds to coordinatively unsaturated species generated by extrusion of olefins and some other ligands. Reference numbers are in brackets.

Sometimes thermal and photochemical activation can result in the formation of different products. For example, heating the solution of the ethylrhodium carbonyl complex **$RhHBPz^*_3(CO)(C_2H_4)$ (Pz^* = 3,5-dimethylpyrazole)** in benzene entails the elimination of the ethylene **π-ligand** and the formation of phenylrhodium hydride (complex **IV-3** in Scheme IV. 11) [20a]. On irradiation of this solution, the hydride ligand adds not to the metal atom but to the ethylene molecule, which results in the appearance of an **σ-ethyl** group in the complex **IV-4** [20b].

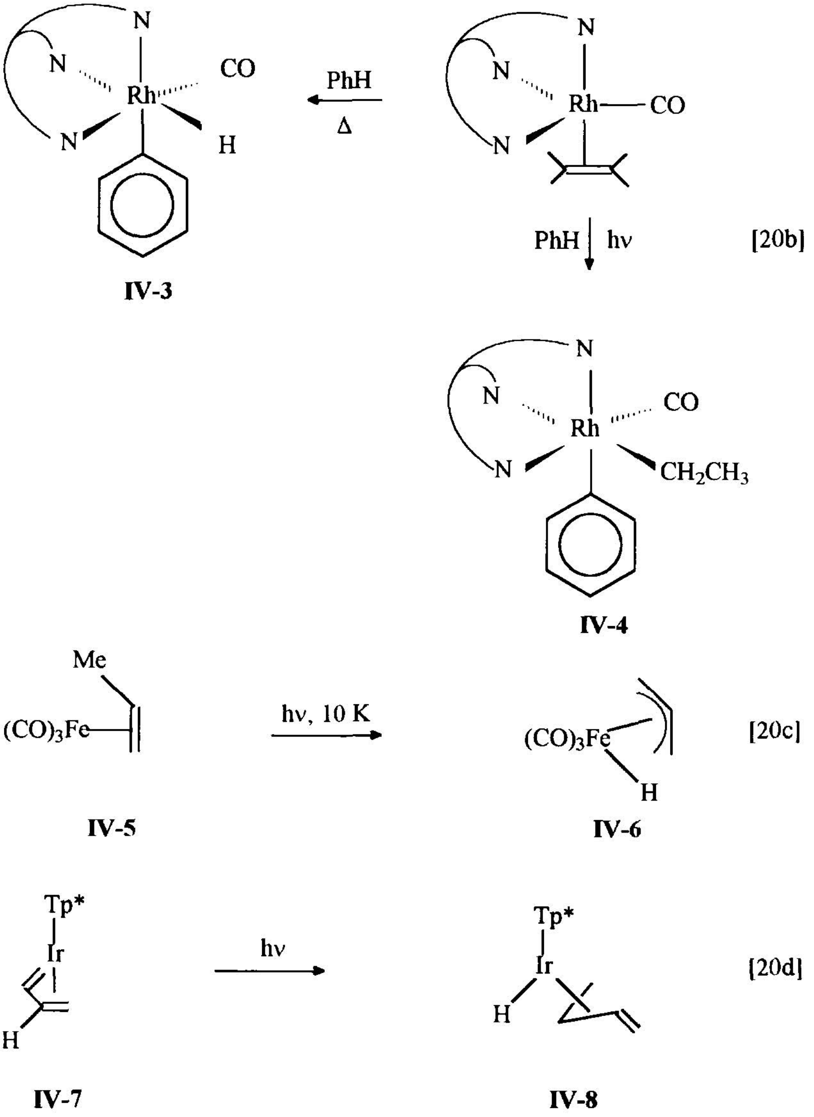
In some cases a coordinatively unsaturated species and then a product of oxidative addition can be formed via a rearrangement of the complex molecule without elimination of any particles (e.g., olefin complex **IV-5** may be converted into the **π-allyl** hydride derivative **IV-6** in Scheme IV. 11 [20c]). Analogously, photolysis of butadiene indium complex **IV-7** gives rise to the formation of a hydrido-allyl isomer **IV-8** [20d].

Transition metal complexes readily cleave the C–H bonds not only in arenes and alkanes, as described above, but can also activate vinylic C–H bonds [21] (Scheme IV. 12) and the C–H bonds in acetylenes [22] (Scheme IV. 13).

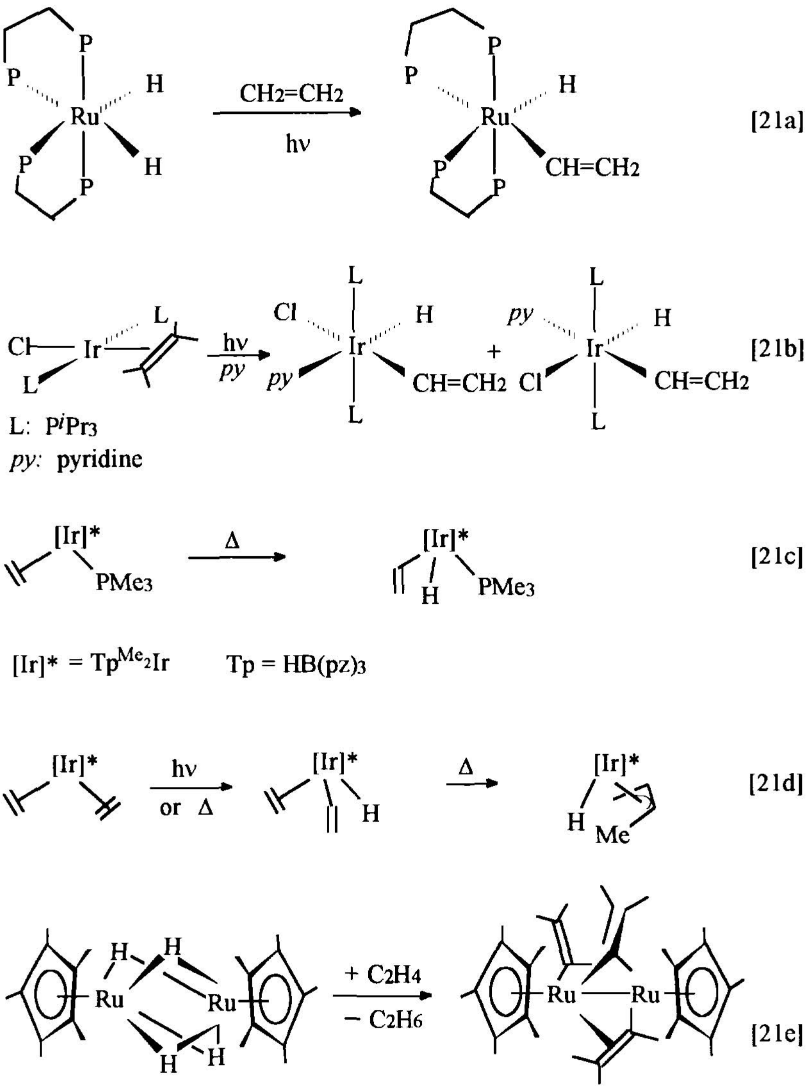


IV-9 **IV-10** **IV-11**

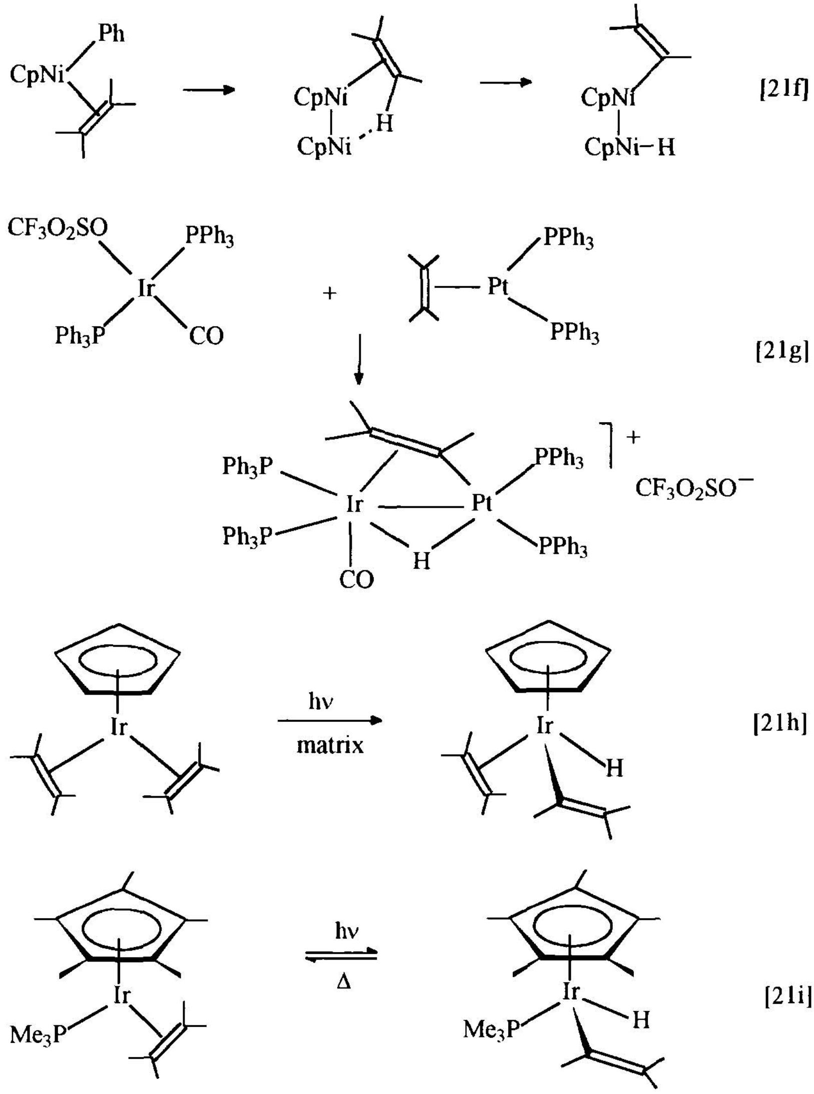
It is important to note that some reactions leading formally to **σ-vinyl**- and **σ-alkynyl** complexes of transition metals can be produced via different mechanisms. For example, the reaction of the ruthenium complex **IV-9** with terminal alkynes gives rise to the formation of vinylidene-metal complexes **IV-10,** which can be converted to the alkynyl-ruthenium derivatives **IV-11** by the action of triethylamine [23].



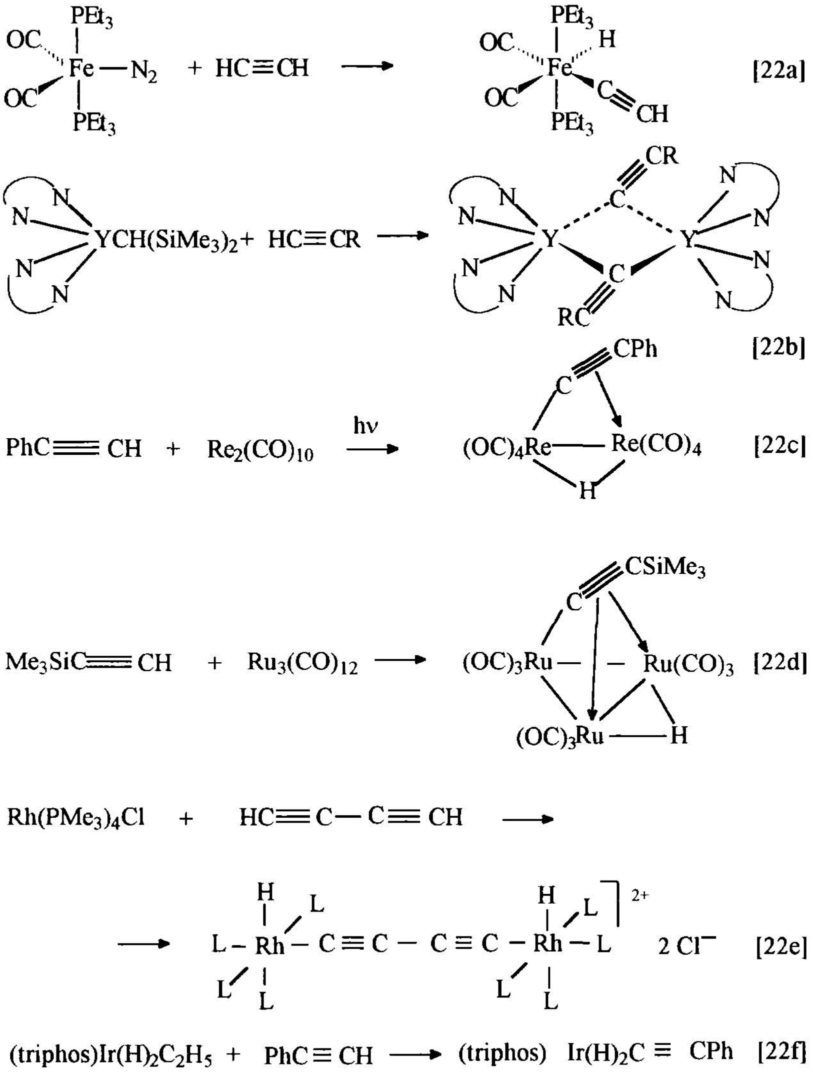
Scheme IV.11. Oxidative addition reactions followed by addition of hydride to olefin and by the formation of allyl complexes. Reference numbers are in brackets.



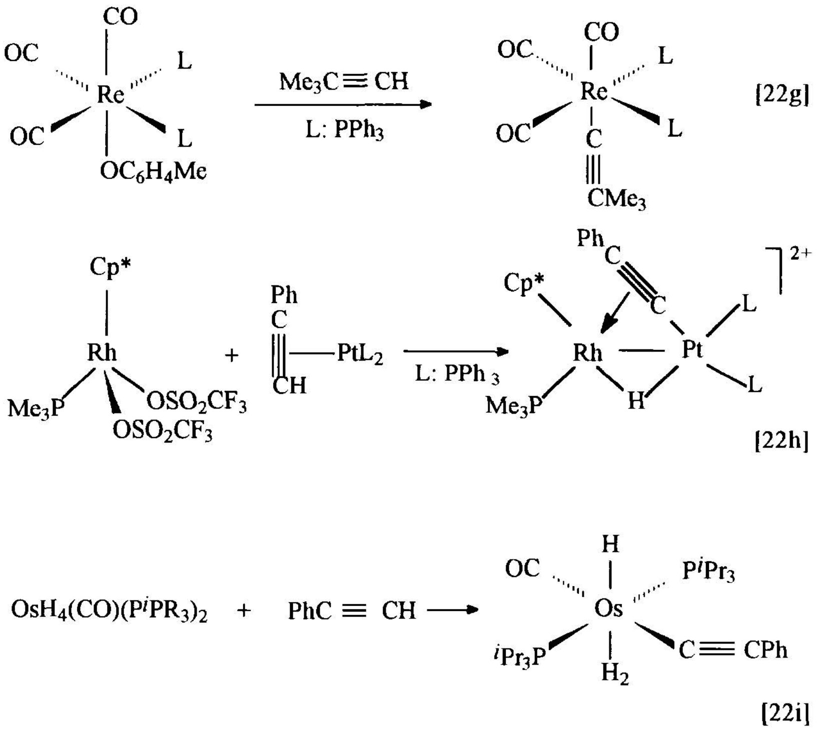
Scheme IV.12 (part 1). Activation of vinylic C–H bonds by metal complexes in a low oxidation state via an oxidative addition mechanism. Reference numbers are in brackets.



Scheme IV.12 (part 2). Activation of vinylic C–H bonds by metal complexes in a low oxidation state via an oxidative addition mechanism. Reference numbers are in brackets.

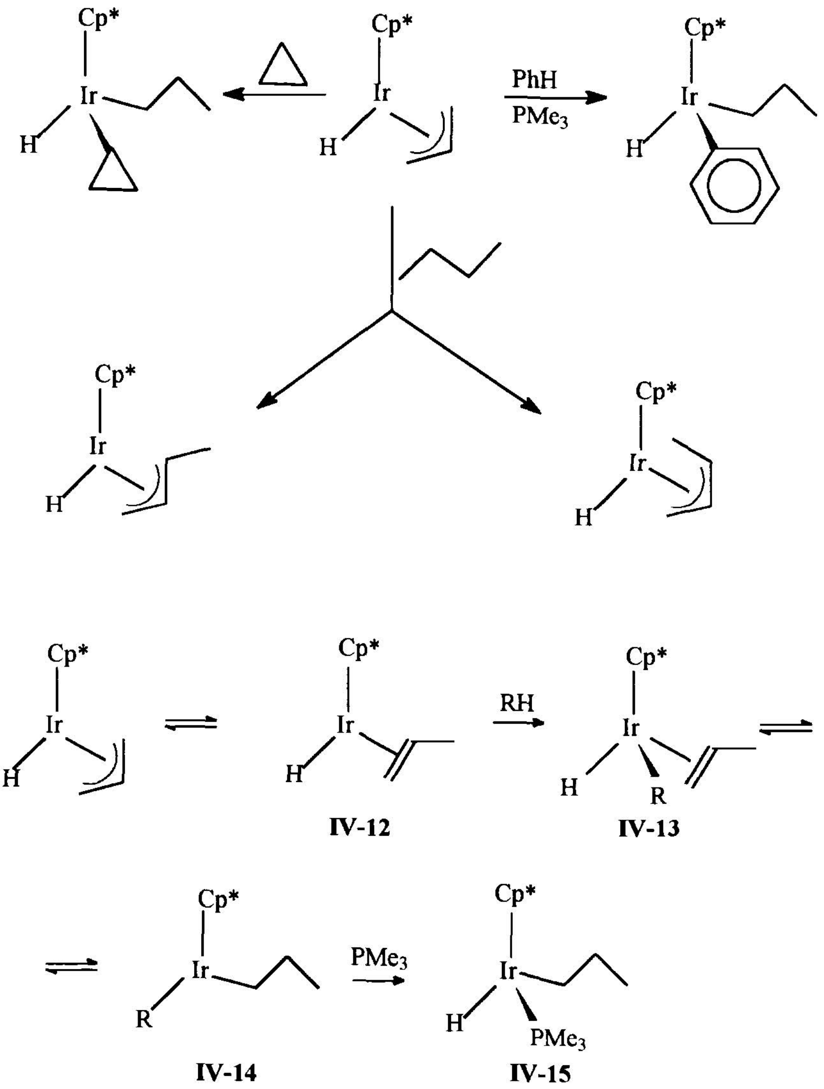


Scheme IV.13 (part 1). Activation of C–H bonds in acetylenes by metal complexes in a low oxidation state via an oxidative addition mechanism. Reference numbers are in brackets.



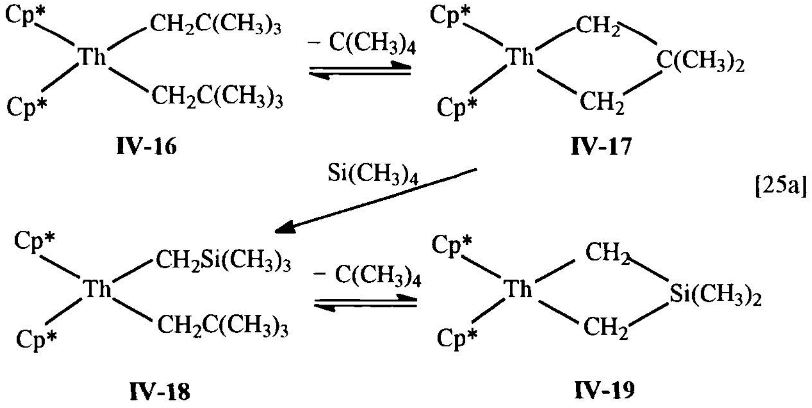
Scheme IV.13 (part 2). Activation of C–H bonds in acetylenes by metal complexes in a low oxidation state via an oxidative addition mechanism. Reference numbers are in brackets.

Iridium **π-allylhydride** complex reacts with various C–H compounds (Scheme 14) [24], oxidative addition of benzene and cyclopropane occurring in the presence of phosphine and giving rise to the formation of products of the hydrogen atom migration from the substrate to allyl ligand. The proposed mechanism includes addition of hydride atom to allyl ligand as the first stage (to produce coordinatively unsaturated species **IV-12** in Scheme IV-14) followed by usual oxidative addition of RH. After this **π–σ-rearrangement** of olefin-hydride complex **IV-13** occurs to give **σ-alkyl** derivative **IV-14**. The last stage is addition of phosphine yielding coordinatively saturated stable complex **IV-15**.



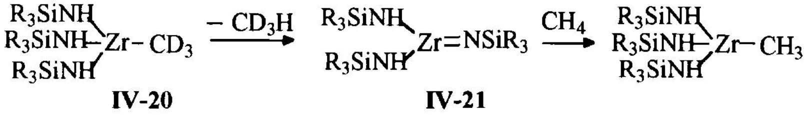
Scheme IV.14. Reactions of the iridium π-allylhydride complex with C–H compounds.

When a cyclohexane solution of thorium complex **IV-16** (Scheme IV-15) containing neopentyl ligands is heated one of the ligands can be eliminated and cyclometalation of a remaining alkyl groups proceeds [25a]. Metallacycle **IV-17** thus formed metalates intermolecularly tetramethylsilane. The reaction does not stop when compound **IV-18** is formed, and cyclometalated complex **IV-19** can be obtained. The thorium complex also readily activates methane. It should be noted that formally thorium is not a low-valent ion in these reactions.

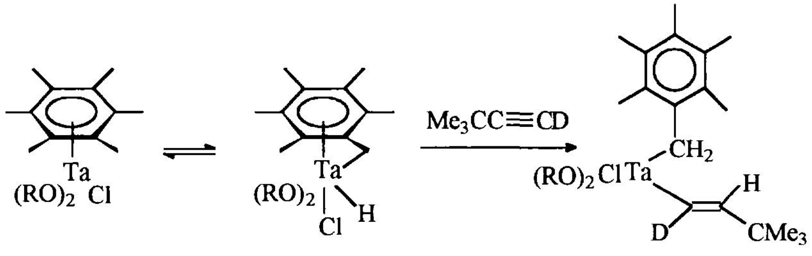


Scheme IV.15. Reactions of the thorium complex.

The hydrogen atom from alkane cannot add to the metal ion but can add to a ligand instead. For example, heating a solution of complex **IV-20** and methane in deuterated cyclohexane leads to the replacement of the CD_3 group by methyl from methane and gives also CD_3H [25b]. Species **IV-21** is assumed to be an intermediate in this process.



The reaction of the tantalum hexamethyl complex **IV-22** with deuterated 3,3-dimethyl-1-butyne proceeds as an intramolecular oxidative addition and gives rise to the **σ-organyl** complex **IV-23** [25c].



IV-22

IV-23

A **$Cp^*Ir(PMe_3)(CH_3)^+$** complex reacts at low temperatures with an alkane, RH, to yield the **σ-alkyl** derivative **$Cp^*Ir(PMe_3)(R)^+$** and methane [26a,b]. Two different mechanisms were proposed for this metathesis:

(i) formation of a four-center adduct between the methyl complex and RH, and

(ii) oxidative addition followed by the reductive elimination of a methane molecule.

Theoretical calculations support a low-energy oxidative addition mechanism [26c]. Reaction of the unsolvated cationic complex **$Cp^*Ir(PMe_3)(CH_3)^+$** with pentane, cyclohexane or benzene in the gas phase also gives **$Cp^*Ir(PMe_3)(R)^+$**as the product. However, a mechanistic investigation of this process by electrospray tandem spectrometry has demonstrated that neither the oxidative addition-elimination mechanism nor the concerted **σ-bond** metathesis mechanism is operative. Instead, the authors proposed a dissociative elimination-addition mechanism which proceeds through a series of 16-electron Ir(III) intermediates [26d].

Various other examples of the activation of C–H bonds by conventional, low-valent metal complexes have been described [27]. Not all of these reactions proceed via an unambiguous, simple oxidative addition mechanism.