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Review

Transition metal-dialkyl compounds (L_xMR_2; R = alkyl; M = metals of groups VI–X)—Synthesis, structure, reactivity and applications

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Contents

Abstract

This review deals with the synthesis, properties and applications of dialkyl complexes of the type L_xMR_2 (R = alkyl; L_x = ligands; M = transition metals of groups VI to X. Discussion on the comparison with analogous monoalkyl-metal complexes is also carried out. Possible reactivity

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Abbreviations: Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Cp′, tetramethylcyclopentadienyl; COD, 1,5-cyclooctadiene; Cn, 1,4,7-trimethyl-1,4,7-triazacyclononane; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dmpe, 1,2-bis(dimethylphosphino)ethane; py, pyridine; bipy, bipyridine; BINAP, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.

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patterns include: insertions of small molecules into the metal and carbon σ-bond, cyclometalations, oxidative addition, transmetalation, and thermal decomposition; these are discussed. The influence of various factors on the stability and reactivity of these title compounds is described. The applications and intermediacy of transition metal-dialkyl species in various catalytic reactions are highlighted.

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Keywords: Transition metal-dialkyl compounds; Synthetic routes; Stability; Reactivity; Thermal decomposition studies; Catalytic applications

1. Introduction

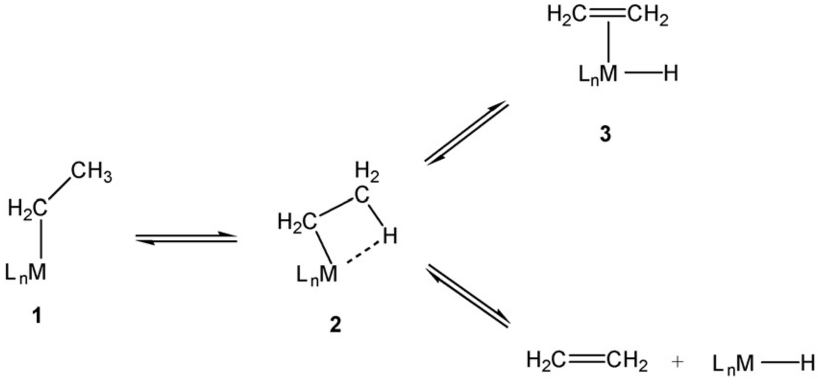
Transition metal complexes containing one or more metal–carbon single bonds are ubiquitous in the field of organometallic chemistry [1]. Transition metal-alkyl complexes are very common and are of great importance in organic synthesis. These complexes are key intermediates in a variety of organometallic, bio-chemical and catalytic reactions, including polymerization [1,2]. A large number of reviews and books on the chemistry of metal-alkyl compounds have been written. However, there has been a growing interest in the elucidation of the mechanistic aspects of metal-mediated reactions, in which metal-alkyls may be present as intermediates. Unlike main group alkyl compounds, transition metal-alkyls often undergo relatively facile reactions, including insertion and isomerization, etc. In general, the relative stabilities of different alkyl ligands often follow the trend: 1-norbornyl > benzyl > trimethylsilyl > neopentyl > Ph ∼ Me ⋙ Et (1° R) > 2°, 3° R. Strong electron donating ligands increase the stability of metal-alkyls significantly. β-Hydride elimination is a fundamental reversible reaction of transition metal-alkyl complexes by which the metal-alkyl (**1**) is converted into the corresponding metal alkene or metal alkylidene hydride complex (**3**) through the formation of an intermediate (**2**) having an agostic interaction (Scheme 1). When β-hydrogens are absent in the alkyl ligand, the free radical $R^{\bullet}$ formed by M–R homolysis can be the predominant product [3]. The factors that influence the stability of isomeric transition metal alkyl compounds have been discussed in detail [4].

Theoretical studies on the dissociation energies of transition metal-alkyl bonds have proven useful in understanding the stability of these complexes [5]. Many transition metal-alkyl compounds, both binary (homoleptic), i.e. of the type MR_n (R = alkyl group), and complex of the type L_xMR_n (L is a ligand such as CO, CN^-, PR_3, etc.), are sufficiently stable below 100 °C [6]. Also, metal-alkyl complexes with various ligands have spurred great interest as possible catalyst precursors for polymerization [7] and for various transmetalation reactions [1]. Among these complexes, transition metal-dialkyl species are an interesting class of compounds which can be more reactive than their monoalkyl relatives.

Dialkyl metal complexes contain two σ-bonded hydrocarbon ligands. They are not as common as mono-alkyl complexes, but as expected they can exhibit similar reactivity to their monoalkyl counterparts. The presence of the second alkyl ligand, however, allows for the occurrence of reactions not possible in monoalkyls [8]. The most striking example of this is the potential for intramolecular coupling of the two carbon groups in dialkyl species [1,2,9], i.e. reductive elimination, which is an important termination step in C–C coupling reactions. Some examples of known dialkyl metal complexes are given in Chart 1.

Metal dialkyls $[M(CH_2R)_2]$ can decompose thermally by intramolecular attack on a C–H bond of an ancillary ligand *via* several modes such as α-, β-, and γ- hydrogen elimination, and reductive elimination, but in some cases they can be stable [9]. Among these pathways, the most common mode of decomposition is the β-hydrogen elimination process. Investigation of the factors that influence the various modes of elimination is important in understanding the mechanisms of the catalytic processes utilizing transition metal catalysts. Metal-dialkyl compounds show similar properties to the metal-dialkenyls that have been reviewed recently, except that the latter complexes have a pendant double bond in the carbon chain [10].

Though metallacycloalkanes also contain two M–C single bonds, the attachment to the metal centre occurs *via* two different carbons on the *same* alkyl chain, thus forming a ring. The principles of reactivity are again comparable to other types of metal alkyls except that the carbon ring, which is more inflexible than



Scheme 1. β-Hydrogen elimination in transition metal-alkyl complexes.

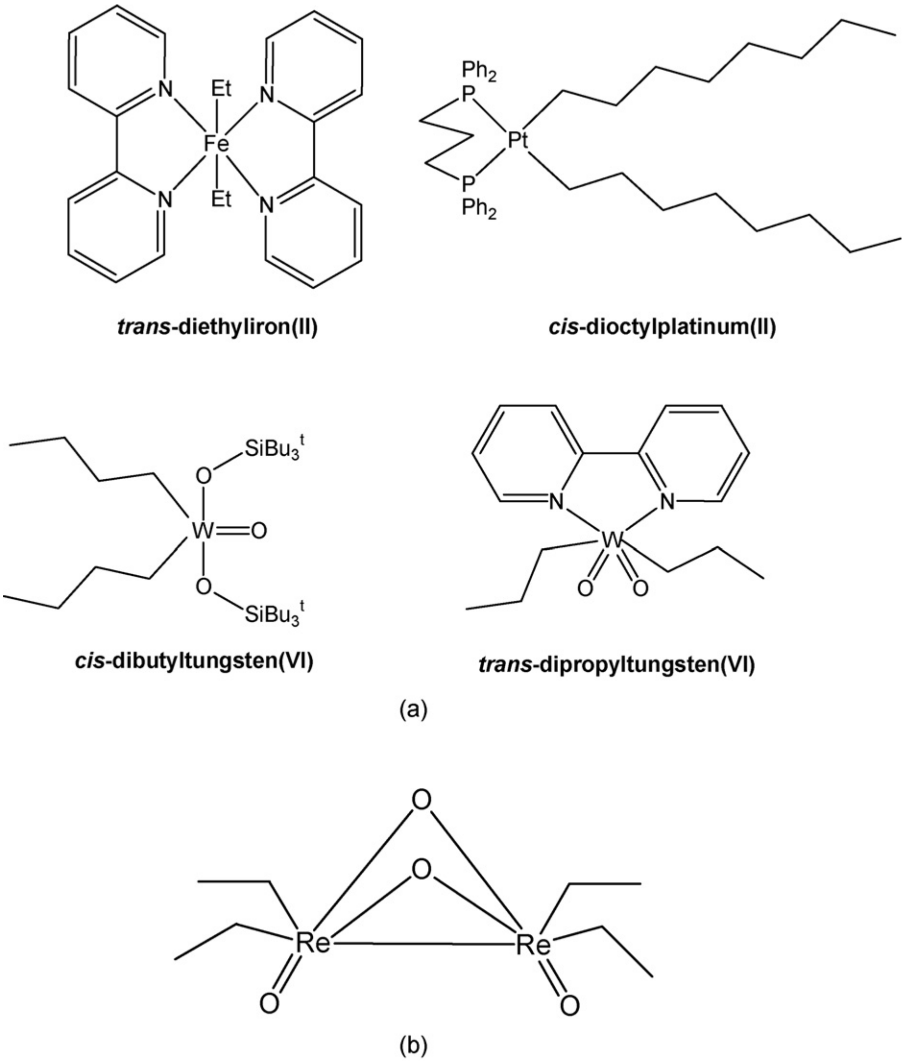


Chart 1. (a) Some examples of dialkyl metal complexes and (b) a dinuclear tetraalkyl complex.

a free alkyl chain, can impose restraints on the reactivity of the metallacycles. Their chemistry and decomposition behaviour are therefore somewhat different from those of the structurally similar dialkyls [11,12]. Metallacycloalkanes are generally observed to be more stable than the metal dialkyls [13], certainly the small to medium ring compounds.

Because of their unique reactivity, dialkyl metal complexes play essential roles, both as catalyst precursors and as intermediates, in numerous catalytic reactions [1d].

Two examples of metal dialkyls are PtL_2R_2 and $MoO_2L_2R_2$, both of which have been studied in detail. Whitesides and co-workers have reported thermal decomposition studies of a number of dialkyl-platinum complexes and discussed the interesting patterns in the organic product distributions [14,15]. Complexes of the type $MoO_2R_2L_2$ ($R = CH_3$, C_2H_5; L_2 = bidentate ligand) have been reported by various research groups during the past decade [16]. A wide range of compounds bearing a variety of bidentate ligands, including substituted 1,4-diazobutadiene, phenanthroline, and substituted bipyridines have been synthesized. Metal-dialkyl compounds are also widely known as key intermediates in many alkane functionalization reactions through the activation of carbon–hydrogen bonds, although sometimes the formed organometallic species is thermodynamically unstable and thus undetectable [17]. It will be useful to compare the reactivity patterns, particularly thermal decomposition studies, of metal-alkenyls and metallacyclic compounds with those of metal-dialkyls.

This article summarizes synthetic routes for the preparation of transition metal-dialkyl compounds. We will focus specifically on the synthesis and applications of metal-dialkyl species with two metal–carbon σ-bonds. We will include alkyl compounds with saturated hydrocarbon substituents on the alkyl chain. However, we will not include compounds with any heteroatom or any unsaturated alkene/alkyne in the alkyl moiety. This review is not restricted exclusively to complexes having β-hydrogens as some of the interesting applications of dimethyl metal complexes are also included. Complexes with substituents on the β-carbons are also mentioned in order to compare reactivity aspects where necessary. This present review discusses complexes of the transition metals belonging to groups VI, VII, VIII, IX and X. Focus will be on mononuclear compounds although some binuclear dialkyls are also mentioned.

2. Synthetic routes

There are numerous methods for the preparation of monoalkyl metal complexes. These include transmetalation, oxidative addition, nucleophilic attack on a metal centre, insertion of an alkene into a metal-hydride bond, and others [18]. Of the above methods, a few have been adapted for the preparation of dialkyl complexes.

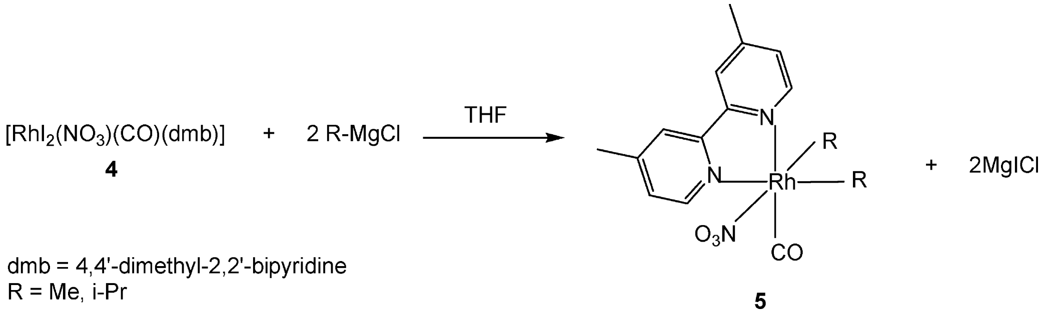
2.1. Transmetalation: the reaction of metal halide complexes with carbon nucleophiles

This is the most common synthetic method for the preparation of alkyl and dialkyl metal complexes [19]. Nucleophilic alkyl groups are transferred from an organometallic alkylating agent such as organolithium or Grignard, to a new metal centre. Metal dihalides can undergo double substitutions in the presence of alkylating agents to afford the corresponding dialkyl species (Eq. (1)).

$$L_nMX_2 + 2M'R \rightarrow L_nMR_2 + 2M'X \qquad (1)$$

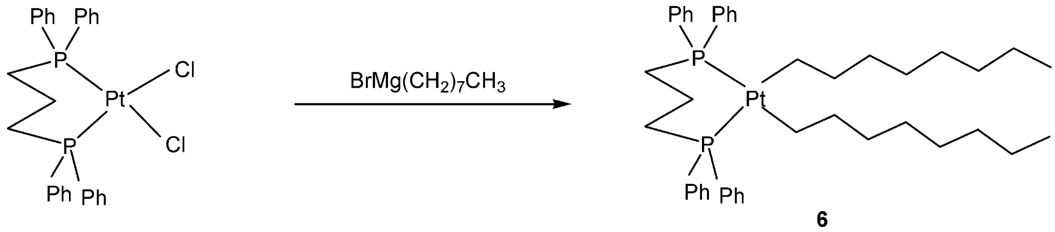
where M′ = Cu, MgX, Li, Zn; X = Cl, Br, I; R = alkyl, aryl, vinyl.

The reaction of the rhodium diiodide (**4**) with two equivalents of alkyl Grignard reagent yielded the first known diisopropyl rhodium complex (**5**) [20] (Eq. (2)).



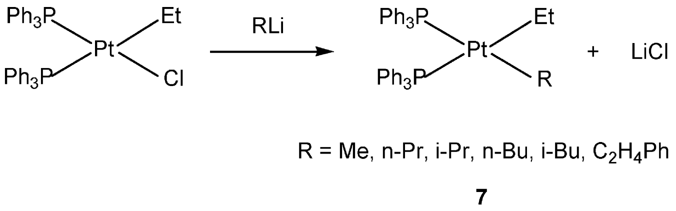
(2)

The Grignard method has also been used by our research group in the preparation of a number of long-chain dialkyl complexes including the dioctyl platinum complex (**6**) [21] (Eq. (3)).



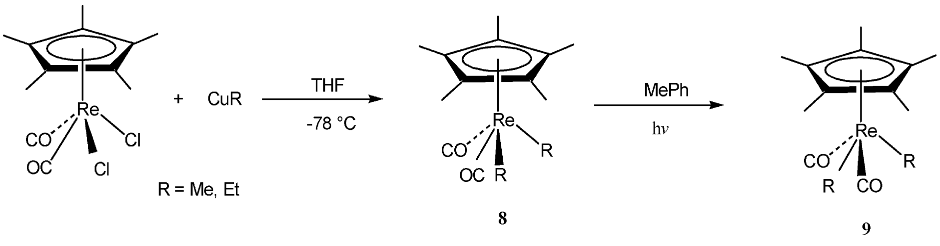
(3)

Unsymmetrical mixed-alkyl platinum complexes (**7**) have been synthesized in a reaction between a monoalkyl platinum halide complex and alkyllithium reagent [22] (Eq. (4)).



(4)

The dialkyl rhenium complexes Cp*ReR$_2$(CO)$_2$ (R = Me, Et) (**8**, **9**) have been prepared by the reaction of organocopper reagents with a rhenium dichloride starting material (Eq. (5)) [23]. Initially the *cis*-isomer (**8**) was formed; UV irradiation of **8** in toluene led to isomerization to the *trans*-isomer, **9**.



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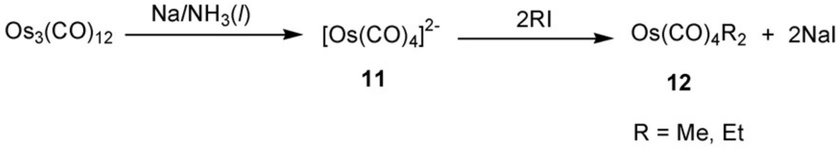
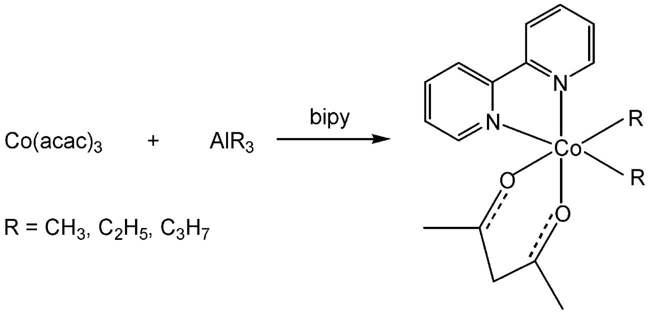


Scheme 2.

Metal complexes that do not contain halide leaving groups can also undergo double alkylations. The iron(III) acetylacetonato complex $Fe(acac)_3$ reacts in the presence of diethylaluminium monoethoxide and bipyridine to form $Fe(bipy)_2R_2$, which has been shown to be a good catalyst for butadiene cyclodimerization [24]. Similarly, $Co(acac)_3$ reacts with trialkylaluminium reagents to give cobalt dialkyls (**10**) (Eq. (6)) [25].



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(6)

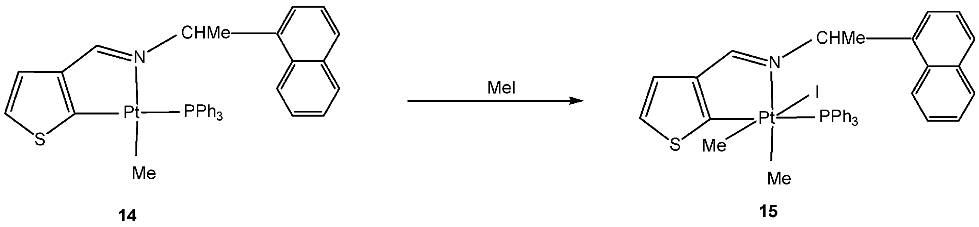
2.2. The reaction of anionic or nucleophilic metal complexes with alkyl halides

Anions generated from carbonyl metal complexes will react with alkyl halides to yield alkylated products [18,26,27]. For example, $Os_3(CO)_{12}$ is easily reduced to its mononuclear dianion (**11**) which can then be alkylated to form mononuclear dialkyl complexes (**12**) (Scheme 2).

Cobalt(III) dialkyls are often synthesized from more nucleophilic cobalt(I) intermediates [28]. Co(II) complexes can be reduced to Co(I) *in situ*, facilitating the addition of two electrophilic hydrocarbon groups to the metal complex [29,30]. Cobalt complexes **13** (Scheme 3) are examples of dialkylcobalt species formed from the reduction of $CoCl_2{\cdot}6H_2O$ by $NaBH_4$ in the presence of alkyl halide and bipyridyl ligand.

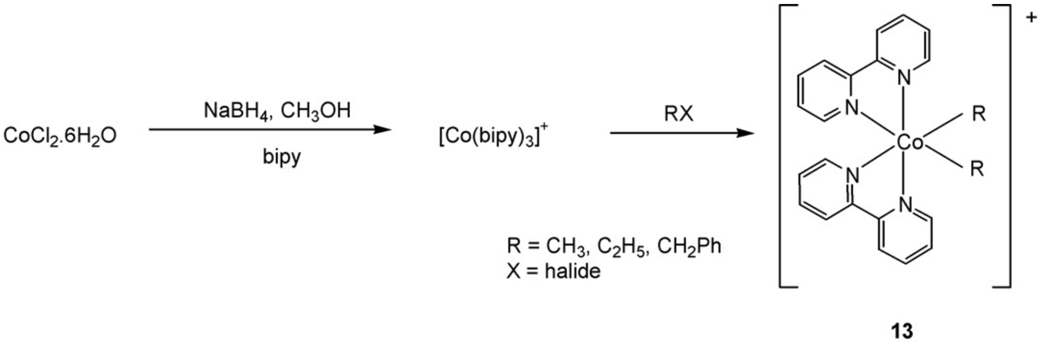
2.3. Oxidative addition reactions

There are several examples of dimethyl complexes prepared *via* oxidative addition of a methyl halide to a metal centre. Platinum(II) monomethyl complex **14** undergoes oxidative addition of methyl iodide, producing a Pt(IV) dimethyl compound (**15**) [31] (Eq. (7)).



(7)

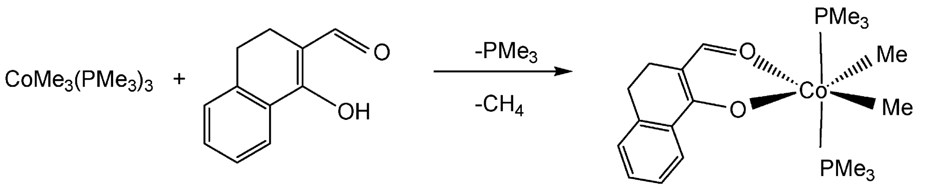
The ionic complex $Cs_2[PtMe_2Cl_4]$ was also synthesized by the oxidative addition of methyl groups from dimethyl sulphate [32].



Scheme 3.

2.4. Generation of dialkyls from polyalkyl complexes

Trialkyl complexes can react to produce an alkane and a dialkyl complex [33]. This has mostly been observed with methyl complexes. Eq. (8) shows how a cobalt trimethyl complex is converted to dimethyl complex (**16**) with the release of methane.

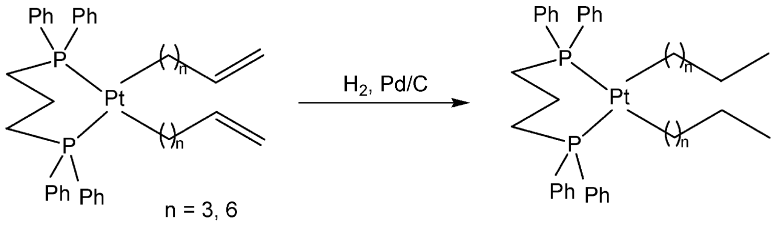


16 (8)

Cationic ruthenium dialkyl complexes have been prepared from tri- or tetramethyl metal precursors. The reaction of $Ru(N)R_3L$ ($R = CH_3$, CH_2SiMe_3; $L = NCCH_3$, pyridine) with HBF_4 in the presence of ligand yielded $[Ru(N)R_2L_2]BF_4$, while the addition of concentrated aqueous HNO_3 to $[Ru(NO)R_4]^-$ gave $[Ru(N)R_2(ONO_2)_2]^-$ [34].

2.5. Hydrogenation of bis(alkenyl) metal complexes

The hydrogenation of monoalkenyl metal complexes to their corresponding monoalkyls has been reported in the literature [35]. We have prepared some long-chain platinum-dialkyl complexes (**18**) by the hydrogenation of the bis(alkenyl) precursors (**17**) [21] (Eq. (9)).



17

18a, n = 3;
18b, n = 3

(9)

3. Structure

A review of the Cambridge Structural Database reveals that relatively few crystal structures of metal-dialkyl complexes of the type discussed in this paper where R > Me have been reported. A summary of bond distances and bond angles related to the dialkyl moiety in dialkyl complexes for which crystallographic data have been published appears in Table 1. Where available, structural details for the analogous dimethyl complexes are included for comparison.

The metal–carbon bond distance is typically in the range 200–220 pm in these complexes. However, no trends can be discerned nor any conclusions drawn due to the diverse nature of metal complexes listed, including a wide range of oxidation states of the metals as well as a variety of ancillary ligand sets.

The alkyl ligands in these complexes adopt either a *cis* or *trans* arrangement. In tetrahedral complexes or octahedral complexes where the arrangement is *cis* the angle formed at the metal centre by the alkyl ligands ranges from 76° to 91°. In the five coordinate trigonal bipyramidal complex, $WO(OSi^tBu_3)_2(^nBu)_2$ a slightly splayed angle of 128° has been measured. Octahedral complexes in which the alkyl ligands are in a *trans* relationship display a bond angle of 147–153°.

4. Stability and reactivity of metal-dialkyl compounds

4.1. Stability

As in the case of metal-alkenyls and metallacycloalkanes, the stability of transition metal-dialkyl compounds strongly depends on various factors such as the steric and electronic properties of substituents on the alkyl chains, nature of the ligand system, metal, solvent and temperature. For instance, the presence of sterically bulky alkyl groups leads to the formation of some interesting cyclometalation products; this is discussed in Section 5 of this review. α,α′-Bipyridine has been reported as an excellent stabilizer of the metal-alkyl bond in various transition metal-dialkyl complexes [48,24]. The dependence of stability on the alkyl chain length is evident in the series of complexes, $Ni(bipy)R_2$ ($R = CH_3$, C_2H_5, n-C_3H_7, i-C_4H_9), where the stability decreases in the order: $CH_3 \gg C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_4H_9$ [49].

The low thermal stability of metal-dialkyls is due to the existence of a number of low energy decomposition pathways that are specific to transition metals. It is well known that some covalent ligands with lone pairs can impart a greater stability to the metal-dialkyl compounds. For example, doubly bound oxygen and nitrogen and triply bound nitrogen greatly influence the stability. Generally, the stability of late transition metal alkyl complexes can be found as follows: 5d > 4d ≫ 3d and in particular, Os, Re, Pt > others. In addition, cyclic metal-alkyls are more stable than their open-chain analogues. Compounds with high coordination numbers are significantly more stable than

Table 1
Selected inter-atomic distances (Å) and angles (°) for complexes L_xMR_2

Complex	M–CH_2	M–CH_2'	CH_2–M–CH_2'	Reference
Ru(Bu^t_2bipy)R_2				
R = Et	2.142	2.138	85.23	[36]
Fe(bipy)$_2R_2$				
R = Et	2.068	2.063	85.01	[37]
Pt(biphen)(OP^{i}Pr)R_2				
R = Et	2.114	2.128	84.40	[38]
WO(OSi^{t}Bu$_3$)$_2R_2$				
R = Bu	2.102	2.151	128.35	[39]
Mo(bipy)(O)$_2R_2$				
R = Et	2.185	2.191	153.99	[40]
R = Me	2.189	2.194	149.02	[50]
W(bipy)(O)$_2R_2$				
R = Pr	2.150	2.166	147.97	[41]
R = Me	2.195	2.195	149.60	
Cr[(Me_2PCH_2)$_3$CMe]ClR_2				
R = Bu	2.113	2.128	91.74	[42]
RuCp*(NO)R_2				
R = Et	2.087	2.168	81.57	[43]
Pt(dbpp)R_2				
R = Et	2.103	2.113	80.93	[44]
ReCp*(CO)$_2R_2$				
R = Et	2.1.61	2.162	138.97	[23]
Mo(η-C_5H_4)CMe_2(η-C_5H_4)R_2				
R = Et	2.244	2.246	76.41	[45]
W(η-C_5H_4)CMe_2(η-C_5H_4)R_2				
R = Et	2.238	2.241	76.78	[45]
R = Me	2.182	2.182	66.41	
Pt(PPh_3)$_2R_2$				
R = Bu	2.106	2.122	83.47	[46]
MoCp$_2R_2$				
R = Bu	2.270	2.275	76.56	[47]

compounds with low coordination numbers. The stability can also be influenced by the number of valence electrons present in the compound as follows: 18 VE > 16 VE > 17, 19 VE. The very stable platinum dialkyls, most of which are 16 VE species, are an exception to this trend.

4.2. *Reactivity*

Like monoalkyl complexes, dialkyl species can react or decompose in several ways. Many of these reactions form crucial steps in catalytic cycles. It is therefore vital to have a good understanding of their mechanisms and the factors that promote or impede their occurrence. Some of the more pertinent reactivity pathways are discussed below.

4.2.1. *Radical reactions*

Metal–carbon bonds can experience homolytic fission to produce radical species (Eq. (10)). This reaction can often be photolytically induced. Metal centres such as Fe(III) [50], Ru(III) [51] and Co(III) [52] are more likely to undergo radical splitting than others.

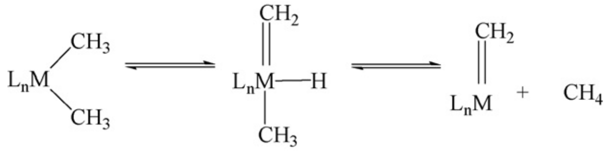
$$\mathrm{R{-}M^{n+1}} \longrightarrow \mathrm{M^{n}} + {}^{\bullet}\mathrm{R} \qquad (10)$$

A dialkyl metal complex is able to produce *two* alkyl radical intermediates; these, then, may couple to form a new organic product [50].

Radical reactions are especially important in cobalt chemistry [52,53]. Vitamin B_{12}, a cobalt-containing corrinoid complex, is an essential coenzyme in human metabolism. Its catalysis of some important biological processes in the body is known to be initiated by homolysis of the metal–carbon bond. Although the complex itself is a monoalkyl species, numerous cobalt corrinoid or macrocyclic complexes, both mono- and dialkyl, have been synthesized and used as model compounds for the investigation of the chemistry of this fascinating biological molecule.

4.2.2. *α-Hydride abstraction*

Transition metal alkyls or dialkyls with no β-hydrogens, such as dimethyl complexes, may undergo thermal decomposition *via*



Scheme 4.

formed olefin ligand dissociates so that the final products of the decomposition pathway are metal hydride and alkene. In the case of metal-dialkyls, the elimination product, after alkene dissociation, is an alkyl-hydrido complex. This can further decompose by *reductive elimination* to yield an alkane.

other, less common routes. One of these is α-hydride abstraction, the mechanism of which is outlined in Scheme 4.

The process is more often observed with early transition metal complexes [54,55] like tantalum, but there are a few examples for the metals in groups 8–10. A square planar iridium methylidene complex was formed by light-induced α-elimination of the (methyl)(neopentyl) starting complex [54].

4.2.3. *β-Hydride elimination*

A large proportion of stable, isolable transition metal-dialkyl complexes are those in which there is no H-atom bonded to the carbon at the position *beta* to the metal centre. Dimethyl species are particularly abundant, but complexes containing benzyl (CH_2Ph) or *t*-butyl (CMe_3) moieties, for example, are also known. This can be explained by the general belief that β-H-containing metal alkyls undergo facile β-hydride elimination, the most frequently observed thermal decomposition pathway for this class of compounds [56]. Scheme 5 shows the process for metal-dialkyls.

In certain cases, the decomposition is complete after the β-H elimination step. The stable η^2-coordinated Pt(0) precursor $Pt(PEt_3)_2(\eta^2\text{-}C_2H_4)$, for example, is easily prepared *via* the β-H elimination of $Pt(PEt_3)_2Et_2$ [57]. Usually, however, the newly formed olefin ligand dissociates so that the final products of the decomposition pathway are metal hydride and alkene.

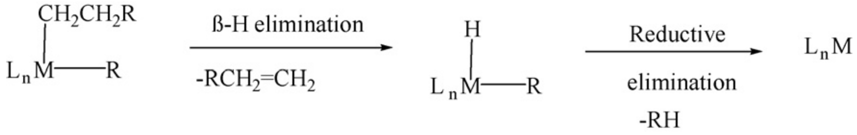
The greater the number of accessible β-hydrogens in the complex, the greater the likelihood of β-H elimination occurring. Yamamoto and co-workers illustrated this after carrying out a study on mixed-alkyl platinum(II) complexes (**19**) through the formation of metal alkyl hydride intermediates (**20**, **21**) [22] (Scheme 6).

The ratios of ethane:ethene and propene:propane generated were found to be 0.64 and 0.60 respectively. This showed that the ethyl group was participating in β-elimination approximately 1.5 times faster than was the propyl group. The results are consistent with the fact that the ratio of β-hydrogens in an ethyl group versus a propyl group is 3:2.

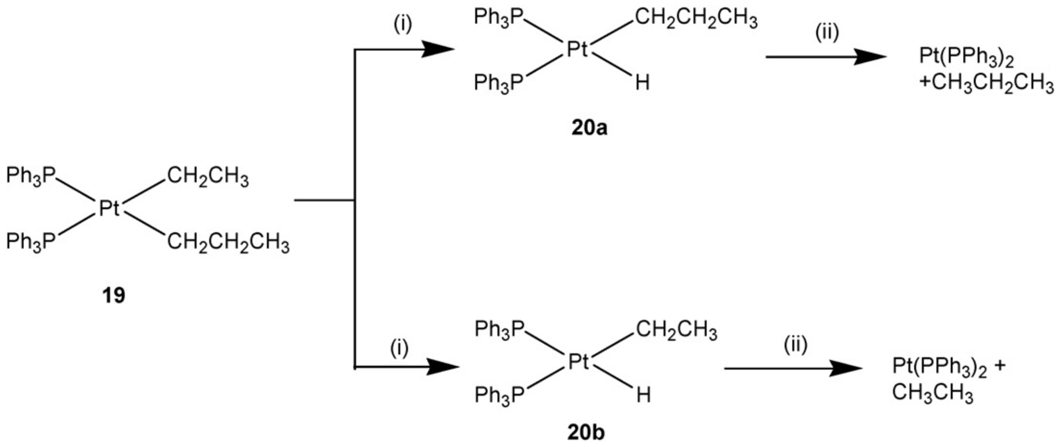
In 2004 Boncella and co-workers reported evidence that the tungsten complex **21a** underwent β-H elimination at 80 °C to form ethylbenzene and **21b**, in which the newly formed alkene molecule remains coordinated to the metal centre even in the presence of phosphine ligand as shown in Scheme 7 [58].

A study of the thermolysis of a range of *trans*-$PdEt_2(PR_3)_2$ complexes in the presence of added ligand showed in all cases the presence of β-H elimination products, ethane and ethene, in a 1:1 ratio (Scheme 8). Similarly, the complexes $PdR'_2(PMe_2Ph)_2$ ($R' = Pr$, Bu) released propane/propene, and butane/butene respectively upon thermolysis [59].

Thermoysis studies carried out on a series of cobalt dialkyl compounds showed that the main decomposition pathway for the diethyl, dipropyl and dibutyl complexes was β-H elimina-

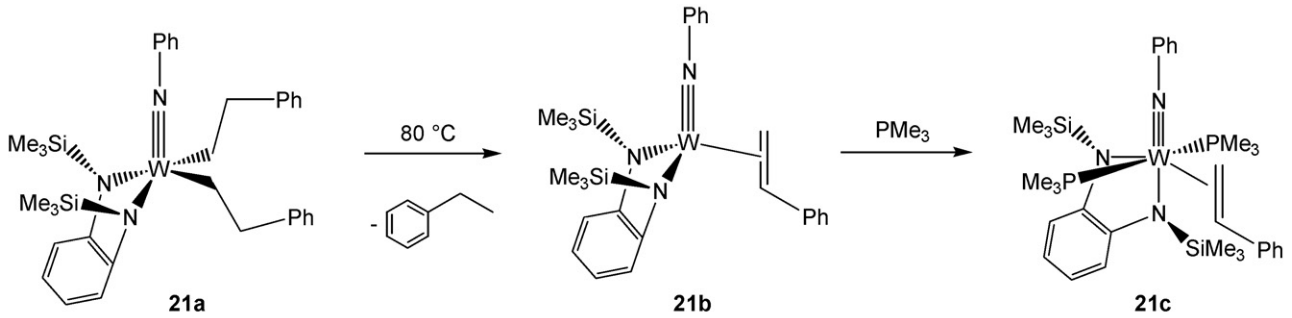


Scheme 5.

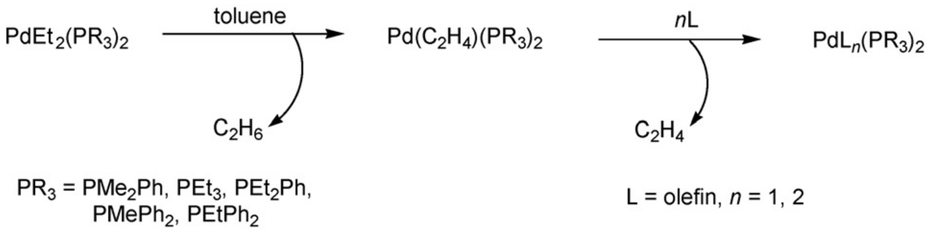


step (i) β-hydride elimination; step (ii) reductive elimination

Scheme 6.



Scheme 7.



Scheme 8.

tion, whereas the dimethyl analogue decomposed *via* reductive elimination [60] (Eq. (11)).

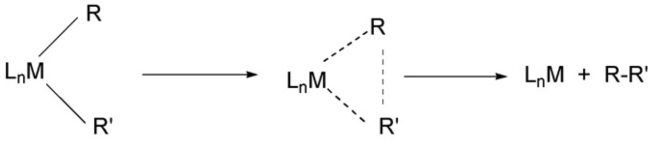
$$CoR_2(acac)(PPhMe_2)_2 \xrightarrow{\text{heat}} \text{alkane} + \text{alkene} \quad (11)$$

R = Et, Pr, Bu.

4.2.4. *Reductive elimination*

Alkyl-halo, alkyl-hydrido, or dihydrido metal complexes can react *via* reductive elimination to yield the products of coupling of the groups concerned: alkyl halide, alkane or dihydrogen respectively. The ability of dialkyls to react in this way leads to the formation of new carbon–carbon bond containing species (**22**) (Scheme 9), an aspect of considerable interest and importance in several catalytic reactions, some of which are of industrial importance [61,62].

As indicated in Scheme 4, it is necessary for the two coupling groups to be situated *cis* to each other for coupling to occur [55,56,61–63]. A study by Yamamoto and co-workers showed how palladium dialkyls with different stereochemical configurations would decompose through different pathways [63]. The palladium complex, *cis*-$Pd(PR_3)_2Et_2$ is able to undergo a facile reductive elimination step to give the ethyl-ethyl coupled product butane. However, the *trans*-isomer is unable to do this, and prefers the β-H elimination decomposition route.



22

Scheme 9.

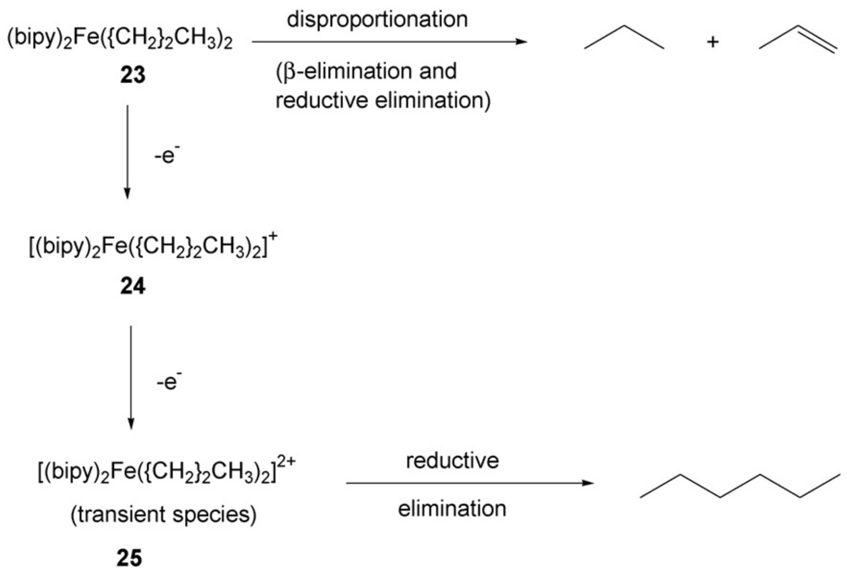
Gillie and Stille [61b] demonstrated that *trans*-$PdMe_2(PMePh_2)_2$ does not undergo reductive elimination under normal conditions. However, in polar, coordinating solvents such as THF or DMF, it was able to isomerize to the *cis* form, and the coupling product ethane could be detected.

The inevitable decrease of a metal centre's oxidation number following reductive elimination makes the process more favourable for metals in higher oxidation states [55,56,61]. Thus the use of oxidants can promote the coupling reaction [56,64]. For instance, the rhodium complex $Cp^*RhMe_2(Me_2SO)$ decomposes in acid to give mostly methane with a small amount of ethane (1–5%). The introduction of one-electron oxidizers, such as $AgBF_4$ or iodine, into the system greatly enhances the percentage of the ethane [65].

Kochi et al. showed a similar trend with a series of neutral $[Fe(bipy)_2R_2]$ complexes (R = Et, *n*-Pr, *n*-Bu) and the electrochemically oxidized products $[Fe(bipy)_2R_2]^{n+}$ ($n = 1, 2$) [50]. The neutral dialkyliron(II) complexes **23** decomposed slowly *via* a disproportionation mechanism, whereas the transient dicationic Fe(IV) analogues **24**, **25** rapidly broke down to release reductive elimination products (Scheme 10).

One other observation is that reductive elimination involving alkyl–acyl [56,62,66] or alkyl–vinyl [62] coupling occurs much more readily than alkyl–alkyl coupling. It was seen that dialkylmonoacyl $PtMe_2(COMe)XL_2$ complexes that decomposed *via* this pathway afforded the acyl–alkyl product propanone rather than the dialkyl product ethane [67]. Yamamoto et al. demonstrated that the cobalt complex **26** (Chart 2) is stable and not susceptible to reductive elimination; however, its acyl relative **27** reacts smoothly to yield the diethylketone product [68].

Although reductive elimination is such an important process from synthetic and industrial points of view, it is not always favoured by metal dialkyls as a decomposition path-



Scheme 10.

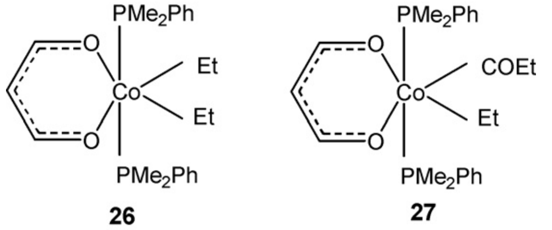


Chart 2. A cobalt dialkyl complex and a cobalt alkyl acyl complex.

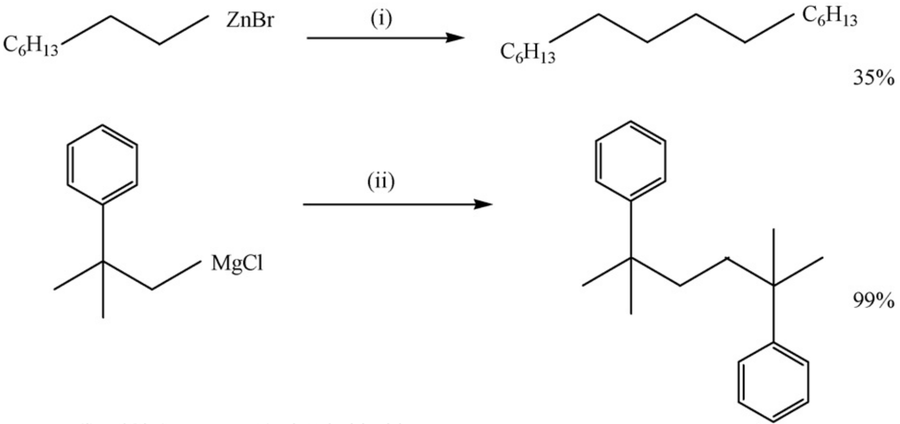
way, and must compete with other, more facile pathways [61,62,69,70]. Lei and Xhang [69] have examined several palladium-catalyzed C$_{sp^3}$–C$_{sp^3}$ coupling reactions in which a key feature is the formation of a Pd-dialkyl intermediate that can undergo reductive elimination to generate the product. While the coupling of carbon chains bearing no β-hydrogens proved to be an efficient and high-yield process, those involving alkyl chains with β-hydrogens proceeded with more difficulty (Scheme 11). The results suggested that a β-H elimination process was in competition with the desired reductive elimination step.

In the case of *cis*-dialkylpalladium(II) complexes, reductive elimination *does* seem to be a favoured decomposition pathway [59,71,72]. The *cis*-Pd(CH$_2$SiMe$_3$)$_2$(PMe)$_2$, complex for example, decomposes to give Me$_3$SiCH$_2$CH$_2$SiMe$_3$ [71]. Similarly, the thermally unstable Pd(Me)(styrene)(PPh$_2$Me)$_2$ undergoes reductive elimination at low temperatures to give propenylbenzene [72].

Nickel, too, can sometimes undergo reductive elimination quite readily [73,74]. Ni(II)(α-diimmine) complexes **28–31** (Fig. 1) decompose to give the organic coupling products [73].

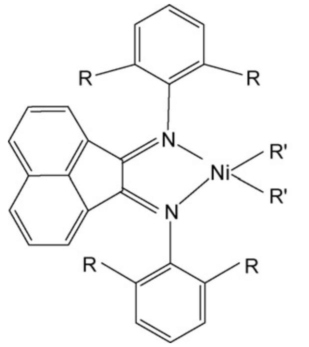
4.2.5. Alkyl migration

Insertion of small molecules such as carbon monoxide into metal–carbon bonds is an important step in many transition



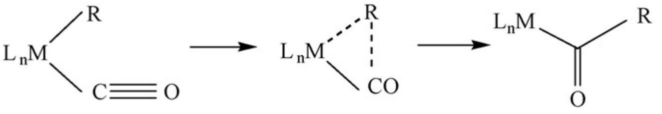
(i) PdCl$_2$(rac-BINAP), desyl chloride
(ii) PdCl$_2$(rac-BINAP), ZnCl$_2$, desyl chloride

Scheme 11.



28, R = Me, R' = Et,
29, R = *i*-Pr, R' = Et
30, R = Me, R' = *n*-Pr
31, R = *i*-Pr, R' = *n*-Pr

Fig. 1. A series of Ni(α-diimmine) complexes that undergo facile reductive elimination.



Scheme 12.

metal-catalyzed reactions. Alkyl migration (often referred to as carbonyl insertion) describes the migration of an alkyl ligand from a metal centre to a CO ligand bonded *cis* to the alkyl on the metal centre (Scheme 12) [56].

The possibility of this process occurring in conjunction with a reductive elimination step in transition metal dialkyls introduces an effective method for the synthesis of ketones [66,75–77]. As previously mentioned, reductive elimination of an alkyl–acyl product from a metal atom is a relatively low energy process. Thus, carbonylation of one alkyl group in a dialkyl complex can easily lead to the formation of a ketone by coupling of the alkyl and acyl moieties. Pampaloni et al. have reported an interesting case relating to $Fe(bipy)_2R_2$ complexes (R = Et, *n*-Pr) [75], confirming similar results obtained by Kochi and co-workers [50]. In the presence of CO these compounds undergo one or two carbonylation steps and subsequent reductive elimination to furnish both the ketone and the diketone products (Scheme 13).

The iron acyl intermediate is able to reductively eliminate a ketone product, or it may undergo a second carbonyl insertion to form a diacyl complex. The likelihood of one pathway being favoured is temperature-dependent; as the temperature decreases, so does the yield of diketone increase.

A convenient synthesis of *trans*-diacyl alkyl complexes of platinum(II) (**32**) involving the CO insertion reaction has been reported by Chen and co-workers [78] (Scheme 14). The unique carbonylation reactions of such complexes, including one with intriguing acyl scrambling, leads exclusively to the *cis*-diacyl products (**33**) and finally to diketones and ketones.

4.2.6. *Alkene insertion*

Alkenes can be inserted into metal–carbon σ-bonds to form extended-chain alkyls through the general mechanism outlined in Scheme 15 [18].

Pardy gained some insight into this process when carrying out a study on a deuterated dimethyl cobalt complex, **34** [79] (Scheme 16).

Extension of the carbon chain by consecutive insertion of multiple alkene molecules into a metal–carbon σ-bond is what makes this process a crucial step in alkene oligomerization and polymerization reactions.

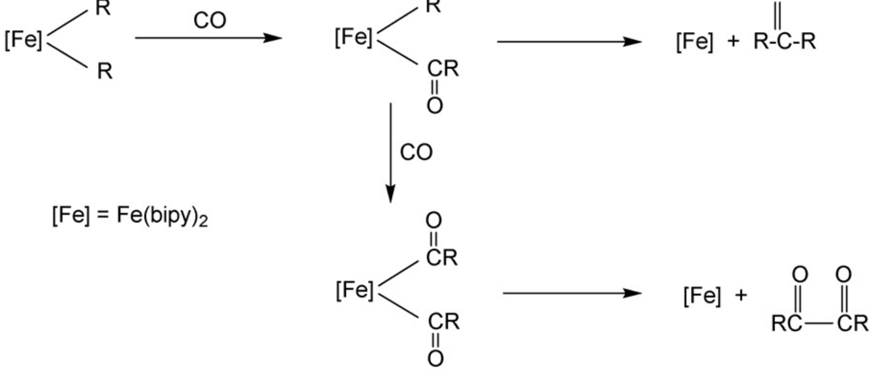
4.2.7. *Oxidative addition*

The oxidative addition of alkyl halides to transition metal-alkyl complexes is a key step in several important catalytic reactions [80]. Usually, the oxidative addition of primary alkyl halides to dimethylplatinum(II) complexes occurs by the S_N2 mechanism and gives *trans* stereochemistry although subsequent isomerization can give products which appear to arise from *cis* oxidative addition as shown in Scheme 17 [81].

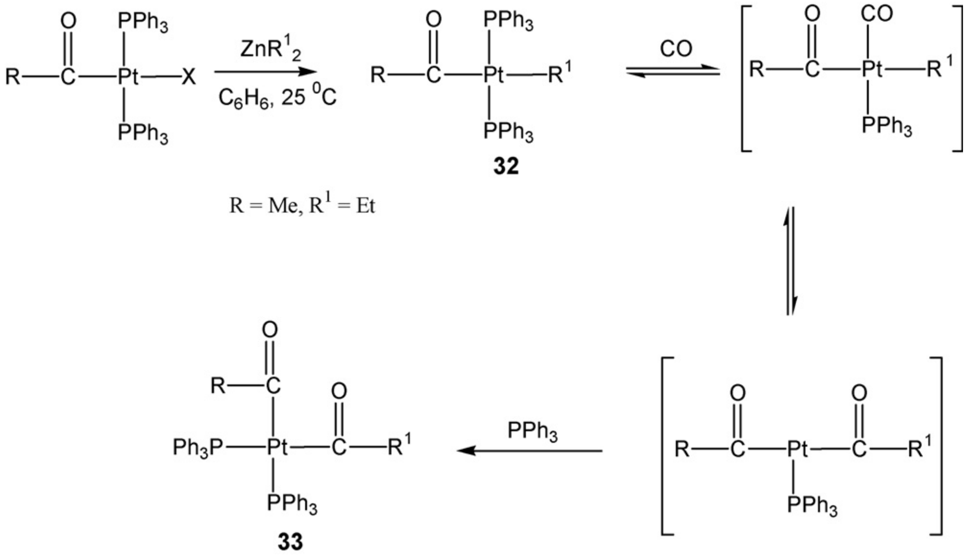
A similar kind of study has also been reported using platinum(II) complexes with metalated diimine ligands derived from *cis*- or *trans*-diiminocyclohexane [82].

5. Thermal decomposition studies

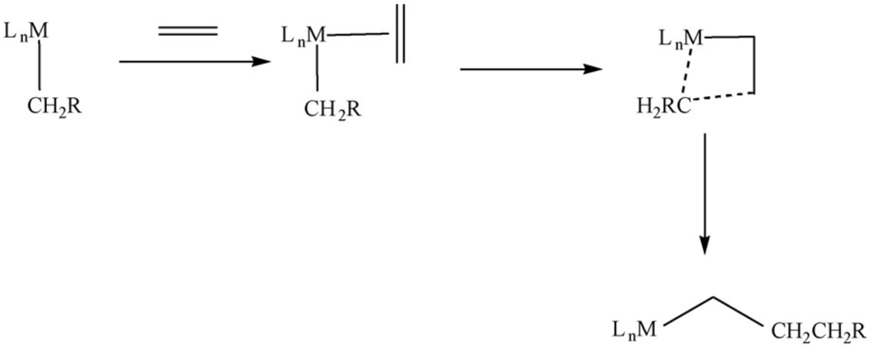
Transition metal alkyl compounds can decompose by several different pathways including: (i) β-hydride elimination, (ii) α-hydride elimination, (iii) γ-hydride elimination and



Scheme 13.

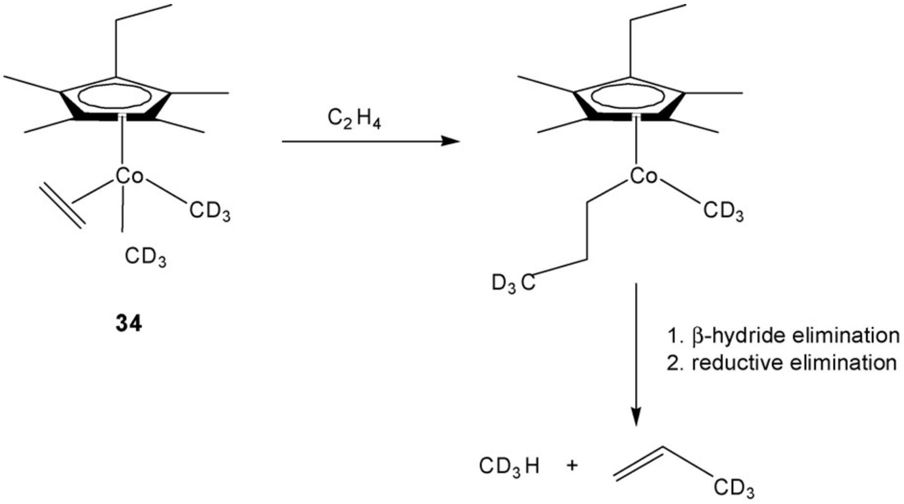


Scheme 14.



Scheme 15.

(iv) reductive elimination. The formation of organic products can vary significantly during the thermal decomposition of metal-alkyl compounds depending on the experimental conditions. The organic products formed are quite similar to the metal-dialkenyl and metallacycloalkane decomposition products. However, the influence of sterically bulky alkyl groups on the types of thermolysis products formed has been described [14,83].



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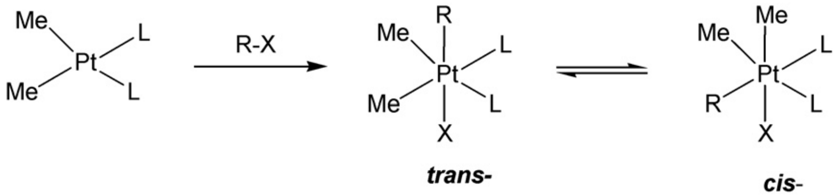
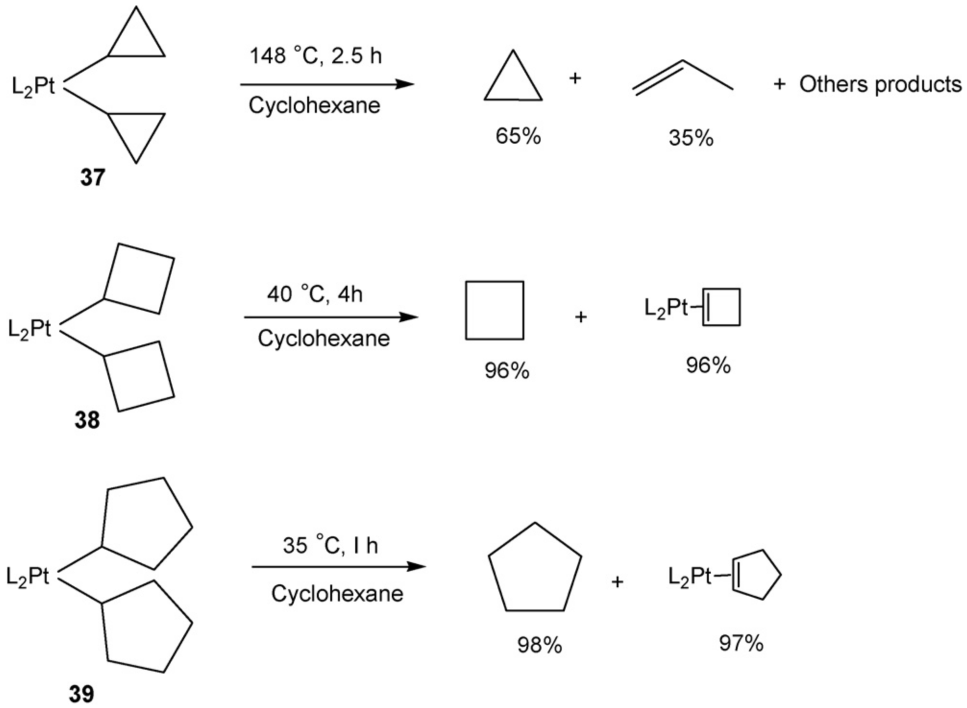
Scheme 16.



Scheme 17.

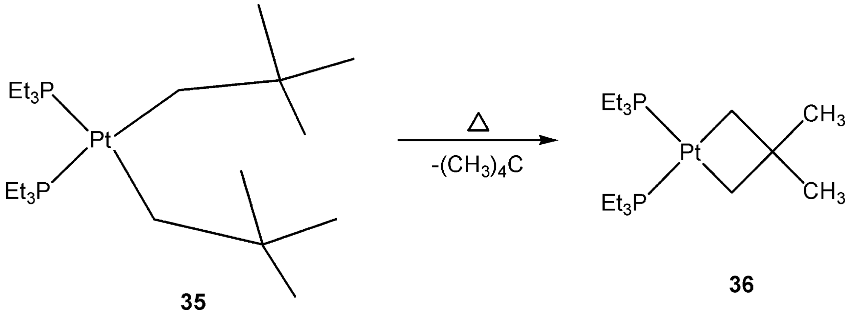


Scheme 18. Thermal decomposition of bis(cycloalkyl)platinum(II)complexes.

Thermolysis reactions of $Pt(CH_2CMe_3)_2(PEt_3)_2$ (**35**) yield Me_4C and bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**36**). A comparison of the structures of these two compounds indicated that **35** is significantly sterically congested, which led to the formation of platinacycle (**36**) [14]. In a similar way, cyclometalation of various $Pt(Et_3P)_2R_2$ (R = alkyl) complexes have also been shown to form their corresponding platinacycles [83] (Eq. (12)).

Studies on the thermal decomposition reactions of di(cycloalkyl)bis(triethylphosphine)platinum(II) complexes (**37–39**) yielded similar products to those established for $Pt(Et_3P)_2Et_2$ when cyclobutyl and cyclopentyl groups are used. However, thermal decomposition of the di(cyclopropyl)platinum(II) compound is too complex as many competitive processes are likely to occur [84] (Scheme 18).

It has also been suggested that the mechanism of thermal decomposition of platinum-alkyl compounds, for example,

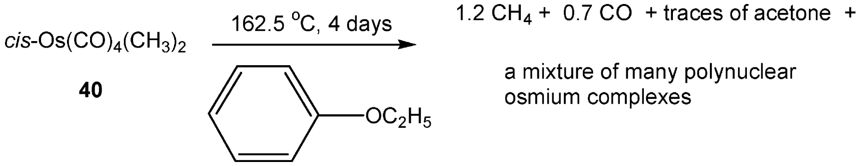


(12)

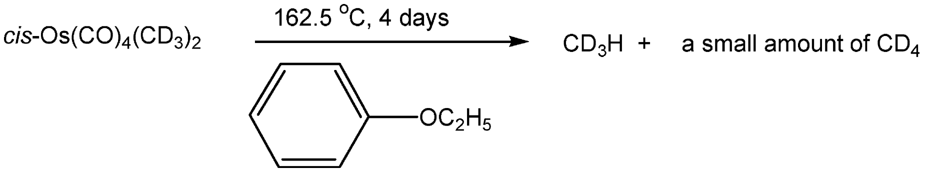
PtL_2Et_2 ($L = PEt_3$) to $PtL_2(C_2H_4)$ and C_2H_6 in cyclohexane depends on the concentration of ligand ($L = PEt_3$) added to the solution [15]. The reactions proceed by sequential dissociation of a phosphine giving a vacant coordination site, oxidative addition of a C–H bond to platinum, and reductive alkane elimination [85] (Eq. (13)). Thermal decomposition of di-*n*-propyl bis(triethylphosphine)platinum(II) complexes in cyclohexane solution yielded one equivalent each of *n*-propane and propylene. The decomposition is strongly dependent on the temperature and ligand, and inhibited by added triethylphosphine.

$$(\text{dmpe})PtEt_2 \xrightarrow[\text{Cyclohexane}, 182\,^{\circ}C]{1\ \text{dmpe}} (\text{dmpe})_2Pt(0) + CH_2{=}CH_2 + CH_3CH_3 \quad (13)$$

Norton and co-workers studied [86] the mechanisms of the elimination reactions of *cis*-$Os(CO)_4R_2$ where $R = CH_3$ and C_2H_5. The formation of methane from *cis*-$Os(CO)_4(CH_3)_2$ (**40**) proceeds *via* an intermediate which displays high H/D selectivity in attacking alkane solvents [Eqs. (14) and (15)]. The formation of ethylene and ethane from *cis*-$Os(CO)_4(C_2H_5)_2$ (**41**) involves a reversible β-hydrogen elimination. The products were ethylene from *cis*-$Os(CO)_4(C_2H_5)_2$ and all possible H/D isomers from *cis*-$Os(CO)_4(C_2D_5)_2$ (**42**). Simple intramolecular reductive elimination has not been observed from these decomposition reactions with *cis*-$Os(CO)_4R_2$ species [Eq. (16)].



(14)

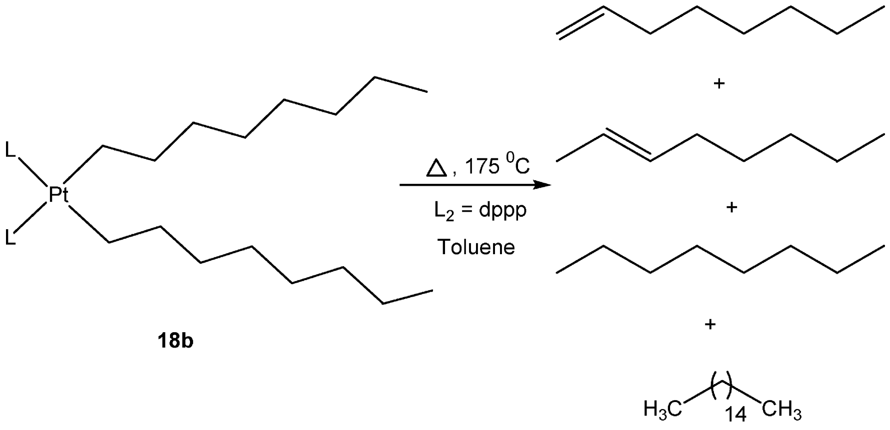


(15)

$$\underset{\mathbf{41}}{cis\text{-}Os(CO)_4(C_2H_5)_2} + \underset{\mathbf{42}}{cis\text{-}Os(CO)_4(C_2D_5)_2} \xrightarrow[n\text{-octane}]{126\,^{\circ}C,\ 3\ \text{days}}$$

$$C_2H_4 + C_2D_4 + C_2H_3D + C_2HD_3 + CH_2{=}CD_2 + cis\text{-}CHD{=}CHD + trans\text{-}CHD{=}CHD \quad (16)$$

Our experiments revealed that the thermal stability of bis(alkyl)platinum(II) complexes strongly depends on the nature of ancillary ligands, and is similar to the platinum-alkenyl analogues. Thus, the cyclooctadiene complex, $Pt[COD]\{(CH_2)_7CH_3\}_2$ decomposes even at 50 °C to yield an intense brown colour. In contrast, the $Pt[dppp]\{(CH_2)_7CH_3\}_2$ complex was quite stable and could be heated up to 100 °C without decomposition. The increased thermal stability could be due to the chelating effect of diphosphine ligand. The organic product distribution observed from the thermal decomposition of the $Pt(dppp)\{(CH_2)_7CH_3\}_2$ complex in toluene [21] (Eq. (17)) indicated the formation of 1-octene (9%), 2-octene (4%, a mixture of isomers) *n*-octane (6%) and *n*-hexadecane (81%). By comparison, the solid-state decomposition showed the formation of *n*-hexadecane (99%) as a major product by an intramolecular reductive elimination of alkyl groups. Our studies also indicated that the thermal decomposition pathway as well as the organic product distributions are strongly dependent on the factors such as nature of ligand, metal, length of alkyl chains and temperature [21].



18b

Thermal decomposition of dioctylplatinum(II) complex (17)

6. Catalytic applications of metal-dialkyl species

It is by virtue of their unique and rapid reactivity that transition metal dialkyls are such an important class of metal complex in the field of catalysis. For this reason, their most important catalytic applications are those in which the metal-alkyl or metallacycloalkane is formed as a transient, non-isolable intermediate that breaks down to form the organic product. Metal-alkyl species are believed to be key intermediates in both homogeneous and heterogeneous catalytic reactions [87].

6.1. Carbon–carbon cross-coupling reactions

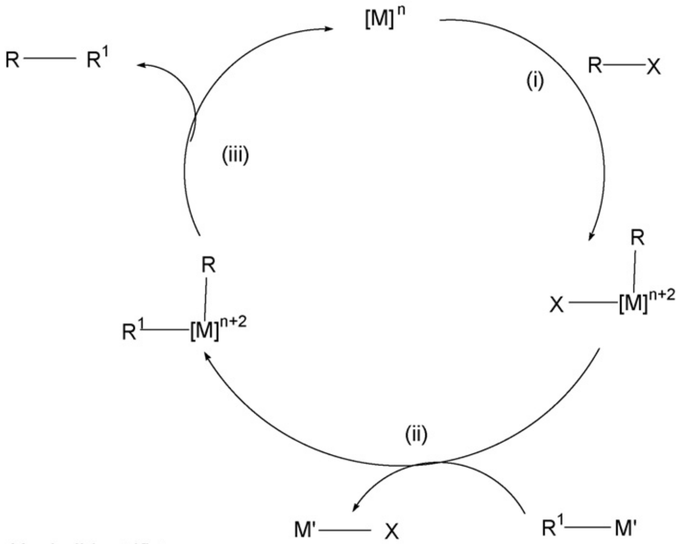
Development of methodologies for the creation of new carbon–carbon bonds is a constant challenge in combinatorial chemistry, and is especially relevant in the synthesis of natural products [88–91]. Cross-coupling reactions catalyzed by transition metals constitute what is probably the most useful method of achieving these bond formations [92,93]. The field has been dominated by palladium chemistry [94], but other late transition metals like Ni, Rh, Pt and Ru have also been known to catalyze the reactions. A simplified mechanism of cross-coupling is depicted in Scheme 19. This is the mechanism that occurs in systems of palladium and many of the other metal-catalyzed reactions.

The crucial step in the cycle is the formation of the dialkyl, which undergoes reductive elimination to release the coupled product. It is important to realise that in most cases the dialkyl complexes, though formed as key intermediates, are not isolated due to their high reactivities. During the reaction, the β-hydride elimination would occur rapidly with an alkyl group [95,96], ending the cross-coupling catalysis. There were few efficient C_{sp^3} alkyl–alkyl coupling systems known until quite recently [97]. Among the more well-known palladium-catalyzed cross-coupling reactions are the Stille [94,98,99], Suzuki [91,94,100] and Sonogashira couplings [94,101].

These reactions have traditionally involved the addition of *aryl* or non β-H containing alkyl halides to various organometallic reagents. Stille coupling has been used, for example, in the convenient synthesis of derivatives of the antibiotic tetracycline, in hopes that the new derivatives would show good antibiotic activity against multi-drug-resistant bacteria [99].

It would be useful to be able to apply these methods using alkyl halides with β-hydrogens. Pioneering research done by Fu and others has proved worthwhile in achieving this end. Use of appropriate ligands is essential. Certain ligands (usually the bulky, strongly-donating molecules) can prevent either the formation of a coordinatively unsaturated metal-alkyl intermediate, or the co-planar geometry required before β-H elimination can take place [97].

Fu and Menzel discovered that a Pd/P(*t*-Bu)$_2$Me catalyst system, unlike most other palladium systems, was able to effect the cross-coupling of alkyl halides with various alkenyltin reagents [98].



X = halide, triflate
R = alkyl, aryl, vinyl etc.
M' = MgBr, Li, Zn, Sn etc.

Scheme 19.

As late as 2001, Fu et al. reported the first instance of alkyl–alkyl Suzuki coupling using $Pd(OAc)_2/PCy_3$ in the presence of $K_3PO_4{\cdot}H_2O$ [102]. The catalyst combination was found to bring about effective coupling of alkyl- and vinylboranes with alkyl bromides containing β-hydrogens. In 2003, the same researchers reported the use of sterically large *N*-heterocyclic carbene ligands in Pd-catalyzed Sonogashira couplings of primary alkyl bromides and iodides [101]. The catalyst system was able to tolerate a range of functionalities on the alkyl halide, including olefins, esters, alcohols and others.

Some of the other later transition metals can also catalyze C–C cross-coupling of both C_{sp^2} and C_{sp^3} centres. There are numerous instances of nickel complexes that effect this type of reaction [95,97]. Kambe and co-workers discovered that $NiCl_2$/butadiene was a proficient catalyst for the coupling of C_{sp^3} halides with alkyl or aryl Grignard reagents [95].

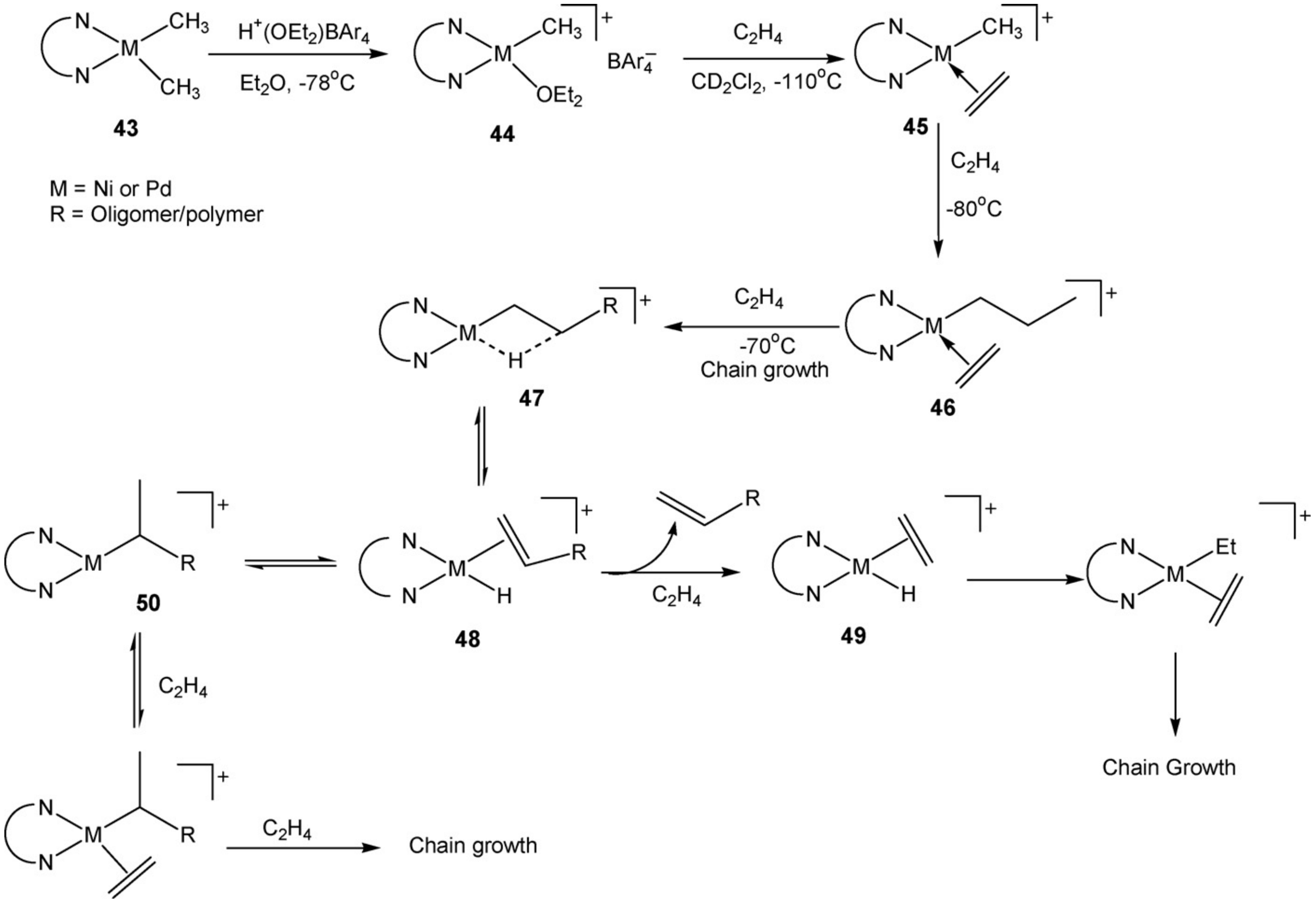
The use of iron cross-coupling catalysts as alternatives to Pd or Ni catalysts is attractive as iron complexes are inexpensive, readily available and environmentally friendly [92,96]. The simple iron complex $Fe(acac)_3$ is able to catalyze coupling of a wide range of aromatic and heteroaromatic halides with primary and secondary alkyl Grignard reagents in the presence of *N*-methylpyrrolidone (NMP) [95]. The development of rhodium cross-coupling catalysts has not been as extensive as for some of the other late transition metals. However, $[RhCl(C_2H_4)_2]_2$ in the presence of phosphine ligand can bring about multicomponent coupling reactions [103].

These are just a small selection of the many examples of useful carbon–carbon cross-coupling reactions catalyzed by the later transition metals. It is obvious, then, that the metals in groups VI to X play a crucial role in organic synthesis, and especially in the preparation of biologically active molecules. The dialkyl complexes generated in the catalytic cycle are essential to the formation of the final products.

6.2. *Catalytic intermediates in ethylene oligomerization and polymerization reactions*

A series of nickel(II) and palladium(II) dialkyl complexes of the type bearing substituted α-diimine ligands have been prepared and used for olefin polymerization. These complexes have been studied extensively. It is believed that the active species involved in olefin polymerization is a cationic alkyl complex [104–112]. Thus, designing well-defined cationic transition metal catalysts for olefin polymerization allows for detailed mechanistic studies of this important class of catalysts to be carried out [107–112].

Unlike the early transition metal catalysts that produce predominantly linear molecules, late transition metal catalysts (e.g. Ni, Pd) can yield either linear or highly branched polymers



Scheme 20. General polymerization and isomerization mechanism of ethylene.

depending on the type of ligand used [108–111,113]. In order to model the reaction of conventional olefin polymerization activators such as methylaluminoxane (MAO), nickel(II) as well as palladium(II) dialkyl complexes have been prepared and used in subsequent olefin polymerization reactions [108].

The proposed mechanism for ethylene polymerization is given in Scheme 20. This mechanism is similar to that proposed for olefin polymerization with early transition metal complexes. Here, nickel and palladium dimethyl (**43**) complexes are used as catalyst precursors [109,112,114] to generate the active cationic species (**44**). A dimethyl complex (**43**) is reacted with $H(OEt_2)_2BAr^f{}_4$ to produce a cationic diethyl ether adduct (**44**) with loss of methane. Insight into the mechanism was gained using low-temperature NMR studies and reaction kinetics [108,109,112]. These techniques demonstrated that the alkyl–olefin complex (**45**) was the catalyst resting state. Insertion of ethylene into complex (**45**) at −80 °C gave complex (**46**). Upon warming the reaction, a series of new alkyl olefin complexes were observed with ^1H NMR and ^{13}C NMR spectroscopy, which showed the presence of a β-agostic intermediate (**47**) [112].

This β-agostic species subsequently gives rise to an alkyl–olefin intermediate (**48**) which can eliminate to yield a terminal olefin. Further addition of ethylene to the resulting hydride gives rise to intermediate (**49**) which continues to grow, resulting in the formation of a linear polymer upon insertion of ethylene. Following β-hydride elimination the resulting olefin can reinsert with opposite regiochemistry (**50**) to produce a polymer with longer branches [112].

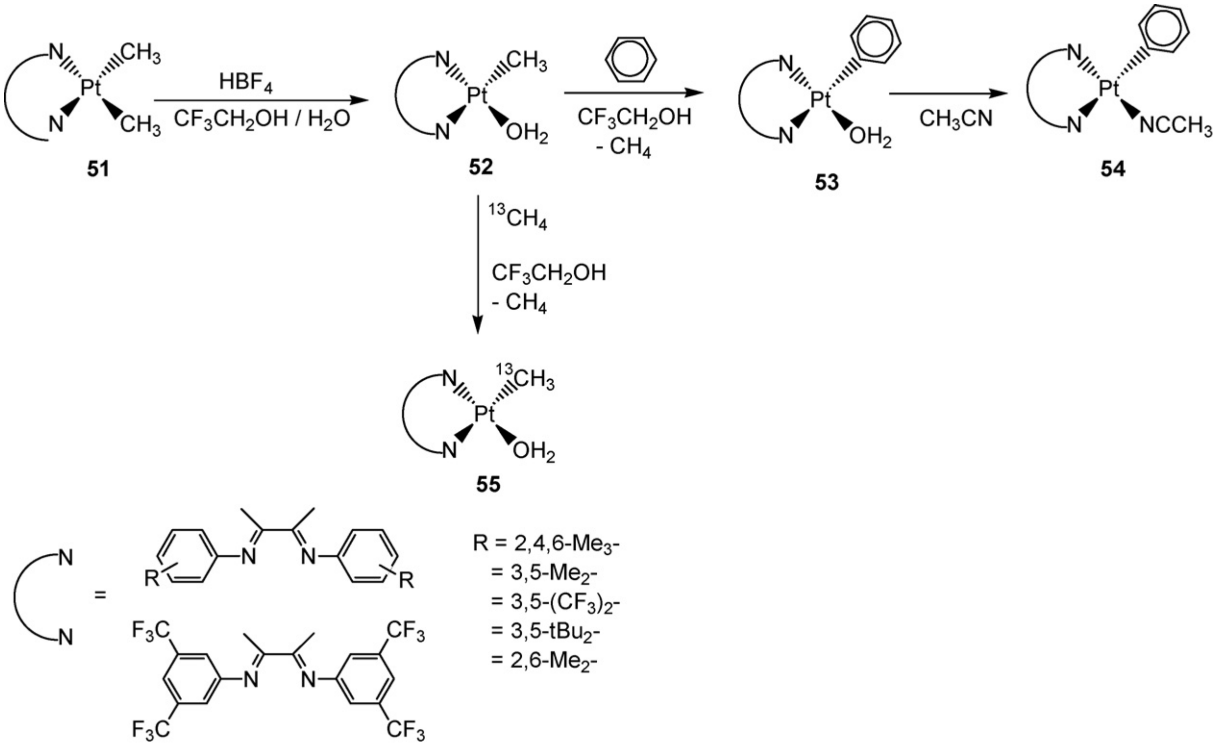
Recently, some iron dialkyl complexes of the type $FeR_2(py)_2$ ($R = CH_2SiMe_3$, CH_2Ph, $CH_2(CMe_2Ph)$) were prepared and found to be useful as models for iron-catalyzed olefin oligomerization/polymerization. $Ni(bipy)Et_2$, as well as other late transition metal dialkyl catalysts, have been shown to facilitate polymerization of acrylonitrile. Both $Ni(bipy)Et_2$ and $Fe(bipy)Et_2$ have been reported to catalyze cyclooligomerization of butadiene [115,48].

6.3. C–H activation reactions

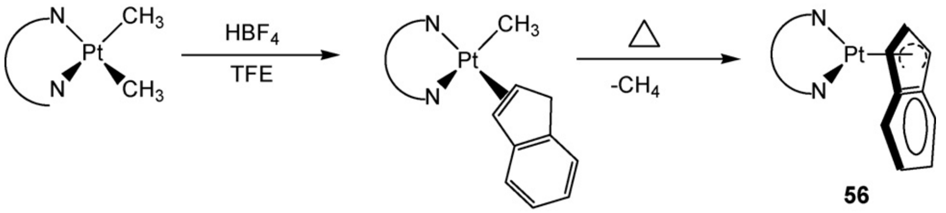
Development of selective catalytic transformation of alkanes has been one of the challenges facing organometallic chemists, owing to the difficulty in functionalizing a relatively inert C–H bond. Selective C–H bond activation is a potentially valuable approach to synthetic problems in areas ranging from fuel to fine chemicals. Early demonstrations by Shilov [116] and Garnett [117] that Pt(II)/Pt(IV) alkyl cationic salts could activate methane and benzene, spurred extensive research effort in the understanding of the electrophillic C–H activation process on the Pt center [118–121].

These cationic catalysts are generally prepared from Pt(II) dialkyl complexes. Catalysts containing diimine ligands have been studied extensively due to their ability to activate the C–H bond of methane and benzene under mild conditions [119] (Scheme 21).

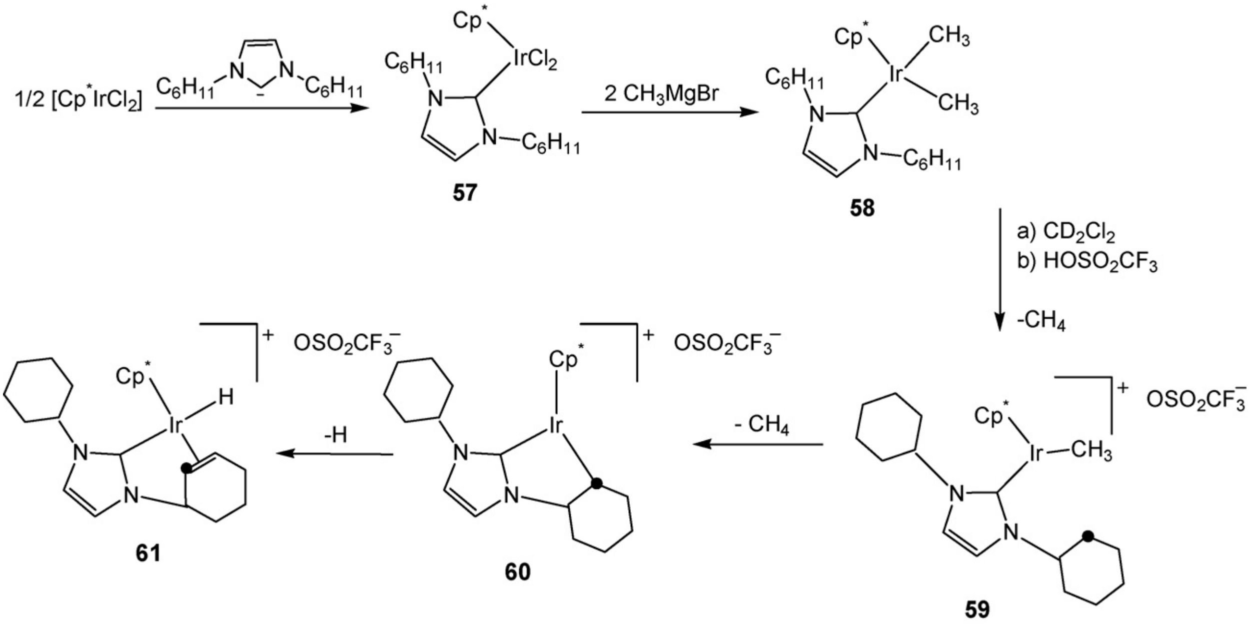
Protonation of the dimethyl complex (**51**) above with HBF_4 occurs in a weakly coordinating solvent that is polar enough to dissolve the cationic complex [119,120,122]. In the above case



Scheme 21. C–H activation of C_6H_6 and $^{13}CH_4$ [34,35].



Scheme 22. C—H activation of indene.



Scheme 23. Cyclohexyl C—H activation of the carbine [38].

2,2,2-trifluoroethanol (TFE), which has low nucleophilicity but is a strongly ionizing solvent, was found to be suitable. The water ligand in the aqua complex (**52**) was found to be strongly coordinating even with TFE as a solvent. The aqua complex was isolated and characterized by elemental analysis in addition to NMR spectroscopy. Complex (**52**) readily reacts with the C–H bond of benzene to give rise to a benzene-coordinated complex (**53**) with evolution of methane. Addition of acetonitrile to (**53**) results in formation of the nitrile complex (**54**). In the same way, complex (**52**) readily reacts with methane ($^{13}CH_4$) giving rise to complex (**55**) with evolution of methane (CH_4) [119].

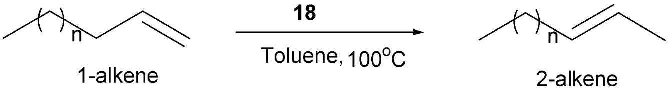
C–H activation of substrates such as indene has been reported in the literature. Firstly, a stable indene complex forms which upon gentle heating results in the formation of an η^3-indene complex (**56**) [120] (Scheme 22).

Sometimes C–H bond activation can take place within a complex, in which an adjacent C–H bond of the ligand can undergo a reaction with the electrophilic metal centre as shown in Scheme 23.

Treatment of iridium dichloride complex (**57**) with two equivalents of CH_3MgBr yield the corresponding dimethyl complex (**58**) which is easily protonated by replacement of one CH_3 with a trifluoromethylsulfonic acid to yield complex (**59**) with immediate loss of CH_4. C–H activation of the cyclohexyl ring results in further loss of CH_4 to give complex (**60**) followed by an instantaneous formation of the hydride (**61**) [123].

6.4. 1-Alkene isomerization reactions

Our recent studies showed that platinum-dialkyl complexes, for example, dialkylplatinum(II)(dppp) (**18**), can act as useful catalysts for the quantitative isomerization of 1-alkenes to 2-alkenes (Eq. (18)) [124]. Experiments are currently being carried out to shed more light on the mechanism of these catalytic reactions [21].



(18)

7. Conclusions and future aspects

From the present review we see that a fairly large number of dialkyl transition metal compounds are known. Many of these contain alkyl groups with no hydrogen on the β-carbon atoms, e.g. di-methyl, di-benzyl and similar compounds. However there are a significant number of dialkyl compounds known which could either decompose *via* β-hydride elimination or reductive elimination—and yet the compounds can be isolated and characterized and in some cases can be quite thermally stable. Clearly, this depends on the nature of the metal and associated ligands. For example, complexes of the type *cis*-$Os(CO)_4R_2$ are remarkably stable and even when they decompose, they do not undergo reductive elimination. In other cases, e.g. with PdL_2R_2 species, which are key intermediates in catalytic coupling reactions, the reductive elimination step is facile.

Metal-dialkyl compounds can thus undergo reactions that are not possible for mono-alkyl compounds. Metal-dialkyl compounds can also be models for catalytic species where two alkyl groups are bonded to the same metal site in either homogeneous or heterogeneous catalytic reactions. Further studies on metal-dialkyl compounds are likely to reveal new information on the factors affecting their stability and reactivity and the extent of their involvement in catalytic reactions. We expect to see some interesting new chemistry of metal-dialkyl compounds in the future.

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