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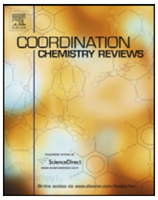

Review

Hydrocarbon (π- and σ-) complexes of nickel, palladium and platinum: Synthesis, reactivity and applications

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ABSTRACT

With the exception of metallocenes, transition metal complexes with hydrocarbon ligands only are rare. However, complexes of this type containing Group 10 metals are known and have been shown to be quite stable. These complexes are versatile precursors for many organometallic compounds. In addition, such compounds can play an important role in many reactions including C–H or C–C activation reactions and have useful applications in the thermal and photochemical production of metal films by chemical vapour deposition (CVD). The present review summarizes the synthesis, properties and chemistry of hydrocarbon complexes of Group 10 metals of the type L_nM or $L_nMR_1R_2$ (where L_n = σ- or π-hydrocarbon ligands; M = Ni, Pd and Pt; R_1, R_2 = σ-hydrocarbon ligands) without the involvement of any hetero donor ligands such as N, P, O and S in the metal coordination spheres.

1. Introduction

Research on hydrocarbon ligands coordinated to transition metals lies at the heart of organometallic chemistry and still continues to attract much research activity [1]. This is partly due to the importance associated with the functionalization of hydrocarbons through activation of C–H bonds. The oxidative addition of C–H bonds and even C–C bonds to metals is a highly topical area of research. The activation of inert hydrocarbons by binding to transition metals with subsequent functionalization could lead to new processes in organic synthesis

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Abbreviations: COD, 1,5-cyclooctadiene; COT, cyclooctatetraene; Cp, cyclopentadienyl; Cp„ pentamethylcyclopentadienyl; Cp^{1}, tetramethylcyclopentadienyl; py, pyridine; bpy, bipyridine; nor, norbornyl; tmsb, 1,4-bis(trimethylsilyl)-1,3-butadiyne; dpbd, 1,4-diphenylbutadiene; c,c,c-cdt, *cis,cis,cis*-1,5,9-cyclododecatriene; acac, acetylacetonate; Isodicp, isodicyclopentadienyl.

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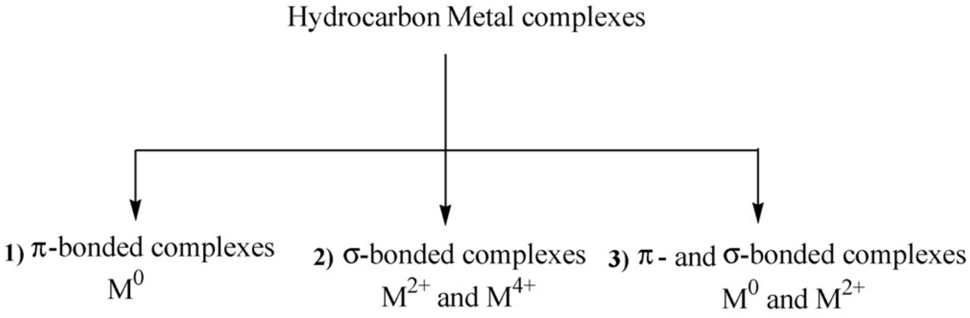


Scheme 1. Classification of hydrocarbon metal complexes.

and the conversion of hydrocarbons into more useful products [2].

The nature and reactivity of organic ligands are influenced by transition metals in terms of redox potential, polarity, steric, stereo chemical and regiochemical properties. In many cases, coordination to the metal imparts significant electrophilic character to the hydrocarbon moiety. Many transition metal complexes containing cyclic π-hydrocarbon ligands are also known, in particular cyclic dienyl and trienyl complexes [3]. During the past few decades, a large amount of work has been devoted to mechanistic and structural studies as well as the synthesis and applications of organometallic compounds. The reactivity of these complexes as well as their reaction mechanisms with nucleophiles including single and double addition to the coordinated ring, substitution of a ring substituent, e.g. chloride, deprotonation of the coordinated ring or a side chain, ligand substitution and single electron transfer have been studied [3].

The main focus of this review is to survey the synthetic procedures, chemical properties and the applications of hydrocarbon complexes of nickel, palladium and platinum where the metal atom is coordinated only to hydrocarbon ligands. These complexes have been known from the early days of organometallic chemistry [1,4] and have been shown to be valuable starting materials in many synthetic procedures as well as key intermediates in many industrial catalytic processes. In addition, they are involved in fundamental organic transformations such as C–H bond activation through cyclometalation and β-hydride elimination [5]. These metal–hydrocarbon complexes also serve as models for understanding the interaction of organic moieties with metal surfaces.

The presence of metal–hydrocarbon species in catalytic cycles as intermediates and their highly reactive nature have spurred the development of interesting and useful chemistry of various metal-alkyls, metal-alkenyls and metallacycloalkane compounds [6–9].

Group 10 metal complexes with coordinated ethylene or cycloalkenes have been known for decades and complexes such as $M(COD)_2$ (**1**) have been reported widely and are used in many synthetic procedures [10]. There is also a broad knowledge base of the chemistry of the phosphine derivatives of these species, such as PtL_2R_2 (where L = P donor ligand) [1].

However, stable metal alkyl complexes without ancillary donor ligands, are very rare with exception of the controversial $[Pt(CH_3)_4]_4$ (**10**) and $Pt_2(CH_3)_6$ (**11**) complexes [11]. Several early reports of these species were subsequently shown to be incorrect and both species are now presumed nonexistent [11]. A significant number of theoretical investigations on the stability and reactivity of M-dialkyl and M-tetraalkyl (M = Pt, Pd, Ni) species have also been reported [12]. Apart from this, an elegant synthesis of nickelaspirocyclononane, a stable tetraalkyl complex of nickel(IV) has also been reported recently [13]. Some of our recent research has revealed the formation of a variety of 12 and 14 electron “naked” organoplatinum complexes from olefin–metal complexes [14]. This prompted us to determine the scope of this field and hence this review.

Reactions catalyzed by transition metals proceed through catalytic cycles involving metal complexes in different oxidation states. Gaining understanding of the mechanistic details of catalyzed reactions may pave the way for the design of new and improved catalysts. Consequently, metal complexes with higher oxidation states can be readily detected and characterized by various spectroscopic and electro-analytical methods [15].

The catalytic applications of hydrocarbon metal complexes have been explored extensively [16]. The Fischer–Tropsch reaction, the conversion of synthesis gas (a mixture of carbon monoxide and hydrogen) to hydrocarbons is a good example of a process in which bridged-intermediates of the type $M–(CH_2)_n–M$ play key roles in the reaction pathway, a view that has received some support from very recent mechanistic studies. Olefin polymerization, catalytic reforming for the production of gasoline and aromatic hydrocarbons as well as the catalytic tetramerization of butadiene are also known to proceed via $M(hydrocarbon)_n$ intermediates [17].

Even though the participation of organometallic complexes *in vivo* is known, the bioorganometallic chemistry of olefin, cyclopentadienyl and arene metal complexes has not yet been explored. Nickel–carbon bonds are strongly suspected of participating in biological processes since Ni has been shown to be present in a variety of enzymes, which catalyze several processes [18].

To the best of our knowledge, this is the first direct review article on Group 10 metal complexes where the metal is surrounded solely by hydrocarbon ligands in various bonding modes. The scope of this review will be limited to hydrocarbon ligands only and we will not include compounds to which any heteroatoms such as P, N, O and S are bonded directly to the metal atom. But the option of keeping these hetero donor ligands as well as other heteroatoms present somewhere in the molecule away from the metal centre is considered in order to assess the factors associated in the stability of these compounds. These compounds are classified as shown in Scheme 1. Chart 1 shows some examples of each type of hydrocarbon metal complexes.

2. Synthesis and reactivity of hydrocarbon complexes of nickel, palladium and platinum

Despite their significance and importance in organometallic chemistry, catalysis as well as other applications, $metal(hydrocarbon)_n$ complexes have proved to be remarkably difficult to isolate and characterize completely. Many compounds, however, have been successfully characterized by increasing their stability through addition of various hetero donor ligands such as tertiary phosphines. Some of the hydrocarbon–platinum compounds that we have prepared have been structurally characterized by X-ray crystallography as well as by various spectroscopic techniques. Most of these compounds have been found to be ther-

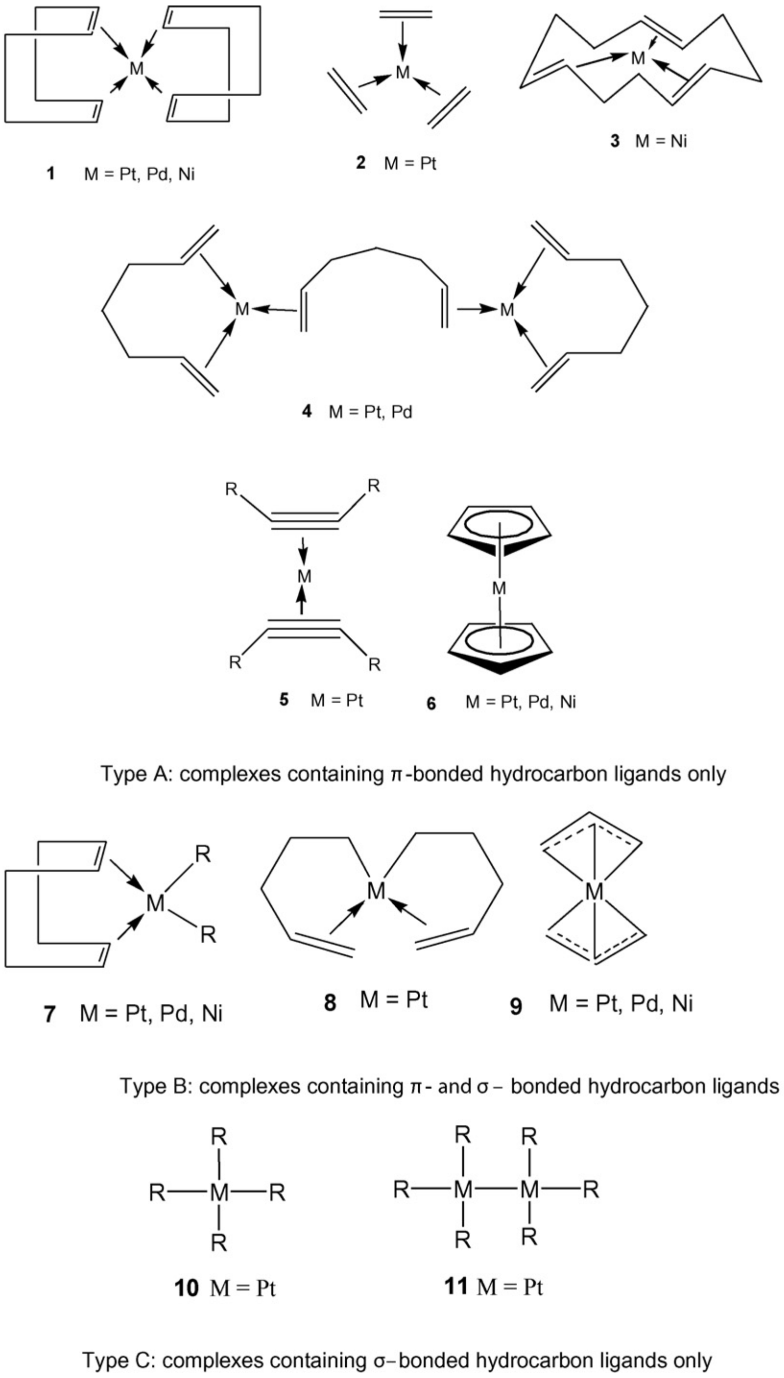


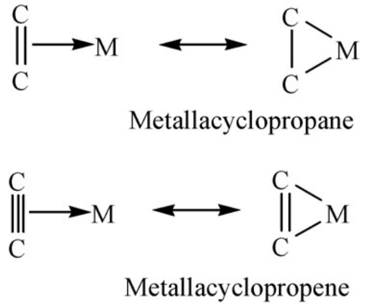
Chart 1. Type A: complexes containing π-bonded hydrocarbon ligands only. Type B: complexes containing π- and σ-bonded hydrocarbon ligands. Type C: complexes containing σ–bonded hydrocarbon ligands only.

mally sensitive and degrade readily to form their corresponding zerovalent metal species. We have also observed that σ-bonded platinum complexes containing β-hydrogen are much more reactive than the π-bonded platinum complexes. However, a significant problem with metal–hydrocarbon complexes in various reactions is identifying the active species in the process and thereby establishing the mechanism of the reaction. The stability and reactivity of these complexes have been found to be sensitive to the experimental conditions.

Firstly we summarize and assess key synthetic routes which have been used to prepare hydrocarbon–metal complexes. In this review, synthesis and reactivity sections are inseparable as the reactions of these metal–hydrocarbon complexes with various reagents lead to a variety of novel organometallic compounds.

2.1. Metal–olefin complexes

Metal–olefin complexes of the types **1**–**6**, with π-bonding, are very well known as useful precursors for many interesting organometallic reactions [19]. Preparation of the tris(ethylene)platinum complex, **2** by Stone and co-workers [20], opened a new area of research with many potential chemical applications. Factors that can influence the reactions of unconjugated metal–olefin complexes are: (1) the thermodynamic stability



Scheme 2.

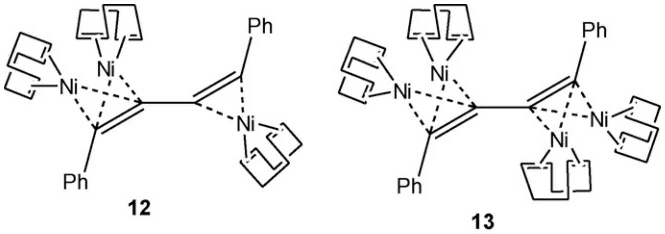


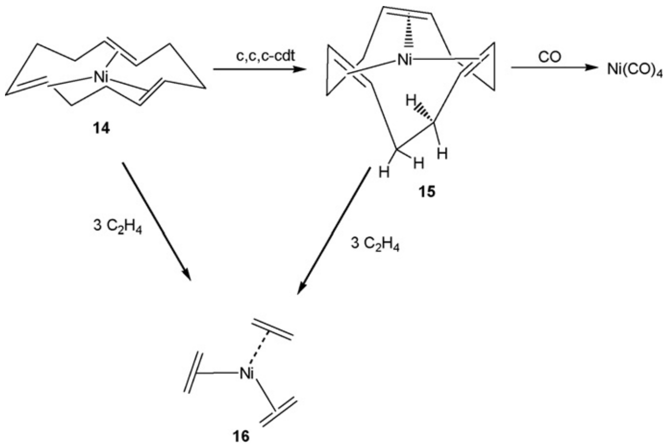
Chart 2.

of these complexes which is strongly influenced by the nature of the olefin, (2) the presence of electron withdrawing substituents on the olefin which increases the stability of the complex, (3) the geometry of the more stable complex is invariably formed with *cis* olefins, (4) complexes of ring-strained cycloalkenes such as cyclopropene, *trans*-cyclooctene and norbornene are surprisingly stable and (5) a high stability is exhibited by chelating olefins in various complexes. Studies on the platinum–olefin and –acetylene complexes also show that the nature of the bonding can be better described as being metallacyclopropane or metallacyclopropene in some of their reactions as shown in Scheme 2 [20].

The yellow crystalline complex $Ni(COD)_2$ is synthesised through reduction of nickel-bis(acetylacetonate) in the presence of 1,5-cyclooctadiene (Eq. (1)) and serves as an alternative and less toxic source of Ni(0) and $Ni(CO)_4$ [21,22]. $Ni(COD)_2$ is air sensitive as a solid and is even more so in organic solvents [21,23]:

$$Ni(C_5H_7O_2)_2 \xrightarrow[\text{[COD]}]{Et_3Al} Ni[COD]_2 \qquad (1)$$

Reaction of $Ni(COD)_2$ with 1,4-diphenylbutadiene (dpbd) in *n*-pentane for 2 h produced the trinuclear nickel compound **12** whilst a similar reaction stirred for 18 h produced the tetranuclear nickel cluster **13** with the hydrocarbon ligand in an η^2,η^2-bridging mode (Chart 2). Coordination of the dpbd ligand in **12** and **13** results in bending of the butadiyne moiety backbone from the normal 180° for free butadiyne to 146°. Also observed is a lengthening of acetylenic bonds to which the two nickel atoms, coordinated with distorted tetrahedral geometry, are bound at distances comparable to those for C–C double bonds. This is as a result of significant back-bonding from the Ni atoms to dpbd [24,25].



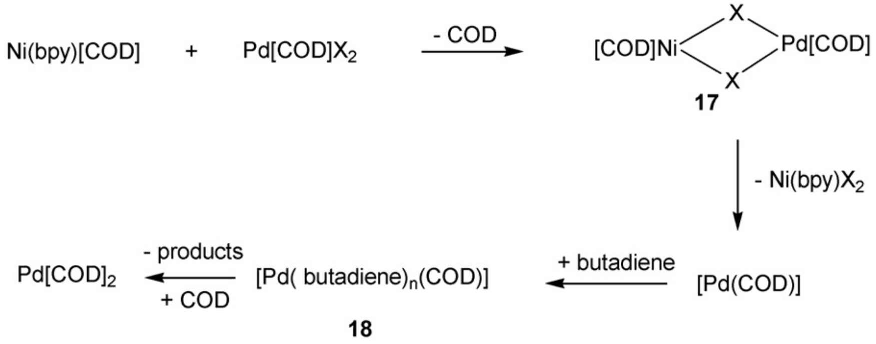
Scheme 3.

Maekawa and co-workers have reported multinuclear nickel(0) complexes of the type $[Ni_4(dpbd)(COD)_4]$ with the dpbd ligand coordinated in an η^1, η^2-bridging mode and $[Ni_3(tmsb)(COD)_3]$ [26].

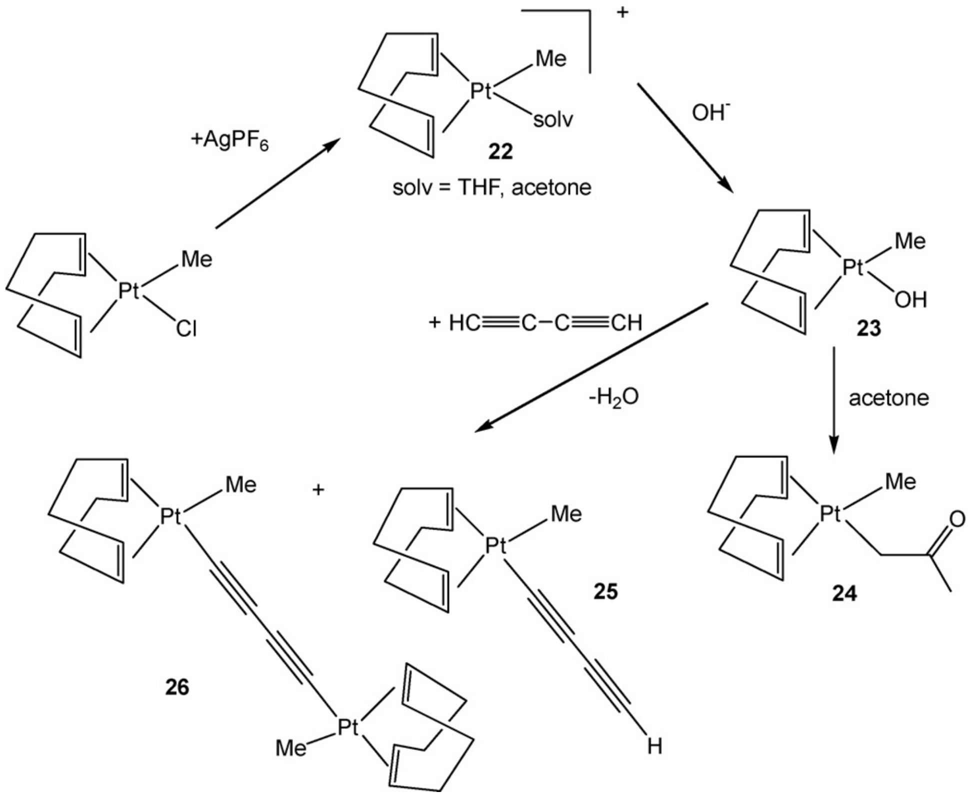
The reaction of **14** with 1 equiv. of c,c,c-cdt yielded the complex **15**. At low temperatures, complex **15** reacts with ethene to afford **16**. This result is in accord with restricted back-bonding between Ni and the olefinic carbons in **14** and **15**. The formation of **16** is a sharp contrast between stability and reactivity of **14** and **15** and those of similar Cu(I) complexes as the stabilization of the Ni(0) complexes by the chelate and macrocyclic effects in cyclopolyene ligands is not sufficient to retard the reactions with ethane to give **16**. In a similar way, **15** reacts with 4 equiv. of CO by displacement of the c,c,c-cdt ligand to yield $Ni(CO)_4$ (Scheme 3) [27].

Reactive low-valent palladium-alkene complexes of the type $Pd[COD]_2$ and $Pd(nor)_3$ compounds were prepared from $Pd[COD]X_2$ using also synthesized by zerovalent complex [Ni(bpy)(COD)] as a mild reducing reagent (Scheme 4). A possible mechanistic pathway for the formation of $Pd[COD]_2$ via the formation of the intermediate species **17** and **18** has been proposed [28].

The homoleptic dinuclear $M_2(\eta^2\text{-1,6-diene})_3$ (**19**) complexes were synthesized by the reaction of $M[COD]Cl_2$ with $Li_2(COT)$ in a 1,6-diene/diethyl ether mixture (M = Pd, Pt; 1,6-diene = 1,6-heptadiene or diallyl ether; COT = cyclooctatetraene) [29] (Eq. (2)). Upon treatment with additional 1,6-diene mononuclear complexes of the type $M(\eta^2\text{-1,6-diene})_2$ were obtained. Reaction of

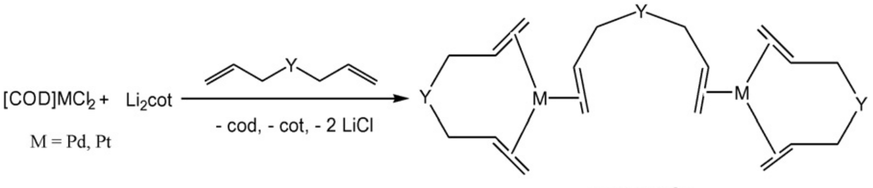


Scheme 4.



Scheme 5.

the dinuclear complexes with ethene resulted in the formation of mononuclear M(η^2-C_2H_4)(η^2-1,6-diene) complexes. The dinuclear M_2(η^2-1,6-diene)$_3$ (**19**) and M(η^2-1,6-diene)$_2$ complexes (M = Pd, Pt) are among the most reactive sources for naked Pd^0 and Pt^0 [29].



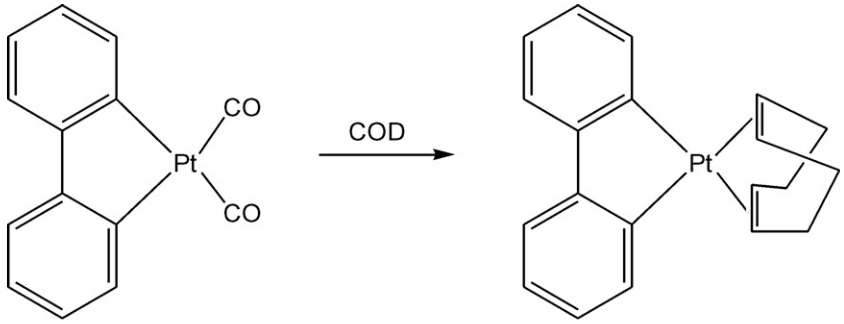
19a: Y = CH_2
19b: Y = O

(2)

The alkene platinum(0) compounds such as Pt(COD)$_2$ and Pt(η^2-norbornene)$_3$ are generally synthesized by the reduction of platinum(II) complexes [30]. Bis(η^2-alkyne)platinum(0) complexes Pt(η^2-R^1CCR^2)$_2$, with substituted alkynols and alkynediols have been prepared by the reaction of Pt(COD)$_2$ with 2 equiv. of R^1CCR^2 [31,32].

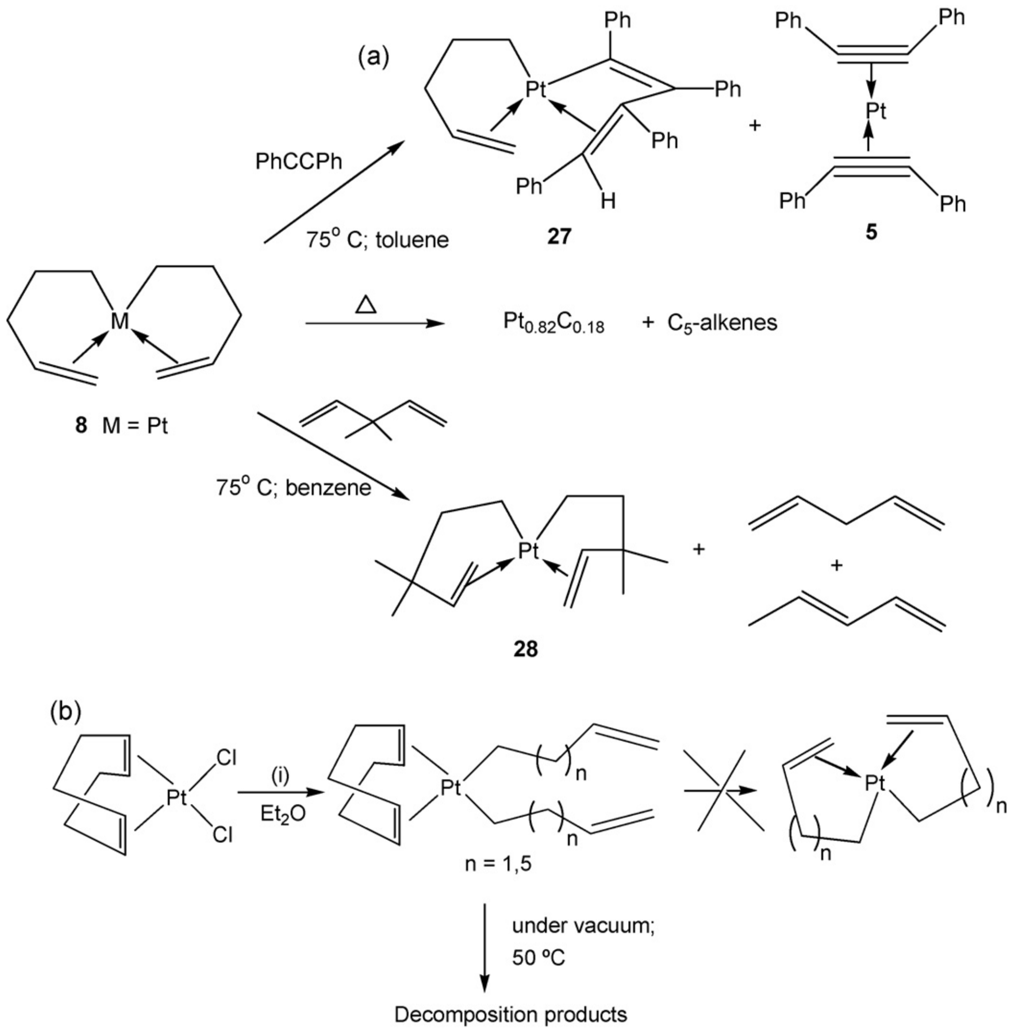
In many reactions, Pt(COD)$_2$ affords products containing a Pt(COD) fragment whilst [Pt(C_2H_4)$_3$] serves as a major source of naked platinum(0). The chemistry of the phosphine derivatives of these species has been extensively studied [1]. Group 10 metal complexes containing coordinated ethylene or cycloalkenes have been known for decades and complexes such as M(COD)$_2$ (**5**) have been reported widely in many synthetic procedures [1].

An interesting neutral platinum carbonyl complex, Pt(biphenyl)(CO)$_2$ (**20**) has been prepared by bubbling CO through a CH_2Cl_2 solution of the dimer, [Pt(biphenyl)(C_2H_5)$_2$S]$_2$ [33]. On reaction with COD, the carbonyl ligands in **20** were displace and Pt(biphenyl)(COD) (**21**) was formed (Eq. (3)).



20 **21**

(3)

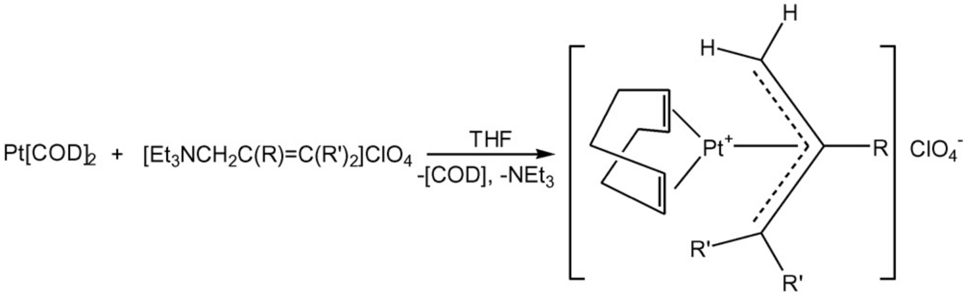


Scheme 6.

The square planar cationic alkylplatinum(II) complexes (**22**) with a labile ligand have been shown to activate methane and benzene as well as insert alkenes or CO into the platinum–carbon bond. Complex **23** reacts with acetone to give **24**. It has been shown that the other C–H acidic compounds such as phenylacetylene and 1,3-butadiyne react with complex **9** to yield dimeric (**25**) and monomeric (**26**) complexes as shown in Scheme 5 [34].

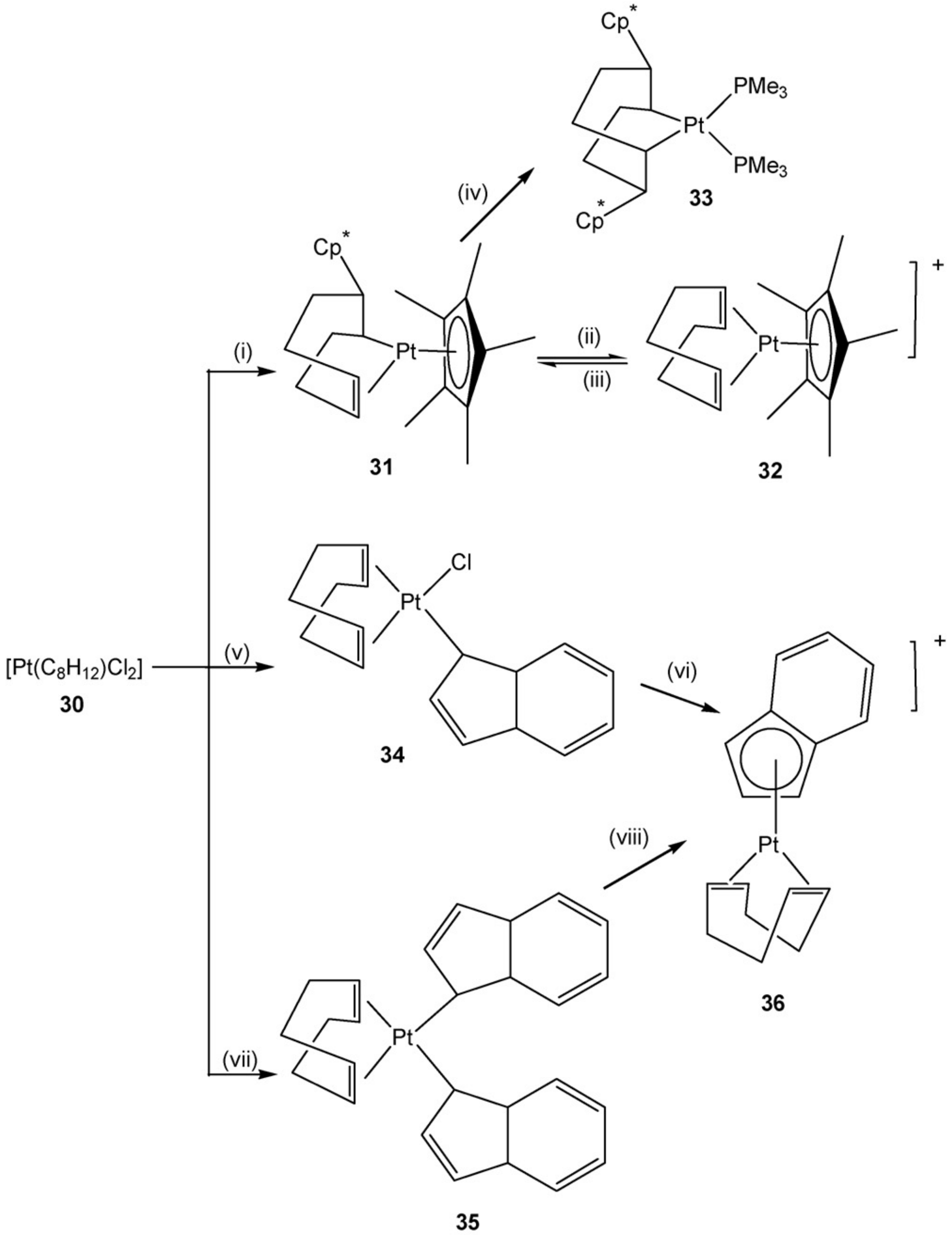
The preparation of the bis(4-pentenyl)platinum complex (**8**) was carried out by the reaction of $PtCl_2(COD)$ with the corresponding Grignard reagent formed *in situ*. Complex **8** was obtained after removal of COD *in vacuo*. The molecular structure of this complex revealed interesting structural features. As the pentenyl ring is puckered, aliphatic hydrogens may appear in a pseudo-axial or pseudo-equatorial position. On thermolysis, **8** produces a Pt–C thin film and can be used in CVD studies as a precursor. In contrast, thermolysis of **8** in the presence of diphenylacetylene completely inhibited the deposition of colloidal Pt(0), leading to the formation of organoplatinum complexes **27** and **5**. The mechanistic aspects of this reaction were discussed [35]. Heating complex **8** in the presence of 3,3-dimethyl-1,4-pentadiene in toluene yielded complex **28** and this complex is more stable than the precursor, **8**(Scheme 6a) [35]. We have attempted to make analogous compounds to **8** with different alkenyl chains (Scheme 6b), but the resulting bis(1-alkenyl)platinum(II)(COD) compounds did not yield the expected alkene coordinated species, i.e. similar to **8** under the experimental conditions used in our study. Instead, it was found that the bis(1-alkenyl)platinum(II)(COD) decomposed at 50 °C under reduced pressure. Further studies on these interesting systems are underway [14].

The complexes $[Pt(\eta^3\text{-}CH_2CR^1CR^2{}_2)(COD)]^+$ (**29a**, R = H, R^1 = H; **29b**, R^2 = H, Me; R^1 = Me, R^2 = H) were prepared from the reaction of $Pt(COD)_2$ as a precursor (Eq. (4)) [36].

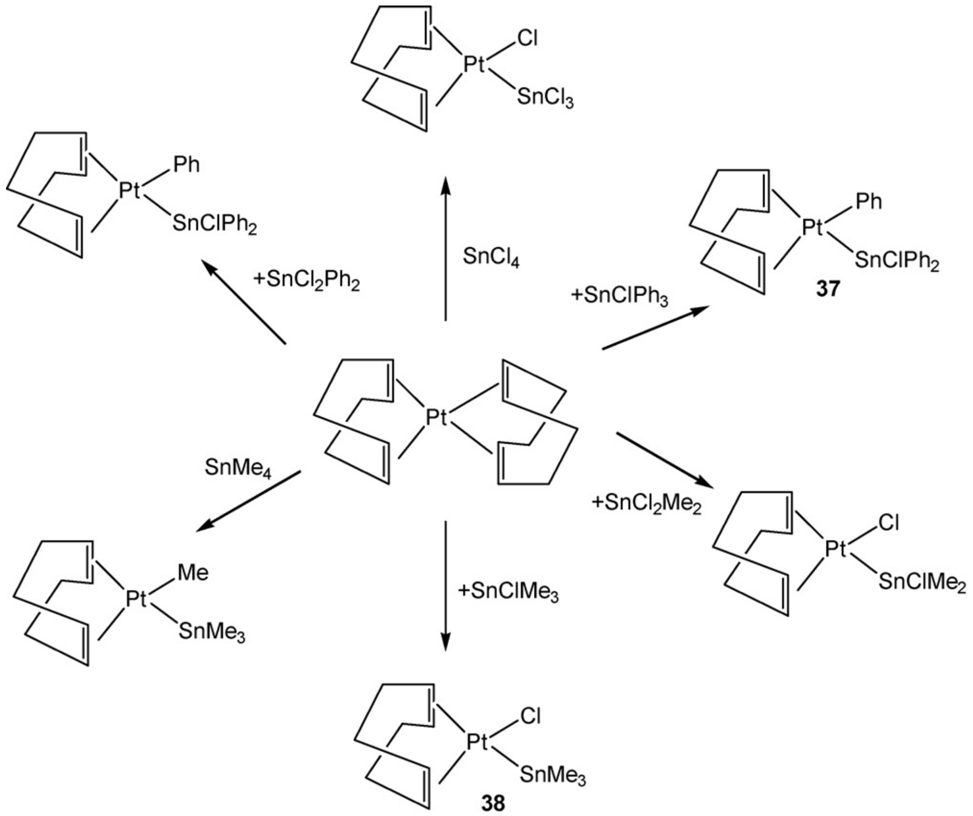


29a, R = R' = H;
29b, R = Me, R' = H;
29c, R = H, R' = Me

(4)



Scheme 7. (i) NaCp* or LiCp* (2 equiv.) in THF; (ii) $HBF_4.Et_2O$ in pentane at −78°; (iii) LiCp* in THF; (iv) excess PMe_3 in THF for 12 h; (v) NaInd (1 equiv.) in THF for 12 h; (vi) $AgBF_4$ (1 equiv.) in CH_2Cl_2; (vii) NaInd (2.5 equiv.) in THF for 12 h; (viii) $HBF_4{\cdot}Et_2O$ at −78°C.

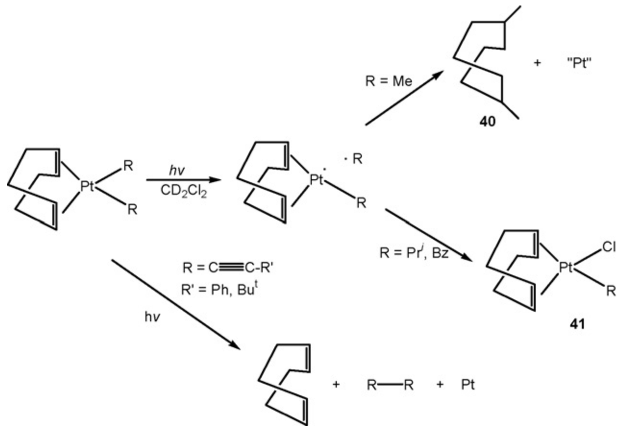


Scheme 8.

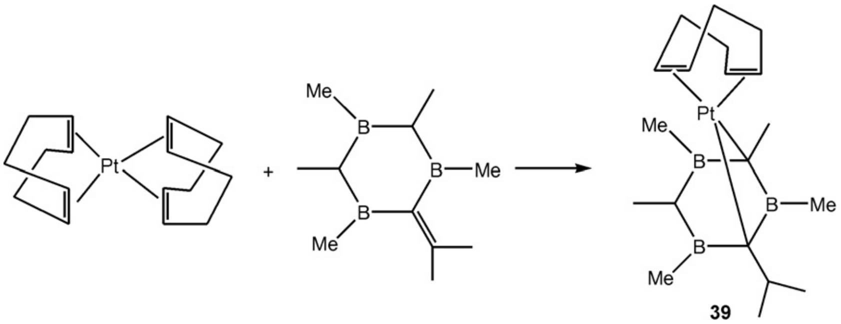
O'Hare has reported a variety of pentamethylcyclopentadienyl platinum complexes using [Pt(η-C_8H_{12})Cl_2] (**30**) as a precursor (Scheme 7) [37]. The reaction of **30** with 2 equiv. of NaCp* or LiCp* in THF yielded [Pt(η-C_5Me_5){σ:η^2-C_8H_{12}(Cp*)}] (**31**), which can undergo an elimination reaction to give **32** on interaction with protic acids. The complex **31** in the presence of an excess of PMe_3 yielded **33** by the addition of two phosphine ligands with concomitant migration of the Cp* ligand to the cyclooctadienyl ligand. In contrast to the chemistry of Cp* derivatives, treatment of **30** with 1 equiv. of NaInd (Ind = C_9H_7) afforded the stable mono(η^1-indenyl) derivative **34**. Abstraction of Cl^- from **34** by $AgBF_4$ resulted in the formation of an isomerised product **36**. The same product, **36** was formed by protonation of **35** with HBF_4 (Scheme 7).

Reaction of chloro(triphenyltin)with $Pt(COD)_2$ yielded the phenylplatinum complex, **37** with a chlorodiphenylstannyl ligand via oxidative addition, in contrast to the reaction with chloro(trimethyl)tin, which yielded **38** [38] (Scheme 8).

The boron substituted platinacyclobutane **39** has been prepared from the reaction of 1,3,5-trimethyl-2-isopropylidene-4,6-dimethyl-1,3,5-triboracyclohexane with $Pt(COD)_2$ (Eq. (5)) [39].



Scheme 9.



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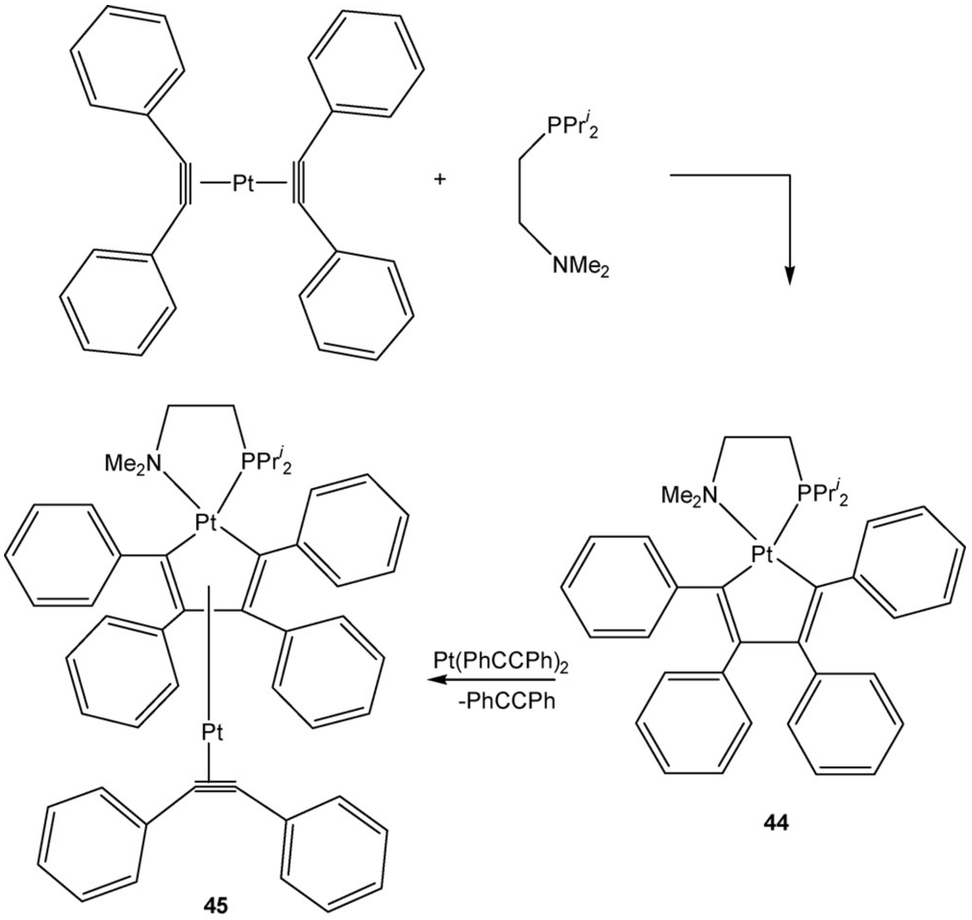
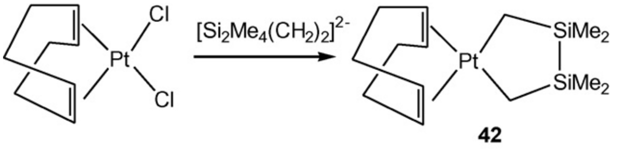


Scheme 10.

Organoplatinum complexes such as $PtR_2[COD]$ (where R = alkyl or aryl) have been synthesized and the chemistry of these precursors has also been explored [40]. These dialkylplatinum complexes with the COD ligand have been shown to undergo photolysis at $\lambda_{max} > 320$ nm in CD_2Cl_2. The products **40** and **41** are formed via photochemically induced homoleptic dissociation of a Pt–C bond as shown in Scheme 9 [41].

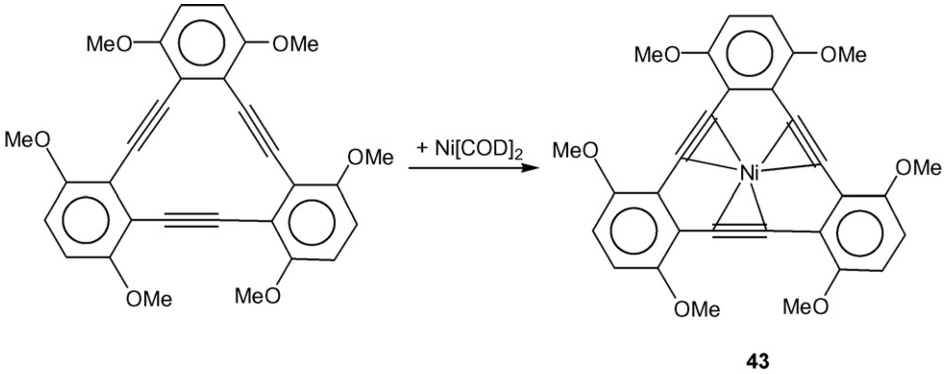
Reaction of the dianion of hexamethyldisilane with $PtCl_2(COD)$ yielded a disila-1-platinacyclopentane with COD ligand, **42** as shown in Eq. (6) [42].



(6)

2.2. Metal–alkyne complexes

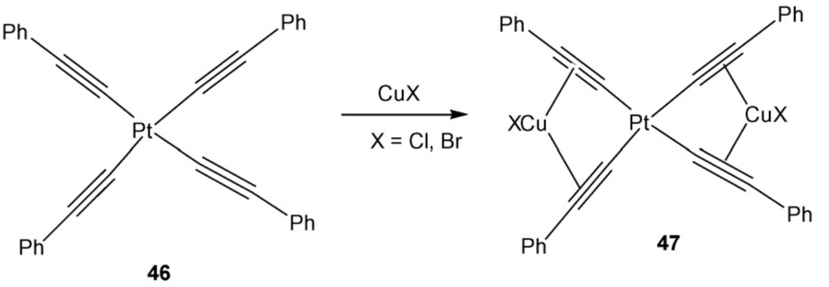
Reaction of $Ni(COD)_2$ with methoxy functionalized tribenzocyclotriynes, substituted with methoxy groups, in benzene resulted in the formation of nickel(0) complex of 5,6,11,12,17,18-hexadehydro-1,4,7,10,13,16-hexamethoxytribenzo[*a*,*e*,*i*] cyclododecene (**43**) as shown in Eq. (7) [43].



(7)

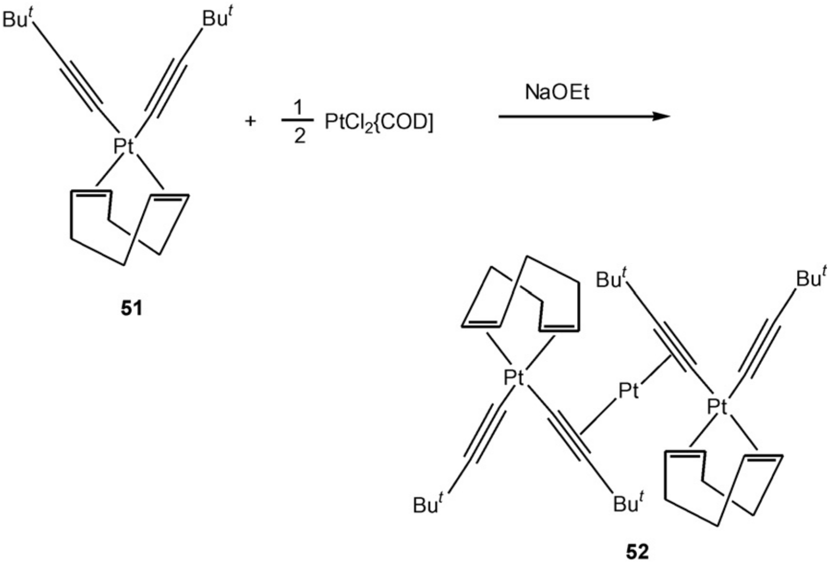
The platinum–alkyne complex $Pt(PhC{\equiv}CPh)_2$ is known as a useful precursor for many interesting organometallic products. This platinum(0) complex reacts with a P,N-chelating ligand to form the platinacyclopentadiene (**44**), and addition of $Pt(PhC{\equiv}CPh)_2$ to **44** gives **45** as stable product where the 5-membered metallacycloalkene ring is coordinated to the Pt(PhC≡CPh) fragment (Scheme 10) [44].

The complex $Pt_2Cu_4(CCPh)_8$ (**47**) has been prepared from **46** [45,46] (Eq. (8)). In a similar way, other metal complexes with Ag [47], Cd [48] and Tl [49] have been prepared and characterized (Scheme 11).



(8)

The dialkylnylplatinate dianion (**48**) with perfluorophenyl ligands has been converted to $Tl_2Pt(C_6F_5)_2(CCPh)_2$ (**49**) and **50** with 2 mol of $[Cu(bipy)]^+$ [50,51]. In a similar way, various derivatives of **48** reacts with $[M(\mu\text{-}Cl)(COD)]_2$ (M = Rh, Ir) to yield the corresponding alkyne coordinated metal complexes [52,53]. A trinuclear platinum [Pt(II)–Pt(0)–Pt(II)] complex, **52** was formed by the coordination of alkynyl ligands in a σ- and π-fashion from **51** [54] (Eq. (9)).



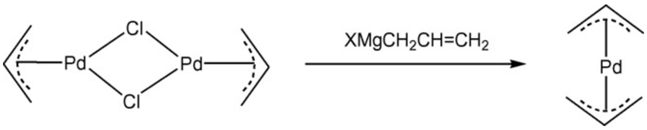
(9)

2.3. Metal–allyl complexes

In contrast to the other group 10 transition metals, very few organopalladium complexes containing only hydrocarbon ligands have been reported. In general, palladium complexes with hydrocarbon ligands are usually stabilized by electron-rich phosphine ligands. The most frequently studied organopalladium complexes of the type under review are $Pd(\eta^3\text{-allyl})_2$ and $CpPd(\eta^3\text{-allyl})$.

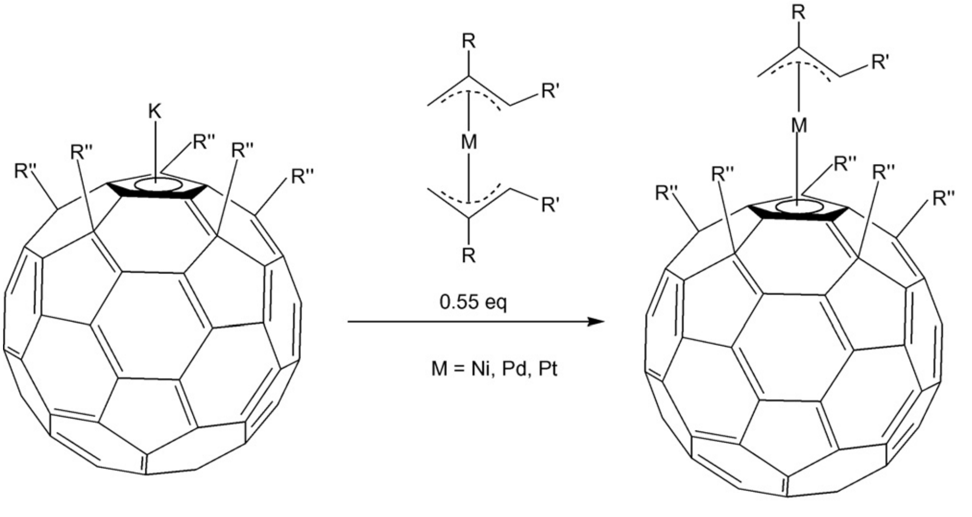
A number of methods are available for the preparation of the homoleptic organopalladium complex $Pd(\eta^3\text{-allyl})_2$. These complexes have been shown to form as intermediates in palladium catalyzed oligomerization, cyclooligomerization and telomerization reactions involving 1,3-dienes and have thus been the focus of a number of studies [55,56].

Reaction of either $PdCl_2$ or the π-allylic palladium chloride dimer $[PdCl(\eta^3\text{-allyl})]_2$ with the corresponding Grignard reagent affords the bis(allyl)palladium complex (Eq. (10)). This compound can also be prepared in high yield by the alkylation of palladium(II) acetate using a Grignard reagent [57].



(10)

The π-allylic metal chloride dimer $[MCl(\eta^3\text{-allylic})]_2$ (M = Ni, Pd and Pt; allylic = allyl, and/or methylallyl and/or crotyl) has also been used as starting material for the synthesis of $(\eta^5\text{-}C_{60}R_5'')M(\eta^3\text{-}CH_2CRCHR')$ complexes where metal is coordinated to a fullerene ligand (**53**, R = R′ = H, M = Ni, Pd; **54**, R = Me, R′ = H, M = Ni, Pd; **55**, R = H, R′ = Me; R″ = Me, Ph, M = Ni, Pd; and **56**, R = Me; R″ = Me, Ph, M = Pt). These complexes were prepared by transmetalation of the potassium salt of Me or Ph substituted C_{60} in yields of 21–71% (Eq. (11)) [58].



53, R = R = H, M = Ni, Pd;
54, R = Me, R = H, M = Ni, Pd;
55, R = H, R = Me; R = Me, Ph, M = Ni, Pd; and
56, R = Me; R = Me, Ph, M = Pt

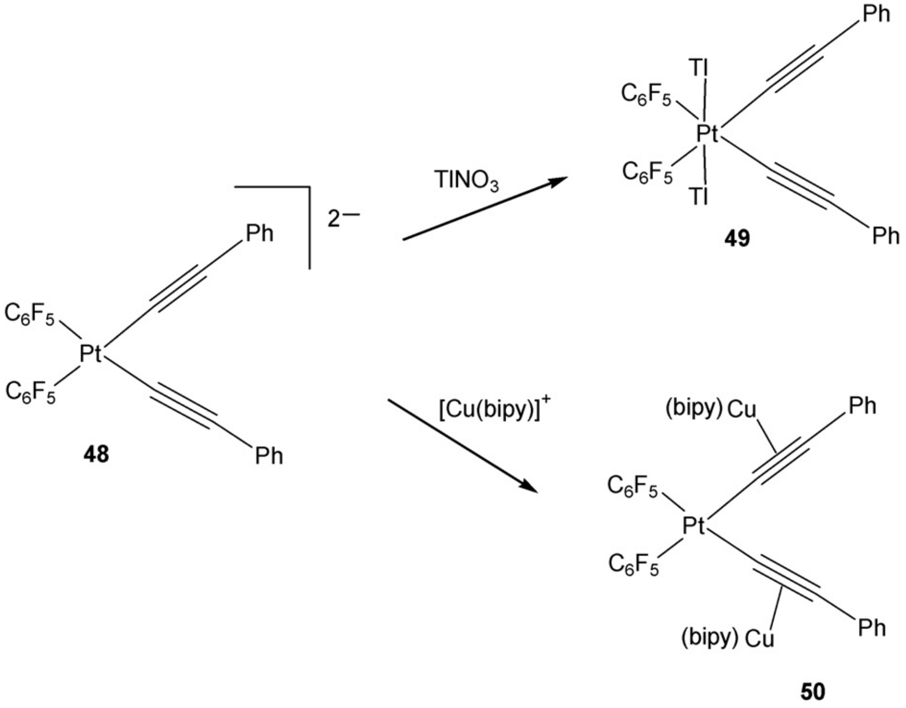
(11)

The structures of the (η^5-$C_{60}Me_5$)Pd(η^3-CH_2CRCHR') complexes (R = R′ = H and R = Me, R′ = H) were determined by X-ray crystallographic analysis. The results show that there is little steric hindrance between the allyl moiety and the bulky C_{60} ligand.

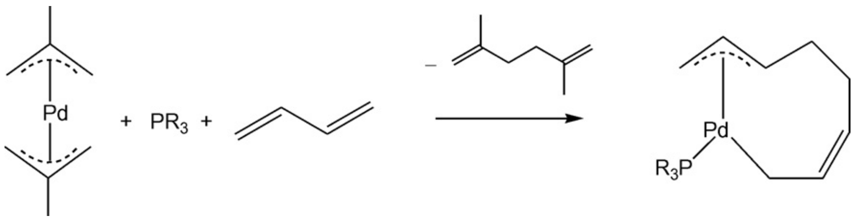
The preparation of the ionic compound, decamethylnickelocenium buckminsterfulleride $[Ni(C_5Me_5)_2{}^+][C_{60}]^-$ has been reported using the reaction of $NiCp^*_2$ with C_{60} in CS_2 [59].

The reactivity of the bis(allyl)palladium complex has been investigated extensively. The Pd(η^3-allyl)$_2$ complex can react with donor ligands to effect the rearrangement or displacement of one or both allyl ligands [60].

The bis(η^3-2-methallyl)Pd complex reacts with butadiene in the presence of PR_3 (R = Me, ^{i}Pr, Cy) to form the octadienyl complex Pd(PR_3)(η^1,η^3-C_8H_{12}) as shown in Eq. (12). The reaction proceeds under mild conditions via a binuclear palladium intermediate [Pd(PR_3)(η^3-2-methylallyl)]$_2$ to give the product in high yield [47]. Reaction of the palladium octadienyl complex with CO or excess PPh_3 results in cleavage of the C_8 chain formed and elimination of butadiene.

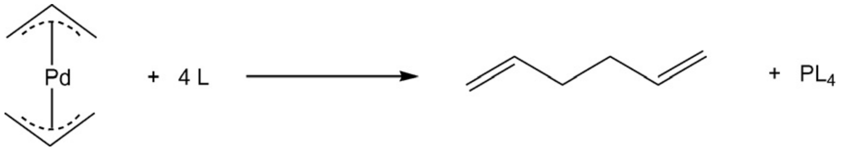


Scheme 11.



(12)

Krüger et al. [60] have reported that reaction of the bis(allyl)palladium complex with excess ligand usually leads to reductive coupling of the allyl moieties followed by elimination (Eq. (13)).



(13)

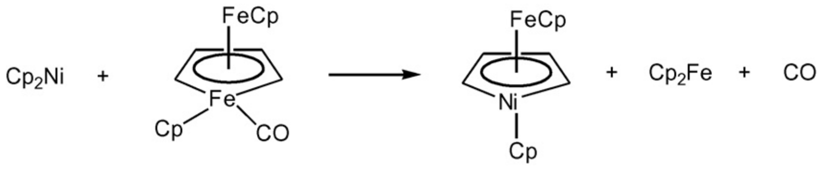
The Pd-π allyl complex reacts with the alkylating agents LiC_3H_5 and $Li_2C_4H_8$ in the presence of tmeda to give the ionic π-allyl palladate(II) complexes $[(\eta^3\text{-}C_3H_5)Pd(\eta^1\text{-}C_3H_5)_2]^-$ (**57**) and the palladacyclopentane $[(\eta^3\text{-}C_3H_5)Pd(C_4H_8)]^-$ (**58**) respectively.

These palladium salts are unstable and decompose at about 0 °C. Interestingly, the bis-σ-allyl complex is reported to be more stable that the corresponding palladacyclopentane (Scheme 12) [61]. This is a reversal of the trend observed for bis-σ-alkyl and metallacycloalkane complexes [9].

2.4. Metallocenes

Unlike palladium and platinum, nickel reacts to form nickelocene, the only 20 valence electron metallocene. Nickelocene is paramagnetic and can be oxidised to form the unstable 19 VE nickelocenium ion. The ability of the Cp rings of nickelocene results in it being a suitable precursor for the synthesis of many organonickel compounds, an array of synthetic chemistry not available to Pd and Pt. Pasynkiewicz and co-workers [67a] have studied and presented a detailed review of the reactivity of nickelocene with a variety of organolithium and magnesium compounds.

The first nickelacyclopentadienyl, **61** was prepared by Simpson and co-workers by an insertion of a ‘NiCp’ species into a labile ferracyclopentadiene (Eq. (14)) [68].



61

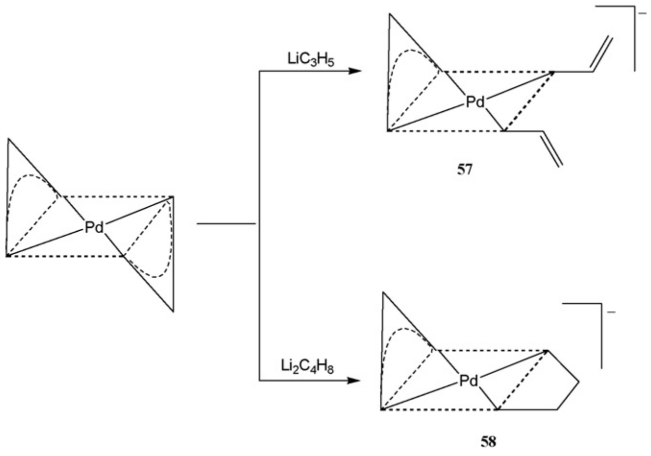
(14)

The stability and decomposition of CpPd(η^3-allyl) has been investigated by Dowben and co-workers using photon- and electron-induced ionization mass spectroscopy [62]. Results from this study indicate that the Pd–Cp and Pd-allyl bonds are of approximately equal strength.

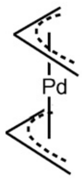
The symmetrical Pd(η^3-allyl)$_2$ complexes can adopt two configurations (Chart 3): **59**, where the η^3-allyl ligands are mutually *cis* and **60**, where the arrangement is *trans*. NMR data indicates that both isomers are present in solution and that rapid isomer interconversion occurs at room temperature. Additional isomers are possible for complexes when the allyl moiety has substituents at the C_1 or C_3 position [56,63].

A theoretical study of the molecular and electronic structure of these bis(allyl)palladium complexes has been conducted using density functional (DFT) methods. Results from this study indicate that for the Pd(η^3-allyl)$_2$ complex in the gas phase, the *trans* isomer is the more stable isomer. A similar result was obtained for the analogous platinum complex, while for nickel the *cis* isomer is computed to be more stable [64]. Wilke and his co-workers [65] reported the first synthesis and distortions of various substituents on *trans*-bis(η^3-allyl)nickel complex. Further studies on the electronic structure and conformational properties of *trans*-bis(η^3-allyl)nickel have been carried out to verify the theoretical investigations [21,65e]. A computational study, using DFT, on the structure and bonding in neutral palladium sandwich complexes of the type Pd_nR_2 (R = benzene, n = 1; R = pyrene, n = 4, 8; R = tetracene, n = 4–9) has also recently been reported by Philpott and Kawazoe [66].

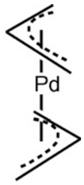
Nickelocene reacts with an array of MR reagents (M = Li or MgX) via the nucleophilic attack of R$^-$ on Ni to form unstable 16 VE {CpNiR} species which are co-ordinately and electronically unsaturated. The {CpNiR} species often proceed to react by a combination of the five modes such as H-elimination [69], coupling [70], homolytic cleavage [71], carbene formation [72] and intramolecular stabilization [73] available to these compounds to produce a variety organonickel compounds as shown in Scheme 13



Scheme 12.



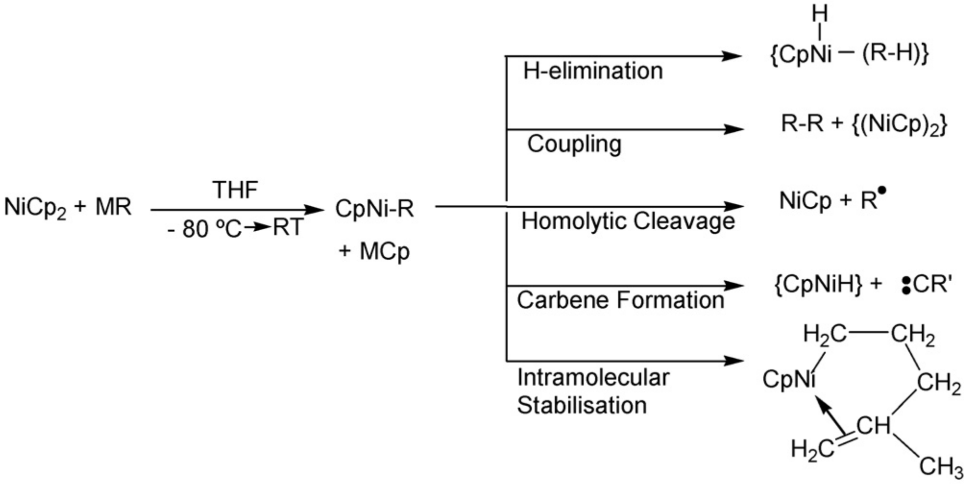
59



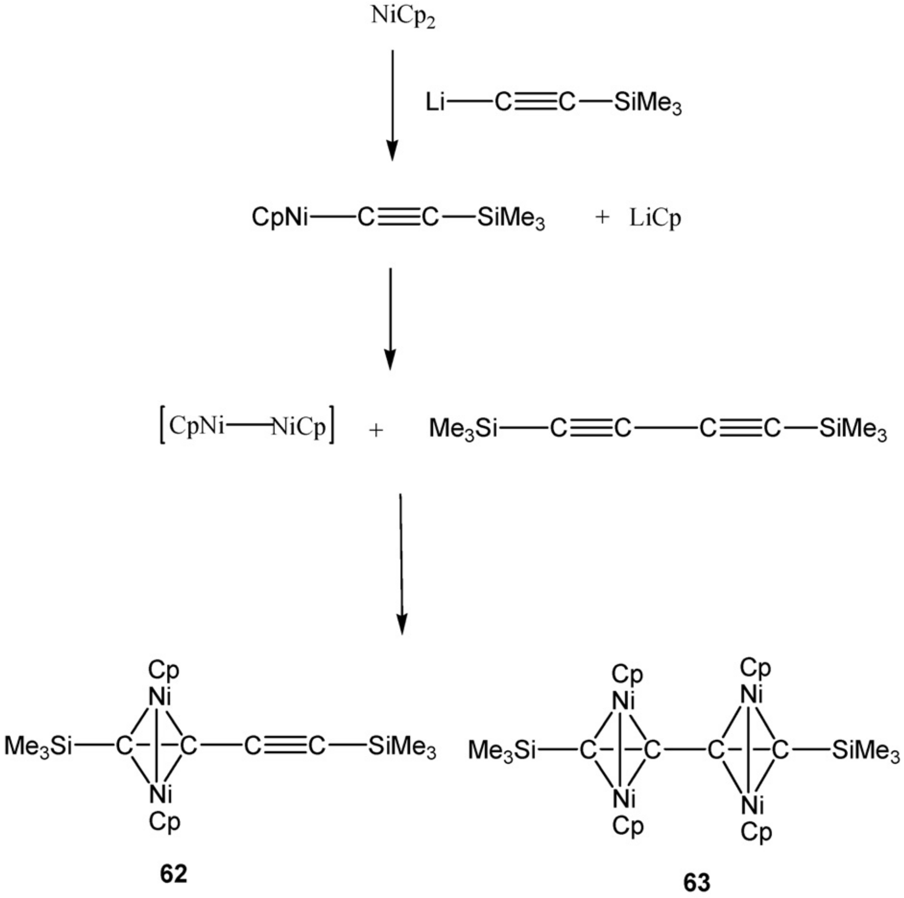
60

Chart 3.

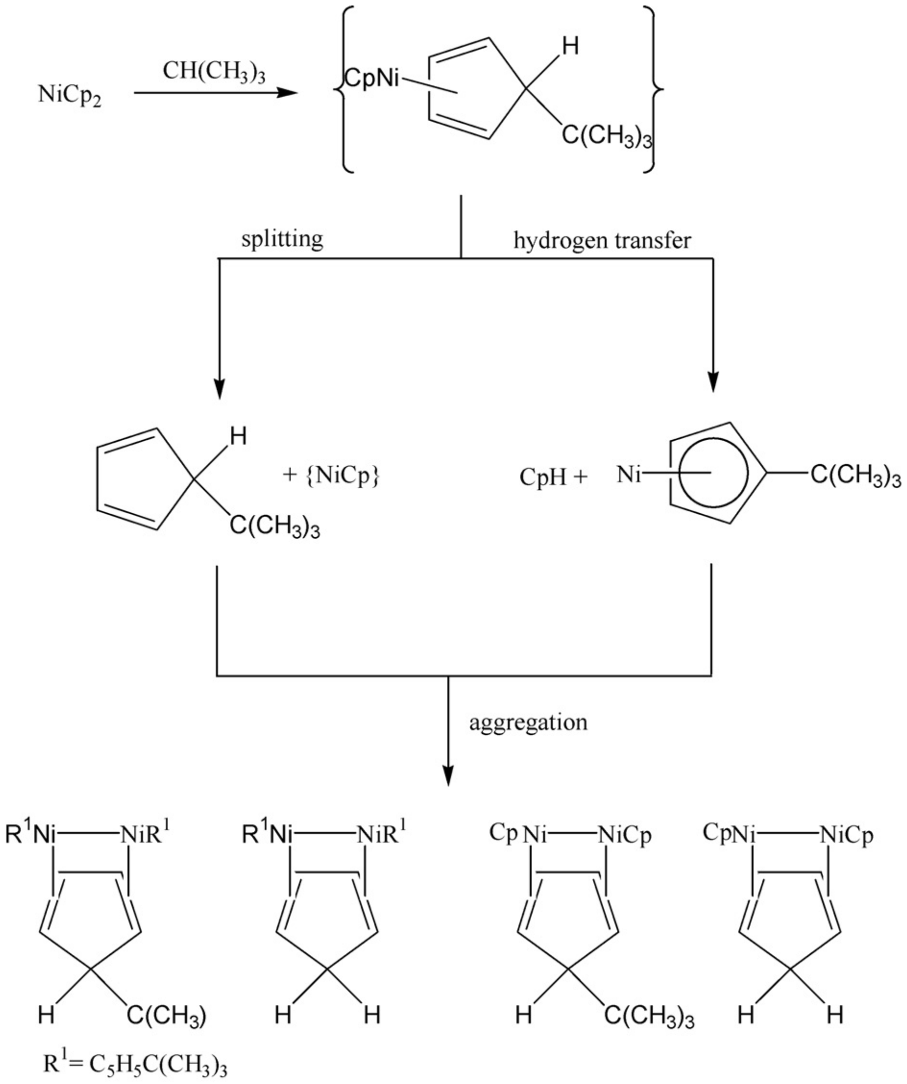
[67]. The complexes of the type CpNiR(alkene) have been prepared by treating nickelocene (**1**) with the appropriate organolithium or organomagnesium halides and can be stabilized by complexation to the C=C bond of an olefin. The CpNiR(η^2-CH_2=CH_2) complexes react with insertion of the coordinated ethylene into the Ni–R bond. The reactivity of the CpNiR(η^2-olefin) complexes with respect to olefin insertion into the Ni–R bond decreases in the order: CpNi-(p-C_6H_4X)(butadiene) > CpNi(*p*-C_6H_4X)(C_2H_4) > CpNi(*p*-C_6H_4X)(C_2H_4) > CpNi(alkyl)(C_2H_4) (alkyl = Me, Et > Pr, Bu) [67].



Scheme 13.



Scheme 14.

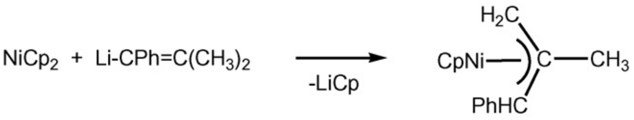


Scheme 15.

α- and β-Hydrogen elimination of CpNiR complexes derived from reaction of nickelocene with organolithium and magnesium compounds provide simple methods for the production of a variety of CpNi clusters and π-allylnickel compounds. The pathway along which the CpNiR species reacts is largely dependent on the nature of the R group and the presence and position of hydrogen atoms therein.

The unstable {CpNiR} can eliminate hydrogen via α-, β- or γ-elimination pathways to produce 18 VE nickel hydrides which are unstable in the absence of carbonyl or phosphorus donor ligands. A key factor of H elimination reactions is the production of the highly reactive {CpNiH} species. The hydride species produced from H-elimination are strong hydrogenating reagents and react with other reactants present to form mononickel, dinickel and trinickel complexes. Noteably, α-elimination of hydrogen atoms of CpNiR species in which the R group contains two α-H atoms is the only efficient route to producing cyclopentadienyltrinickel clusters.

When possible, β-elimination is dominant over α-H elimination and proceeds to form tri-, tetra- and hexanickel clusters together with mono- and dinickel compounds. β-H elimination again produces the reactive {CpNiH} species and alkenes. Vinylnickel {CpNiR} containing γ-H atoms compounds in which α- and β-H atoms are absent react to form π-allyl complexes [69] (Eq. (15)).

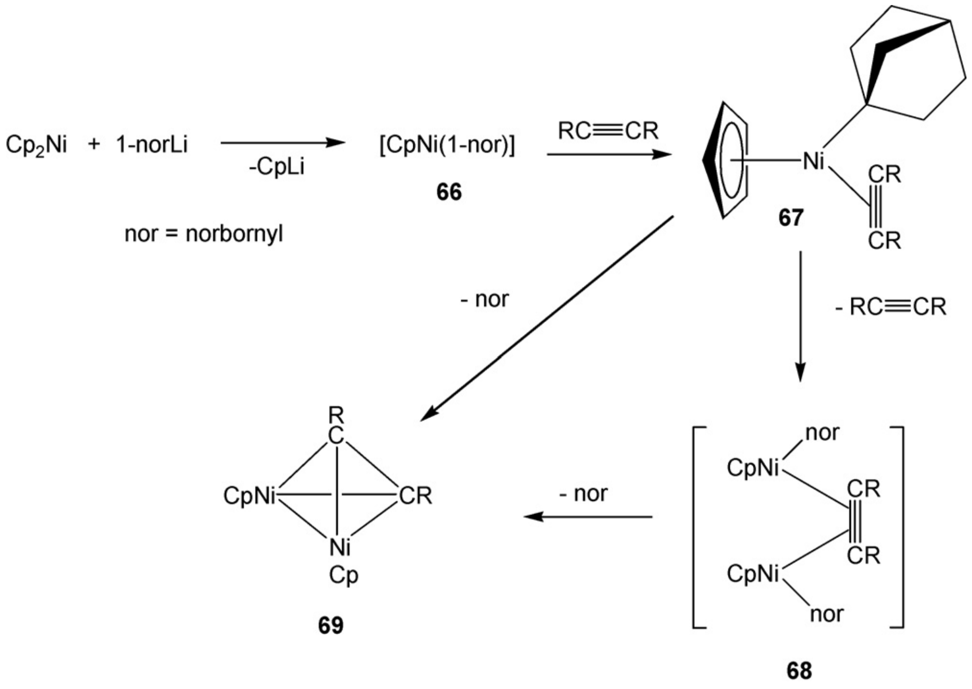


(15)

In a similar way, unstable CpNi(vinyl) compounds of the type CpNi-CR′═CR$_2$ (R′ = CH$_3$, Ph, R = CH$_3$) have also been obtained in the reaction of nickelocene with vinyllithium or -magnesium compounds. CpNi(vinyl) reacts further to form π-allyl complexes [70].

In addition to H-elimination reactions, the unstable CpNiR species can undergo coupling reactions. The ratio of products produced from coupling to that produced by H-eliminations depends on the nature of the R group. For example, when R = CH$_3$ the ratio of the coupling product to the elimination product is 1:6 when R = C$_2$H$_5$ and C$_3$H$_7$, β-H elimination dominates and no coupling product is produced. When α- and β-H atoms are absent (where R = C≡CCH$_3$, C≡CPh, Ph), coupling is the principle reaction (Eq. (16)) [71].

$$2\{\mathrm{CpNi\text{-}R}\} \rightarrow \{(\mathrm{NiCp})_2\} + \mathrm{R{-}R} \tag{16}$$

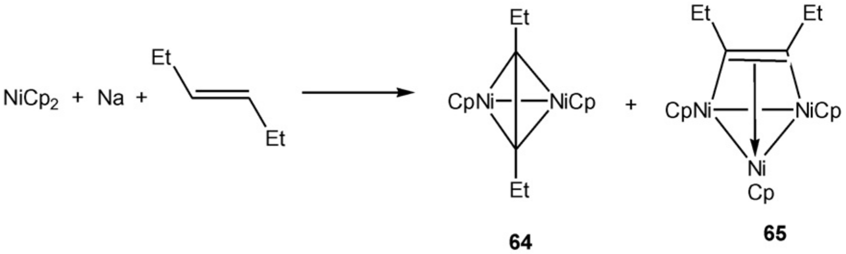


Scheme 16.

The coupling products of these acetylenic compounds react with $NiCp_2$ to form di- and tetracyclopentadienylnickel complexes **62** and **63** through the formation of active $(NiCp)_2$ species as shown in Scheme 14 [67,71].

Homolytic cleavage of the Ni–C bond of {CpNiR} to produce the $R^\bullet$ radical will occur when H elimination and coupling reactions are less dominant. The radical produced reacts with nickelocene to produce a range of hydrocarbons together with mono and dinickel compounds as shown in Scheme 15 [72–74].

The formation of alkynes by the dehydrogenation of internal alkenes in the presence of nickelocene with metallic sodium has been reported. The other products obtained were **64** and **65** (Eq. (17)) [75].



(17)

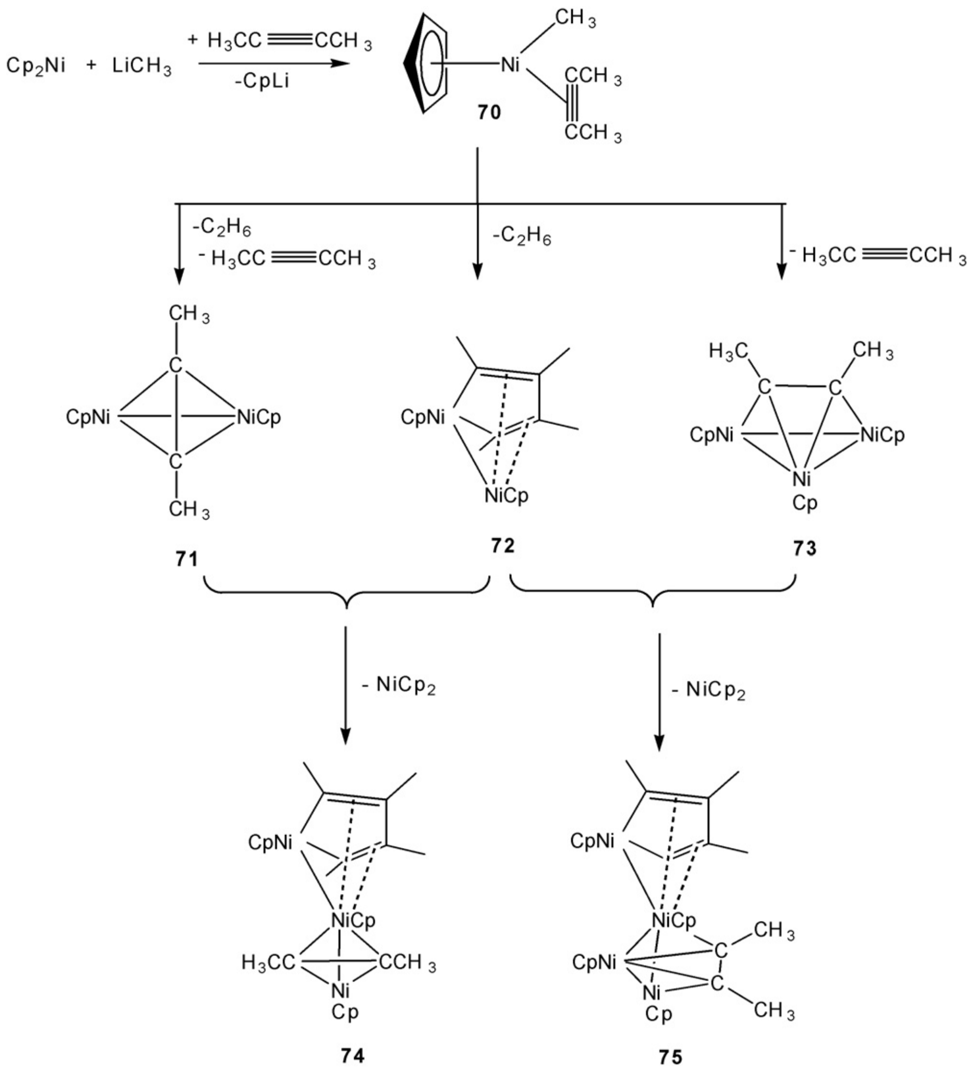
Cp_2Ni reacts at −50 °C with lithiumnorbornyl (bicyclo[2.2.1] heptane-1-yl) in THF to give the CpNi-1-norbornyl complex (**66**) which further reacts with alkynes to yield the complexes of the type CpNi(1-nor)(η^2-RC≡CR) (**67**) where R = Me, $SiMe_3$ and Ph (Scheme 16). On thermal decomposition, low yields of the products of the type **68** and **69** were obtained [76].

Reaction of nickelocene with methyllithium and 2-butyne in the molar ratio of reactants 1:1:1 leads to the formation of several organonickel compounds. In this reaction formation of the unstable nickelocene analogue **71**, and compounds **72** and **73** is observed. Compound **70** reacts with **71** and **72** and as the result of nickelocene elimination two other compounds as trinuclear **74** and tetranuclear **75** clusters are formed as shown in Scheme 17 [77–79]. Similar results were obtained with diphenylacetylene as a reagent [79].

The reaction of nickelocene with diphenylmethyllithium yielded an unstable 16-electron species {$CpNiCHPh_2$} and LiCp. {$CpNiCHPh_2$} reacts in two ways: hemolytic cleavage of the Ni–C bond with the formation of the relatively stable radical $^\bullet CHPh_2$ and α-hydrogen elimination by the formation of hydridocarbene {$CpNi(H)=CPh_2$} (**76**), stabilized by two phenyl groups. This compound **76** can hydrogenate the cyclopentadienyl ring of nickelocene to form the unstable 19-electron species, {$CpNiC_5H_6$} (**77**). This species can be stabilized by (a) the formation of dimer **78**, (b) the addition of {NiCp} species to form complex **79** or (c) further hydrogenation of a cyclopentadiene ring with the formation of the π-allyl complex **80** as shown in Scheme 18 [80].

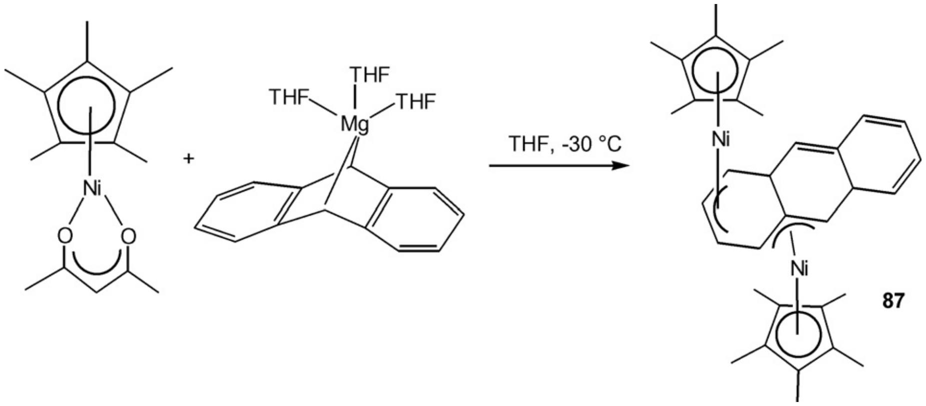
Nickelocene in benzene reacts with the Brønsted acid $H_2O\bullet B(C_6F_5)_3$ to give the salt **81**, which is the first example of a triple-decker nickel sandwich with a bridging η-benzene ligand. Treatment of nickelocene with Brookhart's acid $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ in benzene yields the paramagnetic derivative, **83** in which nickelocene is present as a molecule of crystallization. The same reaction in toluene yielded **82**, a green-blue nickel(III) compound (Scheme 19) [81].

Cp*Ni(η^1,η^2-C_4HPh_4) (**84**) (Cp* = η^5-C_5Me_5) was prepared by reacting Cp*Ni(acac) with 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl. Thermolysis of **84** in THF affords **85** and **86** (Scheme 20) [82].



Scheme 17.

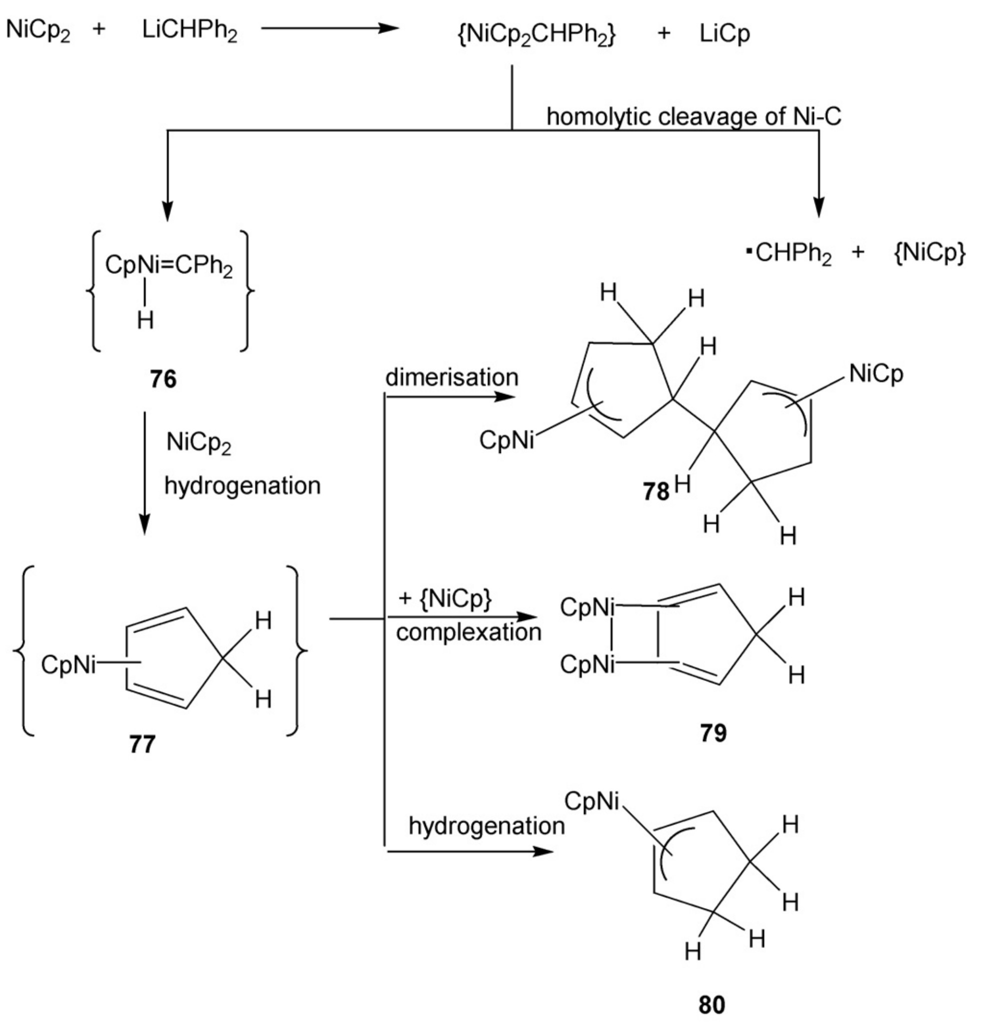
The reaction of magnesiumanthracene with Cp*Ni(acac) yielded the dinuclear compound **87**. In a similar way, other nickel–hydrocarbon complexes have been prepared using dianions of pyrene and pyrylene with Cp*Ni(acac) (Eq. (18)) [83].



(18)

Compounds containing the nickelacyclopentadienyl ring moiety such as **88** have been prepared by the reaction of nickelocene with phenyl lithium and diphenylacetylene [84,85] (Scheme 21). Some of the products of this reaction including compounds **89**, **90** and **91** were isolated as tri- and tetranuclear nickelocenes with Ni–Ni interactions. Also formed in this reaction was (η^5-cyclopentadienyl)(η^5-(1-(η^5-cyclopentadienyl)-2-phenyl-3-methyl-1-nickelaindenyl)nickel (**92**) was structurally characterized.

Platinabenzenes (**93**) which contain an aromatic metallacycle and their derivatives can be prepared as shown in Scheme 21. Complex **93** contains two different rearrangement products of the vinylcyclopropene precursor by the mutual stabilization of the η^5-



Scheme 18.

bonded cyclopentadienyl ligand and the platinabenzene moiety [86]. Hughes and co-workers have reported the synthesis of a platinacyclohexadiene by a similar vinylcyclopropene rearrangement [87] (Scheme 22).

The platinabenzene (**97**) was prepared by the oxidation reaction of $[PtCp^*(CO)]_2$ (**94**) in the presence of iodine to give $PtCp^*(CO)I$ (**95**) and subsequent reaction with a lithiated cyclopropene derivative. Formation of σ-vinyl complex **96** was evident under the shorter reaction times and faster work-up procedures. In solution, it has been found that isomerisation of **96** to the corresponding platinabenzenes **97** occurs at room temperature over 2–3 days (Scheme 23) [88].

Using the isodicyclopentadienyl (Isodicp) ligand (**98**), various neutral (**99**) and cationic (**100**) nickelocenes have been synthesized and studied in order to probe the sign of the unpaired spin density (Scheme 24) [89].

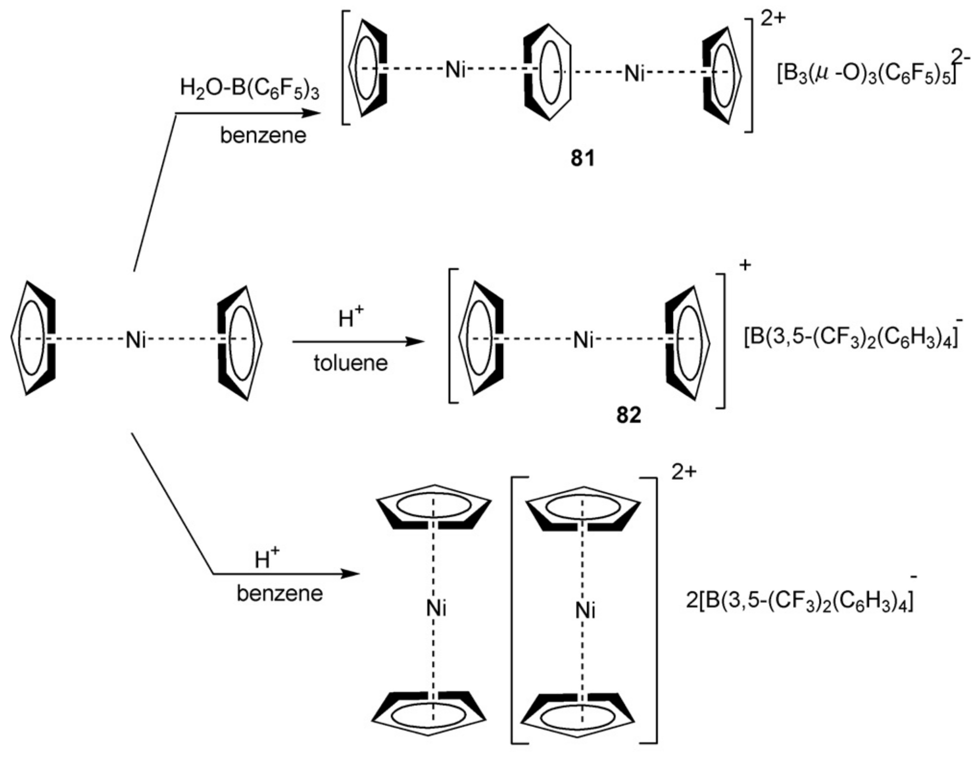
It has been reported that the reaction of **101** with the decacyclide dianion (**102**) produces the π-arene bridged nickel triple-decker complex, $[\{\eta^5\text{-}Me_4EtC_5\}Ni]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-decacyclene})]$ (**103**). The addition of diorganyl dichalcogenides (R-E-E-R) to **103** yielded the complex **104** by reductive cleavage of the E–E bond of the dichalcogenide by reactive $[(\eta^5\text{-}Me_4EtC_5)Ni]$ species (Scheme 25) [90].

Pt(II) and Pt(IV) complexes containing various cyclopentadienyl derivatives bonded in η^1- or η^5 mode to the metal centre are very well-known in the literature as they are of special interest due to structural aspects as well as catalytic applications [91]. With respect to catalytic processes, donor functionalized cyclopentadienyls provide the opportunity to temporarily stabilize a reactive metal fragment by intramolecular coordination, to immobilize or to trap the catalytically active complex as well as to vary the solubility.

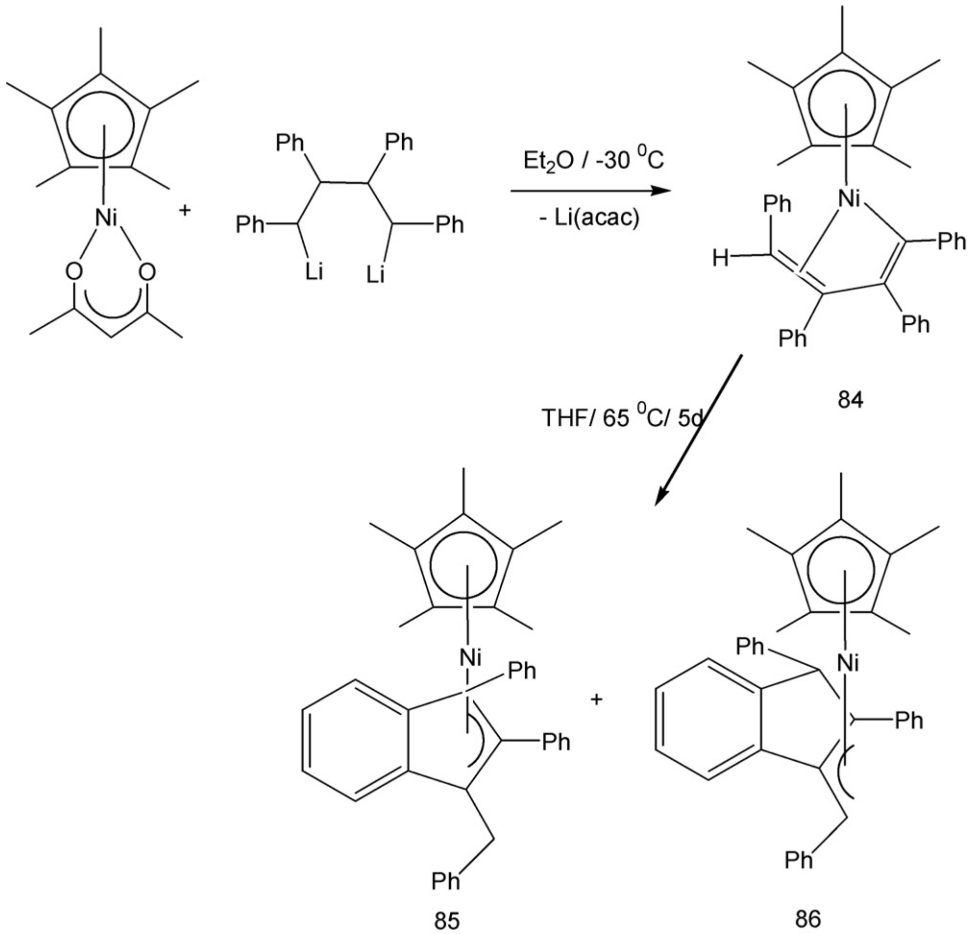
A substituted tetramethylcyclopentadienyl platinum complex with a monodentate COD ligand (**105**) reacts with PMe_3 to give compound **106** by migration of the Cp fragment from metal to COD ligand. Another interesting feature is the metal centre is coordinated to a cyclooctenyl ligand via both σ- and π-bonding modes. Formation of the dinuclear platinum complex, **107** from **105** after losing a COD ligand was observed (Scheme 26). There are few examples of platinum(II) complexes which contain a Cp moiety coordinated in an η^5 bonding fashion, an olefin, and an alkyl group (**108** and **109**) [92] (Chart 2).

2.5. Metal–σ-bond complexes

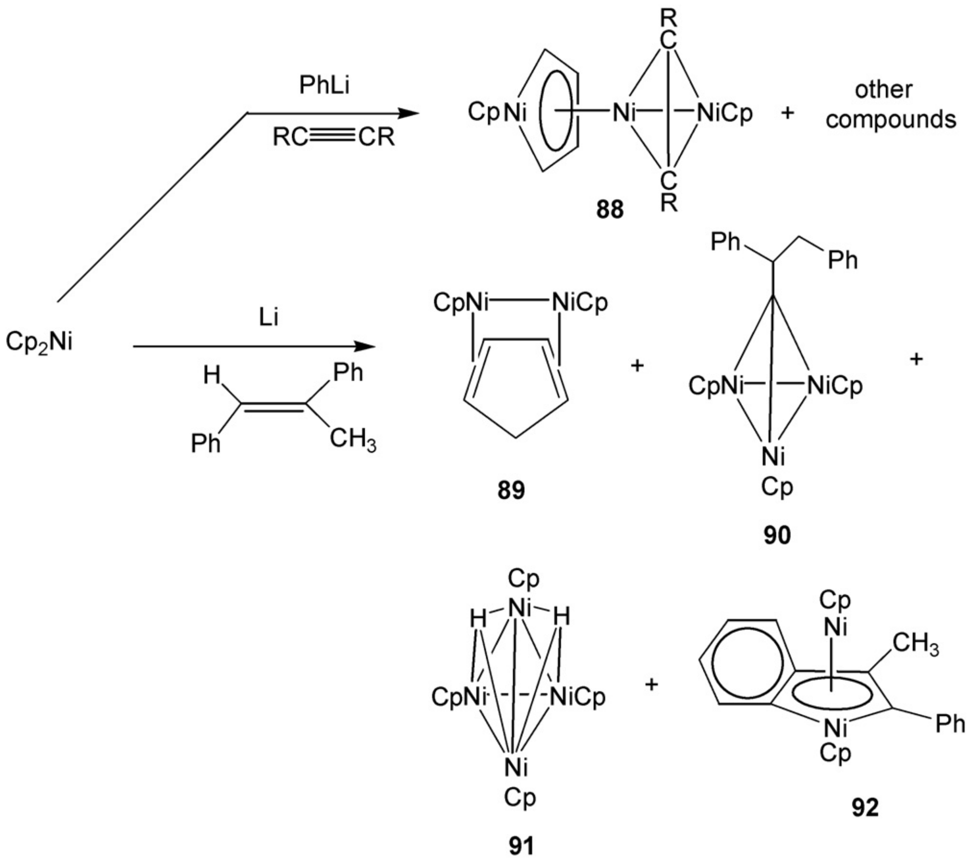
Extensive research has been carried out on the classical σ-bonded alkyl and aryl groups of the d-block transition elements along with the binding of delocalized aromatic or quasi-aromatic entities, alkenes, alkynes, etc., to metals for several years [93]. A number of transition-metal systems are now known which oxidatively add hydrocarbons to form relatively stable alkyl hydride complexes [94]. The interaction of C–H bond with an unsaturated transition-metal fragment has been examined using various spectroscopic techniques [95,96]. There is now substantial evidence in the literature for the intermediacy of metal–hydrocarbon σ-complexes as shown in Scheme 27a [97].



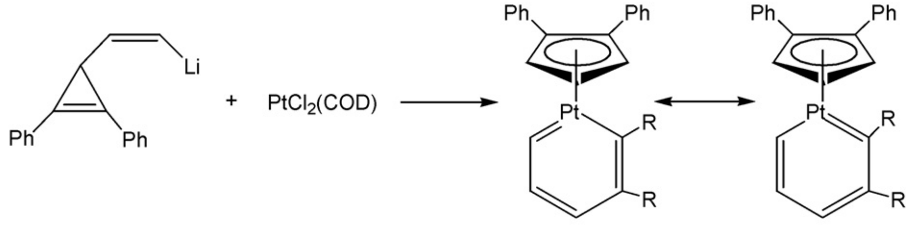
Scheme 19.



Scheme 20.



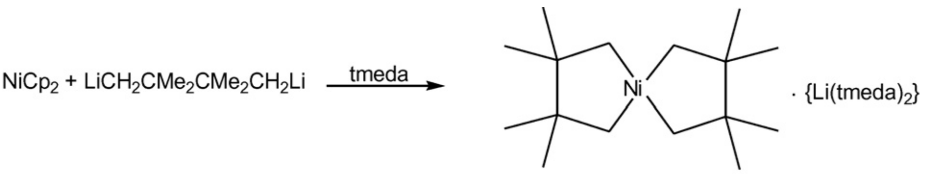
Scheme 21.



93, R = H or Ph

Scheme 22.

When a C–H bond of a free hydrocarbon is coordinated to a transition-metal centre, the C–H σ-electrons serve as the electron donor to the empty metal orbital, and the high-lying C–H σ* orbital serves as a π-acceptor orbital. The structures for these intermediates proposed by several workers are shown as **i**–**iv** in Scheme 27b.

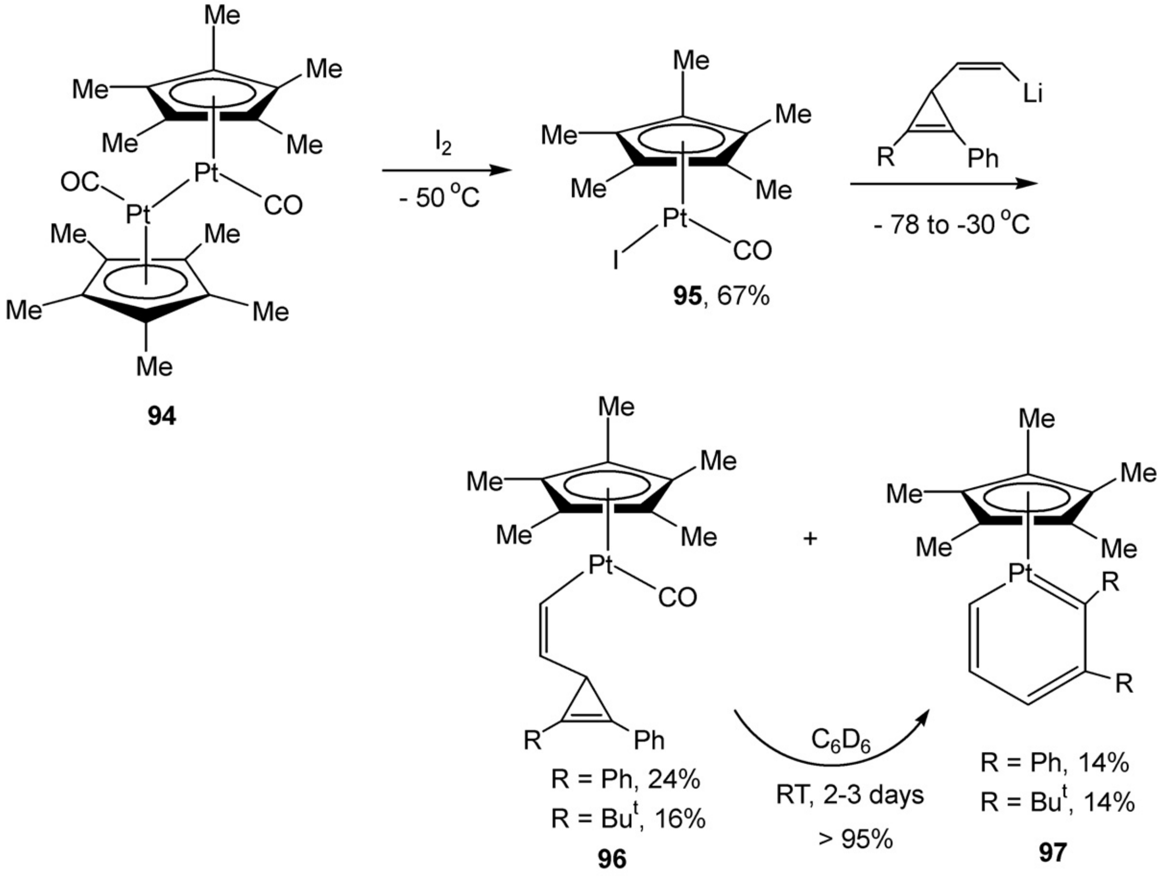


110

(19)

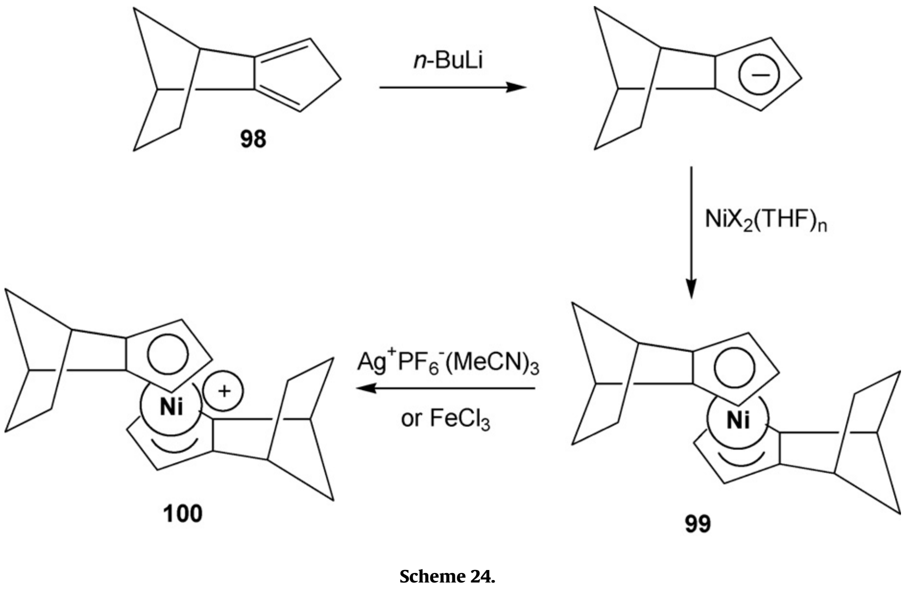
Nickel–hydrocarbon complexes with Ni–C σ-bonds stabilized with organolithium adducts (**110**) as shown in Eq. (19) have been prepared by the treatment of $NiCp_2$ with dilithium compound $LiCH_2CMe_2CMe_2CH_2Li$ [98]. Similarly, $Li_2[Pt(CH_3)_6]$, $Li_2[Pt(CH_3)_4]$, $Li_2[Pt(CH_3)_5C_2H_5]$, $Li_2[Pt(CH_3)_5(n\text{-}C_4H_9)]$ and $Li_2[M(CH_3)_4]$ (M = Ni or Pd) compounds have also been synthesized and characterized by various spectroscopic studies [99]. Thermal decomposition studies of compounds (**111**–**113**) at different temperatures are reported as shown in Scheme 28.

When a strained alkene, **114** reacts with $Ni(COD)(P^tBu_3)$ in cyclohexane, a nickel alkene complex tris((5Z,11E)-dibenzo-[a,e]cyclooctatetraene)nickel(0) (**115**) is formed. This nickel complex **115** with three very bulky alkene ligands is relatively

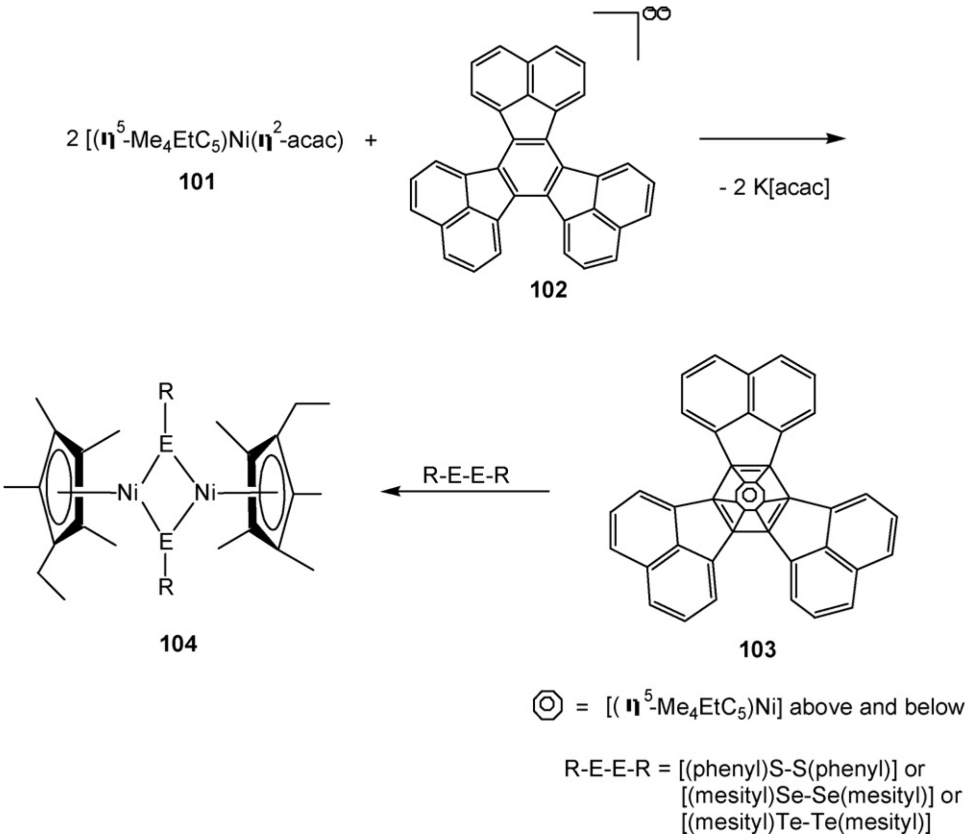


Scheme 23.

stable at ambient temperature and on heating at 60 °C in benzene, a reductively eliminated cyclobutane (**116**) is obtained. It is interesting to note that the reaction of **114** with two-fold excess of Ni(COD)(P^tBu_3) yielded a tetraalkyl complex of nickel(IV) (**117**). Formation of the nickelaspirocyclononane, **117** results in the release of strain in the free ligand and consequently the reverse transformation is greatly disfavoured [Scheme 29]. It is also remarkable that the C–C bond-forming step occurs twice to give a metallaspirocycle. Complex **117** contains two metallacyclopentane units and, especially in view of the very high nominal oxidation state of the nickel centre, appears to be susceptible to reductive elimination [13].



Scheme 24.



Scheme 25.

3. Significance and applications

3.1. Significance of hydrocarbon metal complexes as key intermediates in catalysis

Hydrocarbon–metal complexes are known as intermediates in reactions catalyzed by tri- and polynuclear metal clusters and by heterogeneous catalysts. Multinuclear metal catalysts offer significant stabilization of coordinatively unsaturated intermediates through metal–hydrocarbon bonding via bonding to two, three, or possibly more metal atoms. Thus the chemistry with multinuclear metal complexes may be different from the mono- or even dinuclear metal complexes. However, it is not possible to reconcile the disparity in heterogeneous catalysis by virtue of the fact that the temperatures employed (ca. 500 °C) lie well above those considered as the typical range of stability for coordination complexes.

Hydrocarbon–metal complexes include skeletal rearrangements and dehydrocyclizations of aliphatic hydrocarbons (which feature prominently in catalytic re-forming for the production of gasoline and aromatic hydrocarbons), and the conversion of synthesis gas (mixtures of carbon oxides and hydrogen) to hydrocarbons, i.e. the Fischer–Tropsch reaction. The Fischer–Tropsch reaction is perhaps a good example of a process in which bridged-intermediates are believed to play key roles in the reaction pathway (Scheme 30).

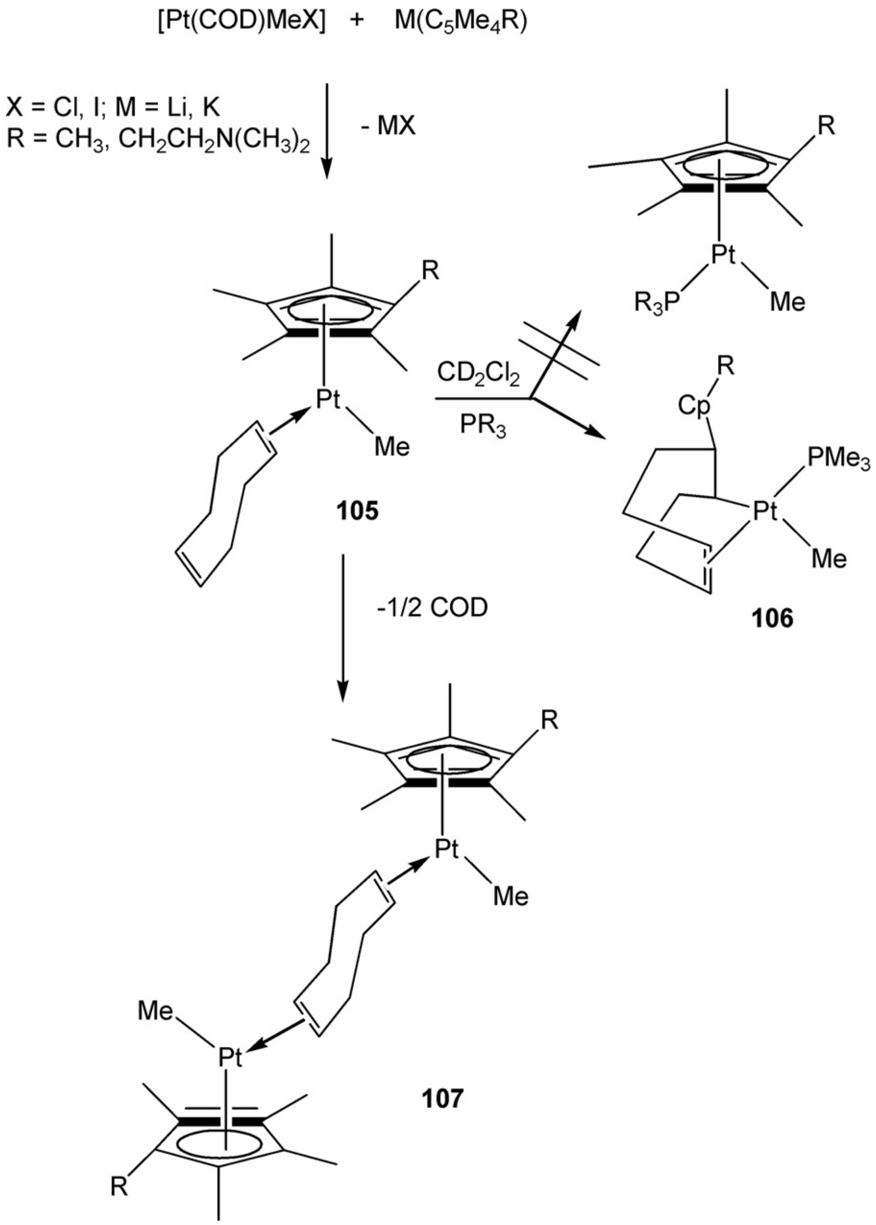
Many recent proposed mechanisms for ethylene hydrogenation have been postulated [100] from this first plausible mechanism shown in Scheme 31 [101]. Whitesides and co-workers have shown a new type of heterogeneous reaction that generates R* of known initial structure under conditions similar to those employed in organic chemistry for the heterogeneous, catalytic hydrogenation of olefins, through the hydrogenation of (diolefin)dialkylplatinum(II) complexes using platinum black suspended in organic solvents as catalyst (Scheme 32). These reactions are very useful for studying the reactivities of alkyl groups on the surface of platinum as this reaction can generate R* having well-defined patterns of isotopic labeling and known regio- and stereochemistry of bonding to the surface [102]. The ability of this type of chemistry to form surface organometallic groups should also be preparatively useful in technologies that involve surface alkyls as intermediates in hydrogenation, hydrogenolysis, isomerisation, Ziegler–Natta polymerization, Fischer–Tropsch and chemical vapour deposition reactions.

Many organometallic complexes including various nickel and palladium containing species are known to catalyze olefin oligomerization and polymerization reactions [103]. Most transition metal-catalyzed alkene polymerization systems occur most importantly via β-H elimination, which results in the formation of dimers, oligomers, or polymers. The most commonly accepted mechanism for chain propagation in alkene polymerization is the one proposed by Cossee and involves alkyl migration to a coordinated olefin (Scheme 33a) [104]. An alternative chain propagation mechanism, originally proposed by Briggs, has been implicated in selective trimerization and tetramerization reactions and involves metallacyclic intermediates (Scheme 33b) [9,105].

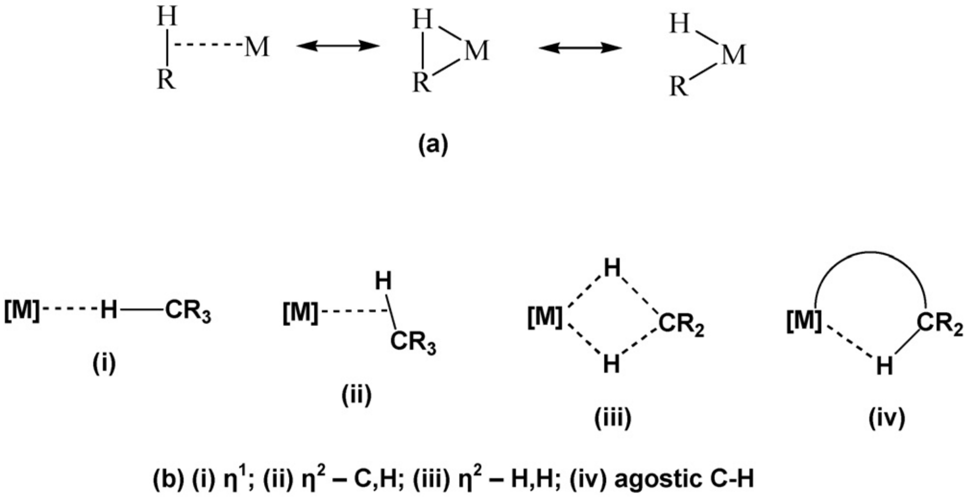
3.2. Applications

3.2.1. Catalysis

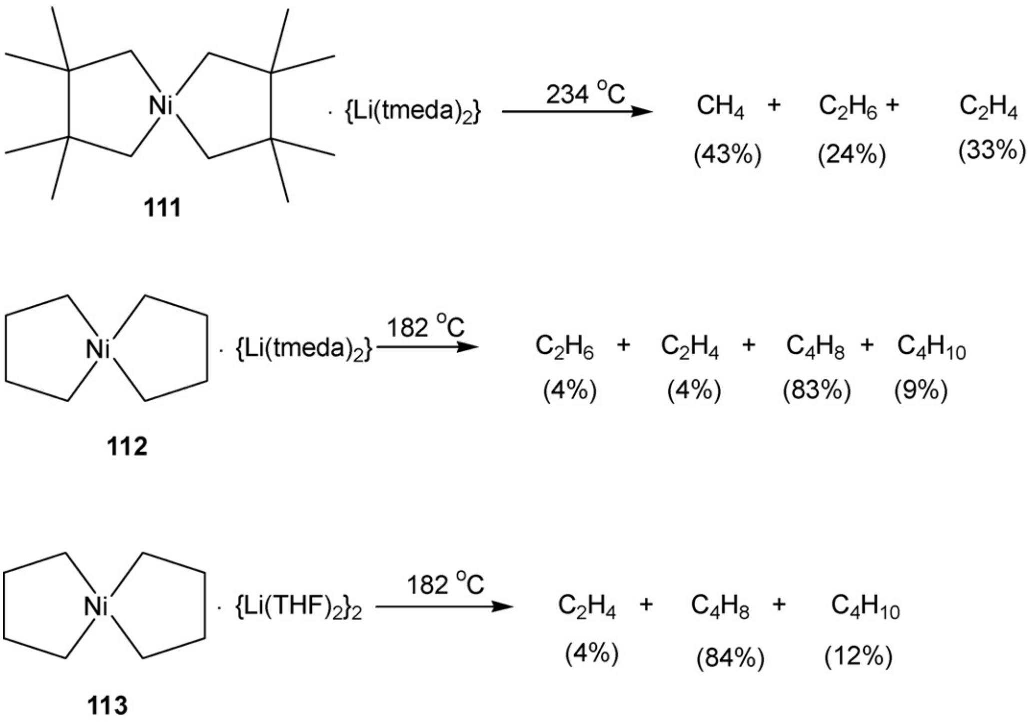
Organometallic complexes (of Ni, Pd, Pt) bearing no heteroatom in the ligand backbone are little known in catalysis. Complexes such as $M(COD)_2$ (M = Ni, Pd, Pt) typically play a vital role as precursors or intermediates in several transition metal-catalyzed organic reactions. For example $Ni(COD)_2$ is not a good α-olefin oligomerization



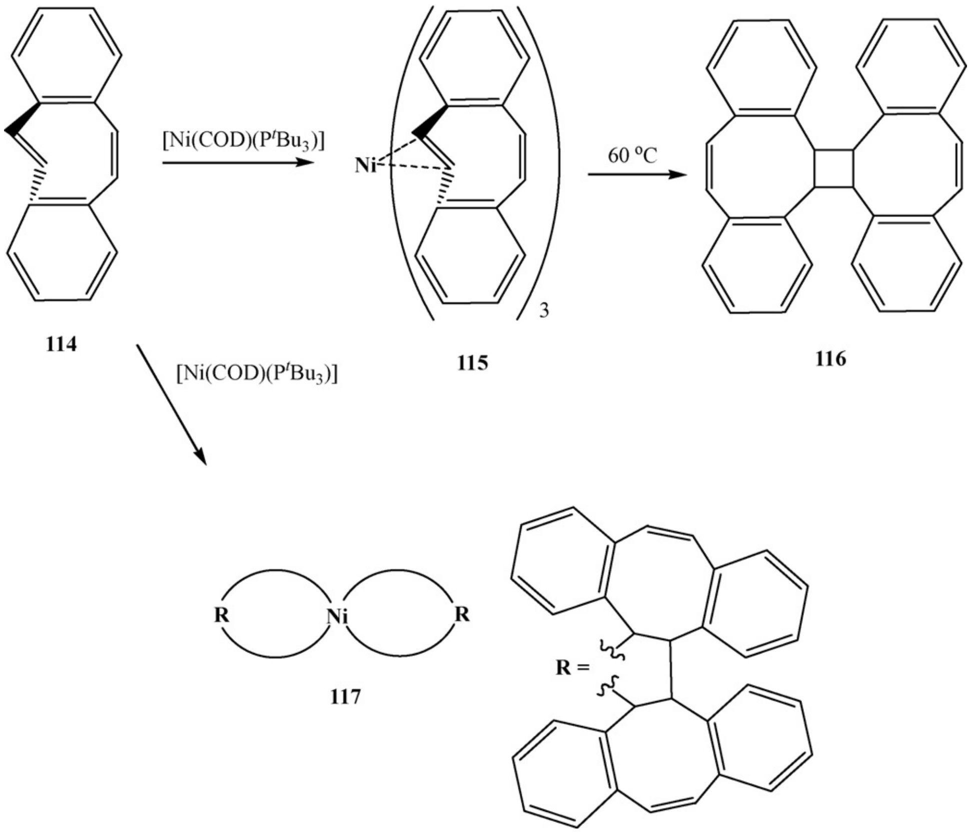
Scheme 26.



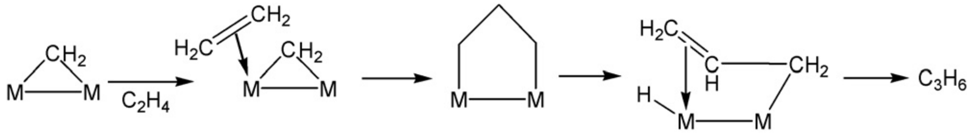
Scheme 27.



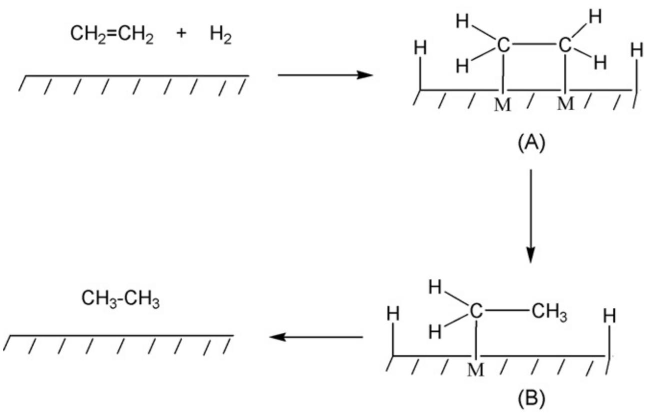
Scheme 28.



Scheme 29.

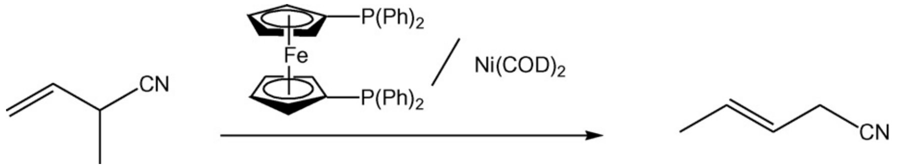


Scheme 30.



Scheme 31. Proposed intermediates for the hydrogenation of ethylene on a metal catalyst surface; (A) the initial state of alkyls on surface; (B) the half-hydrogenated state.

catalyst precursor, however it is known to be a good phosphine scavenger and addition of a ligand containing phosphines can drastically alter the dynamics of catalysis [106–108]. García and co-workers demonstrated the isomerisation of branched nitrile 2-methyl-3-butenenitrile to the linear isomer 3-pentenenitrile by adding Ni(COD)$_2$ to a series of P-donor (ferrocenylphosphines) ligands [107]. An example of one such reaction is shown below in Eq. (20).



(20)

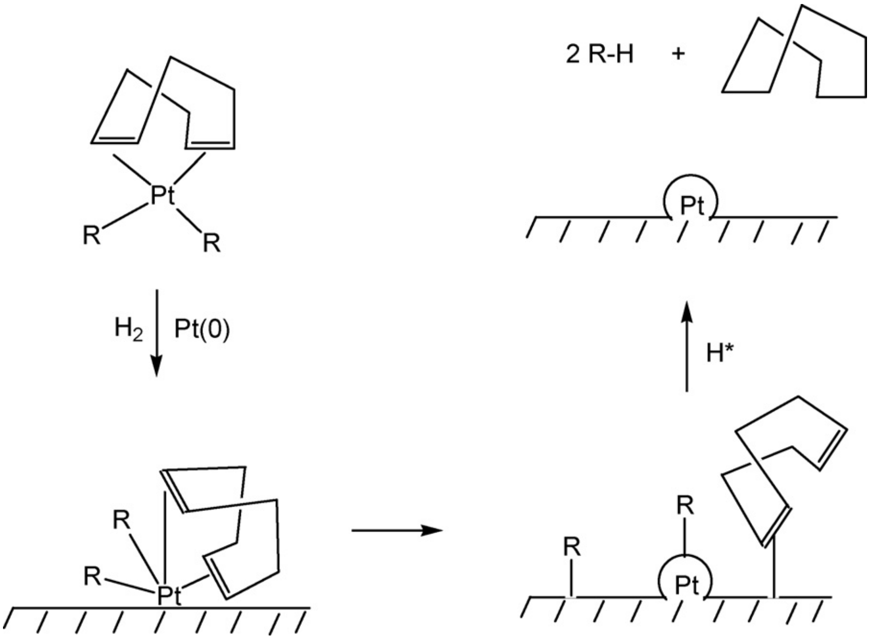
In combination with PPh$_3$, Ni(COD)$_2$ is reported to catalyze the degradation of allyl formate into C_3H_6 and CO_2 at room temperature as described in Eq. (21) [109].

$$\mathrm{HCOOCH_2CH = CH_2 \overset{Ni(COD)_2-PPh_3}{\longrightarrow} C_3H_6 + CO_2} \tag{21}$$

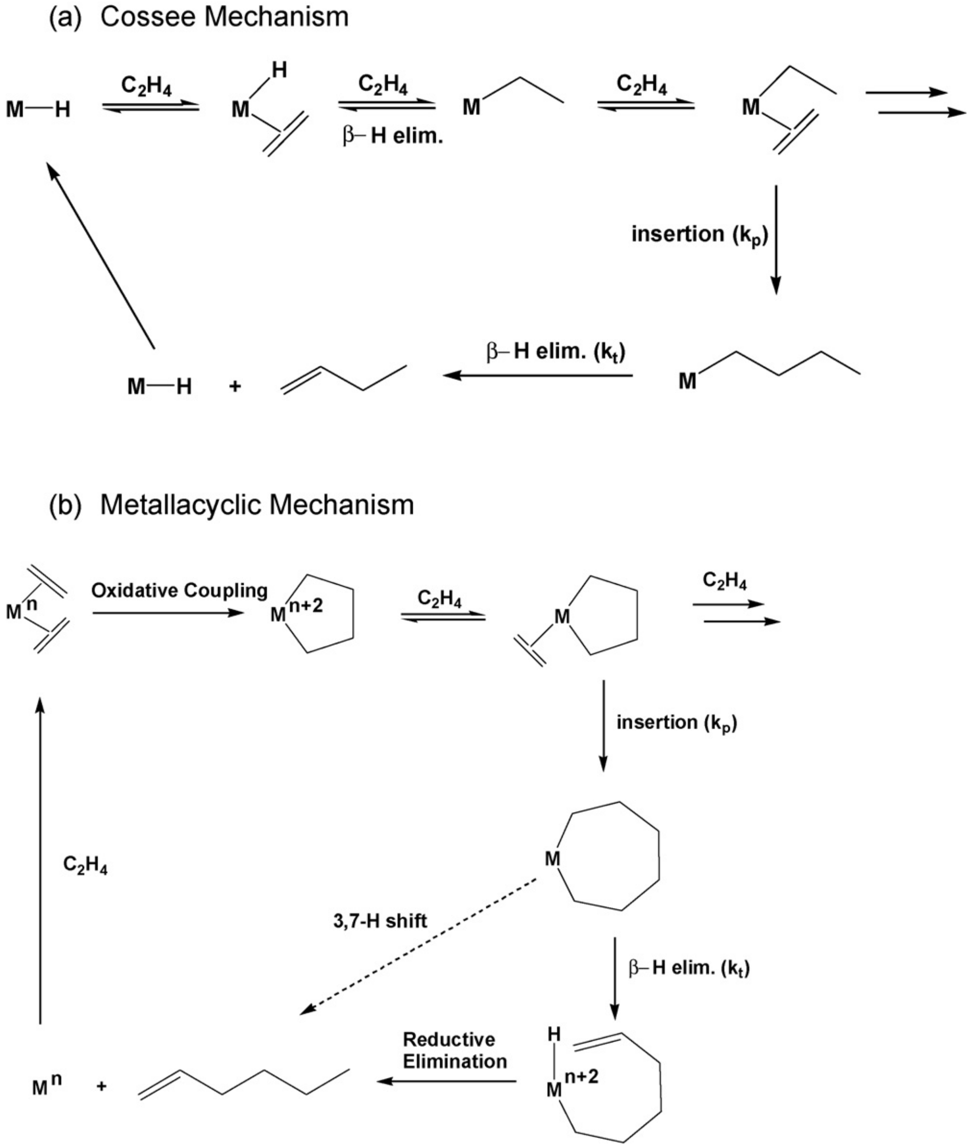
Transition metal complexes bearing η^3-allyl ligands have sometimes been employed in coupling reactions. Kambe and co-workers demonstrated that the presence of η^3-allyl ligands was vital in the cross-coupling of alkyl halides with Grignard reagents [110]. In their experiments they found Pd(PPh$_3$)$_2$Cl$_2$ was not active in these cross-coupling reactions and with (η^3-allyl)PdCl only giving 10% yield. The bis(η^3-allyl)Pd complex on the other hand gave a moderate yield with the analogous bis(η^3-allyl)Ni complex yielding high activity [110]. Scheme 34 delineates a possible reaction pathway by which this cross-coupling reaction proceed.

The bis(η^3-allyl)M **118** (M = Ni and Pd) were reacted with a Grignard reagent to give rise to an anionic bis(η^1,η^3-allyl)M complex **119**. The anionic nature of this complex improves the nucleophilicity at the metal centre towards alkyl halides. Nucleophilic attack of **119** on an alkyl halide gives a dialkyl metal complex **120** followed by reductive elimination to yield the cross-coupled product and **118** [110].

Reductive elimination is an important and vital reaction in chemistry and is often the crucial step for product formation in



Scheme 32. Proposed mechanism for the heterogeneous hydrogenation of (Diolefin)dialkylplatinum(II) complexes.

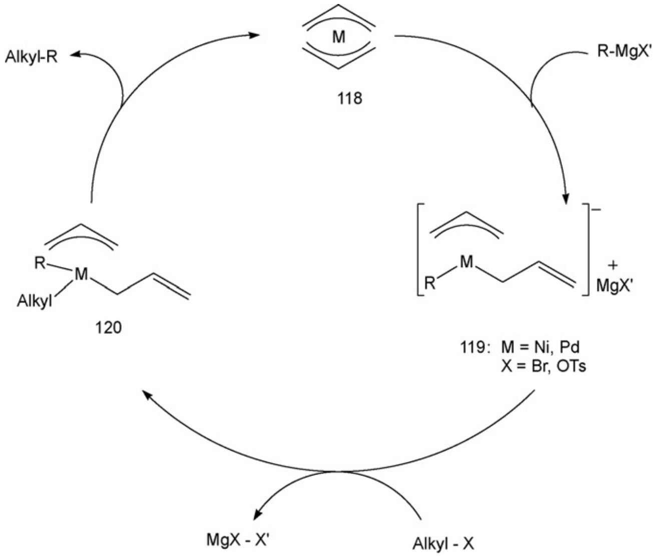


Scheme 33. (a) Cossee mechanism; (b) metallacyclic mechanism.

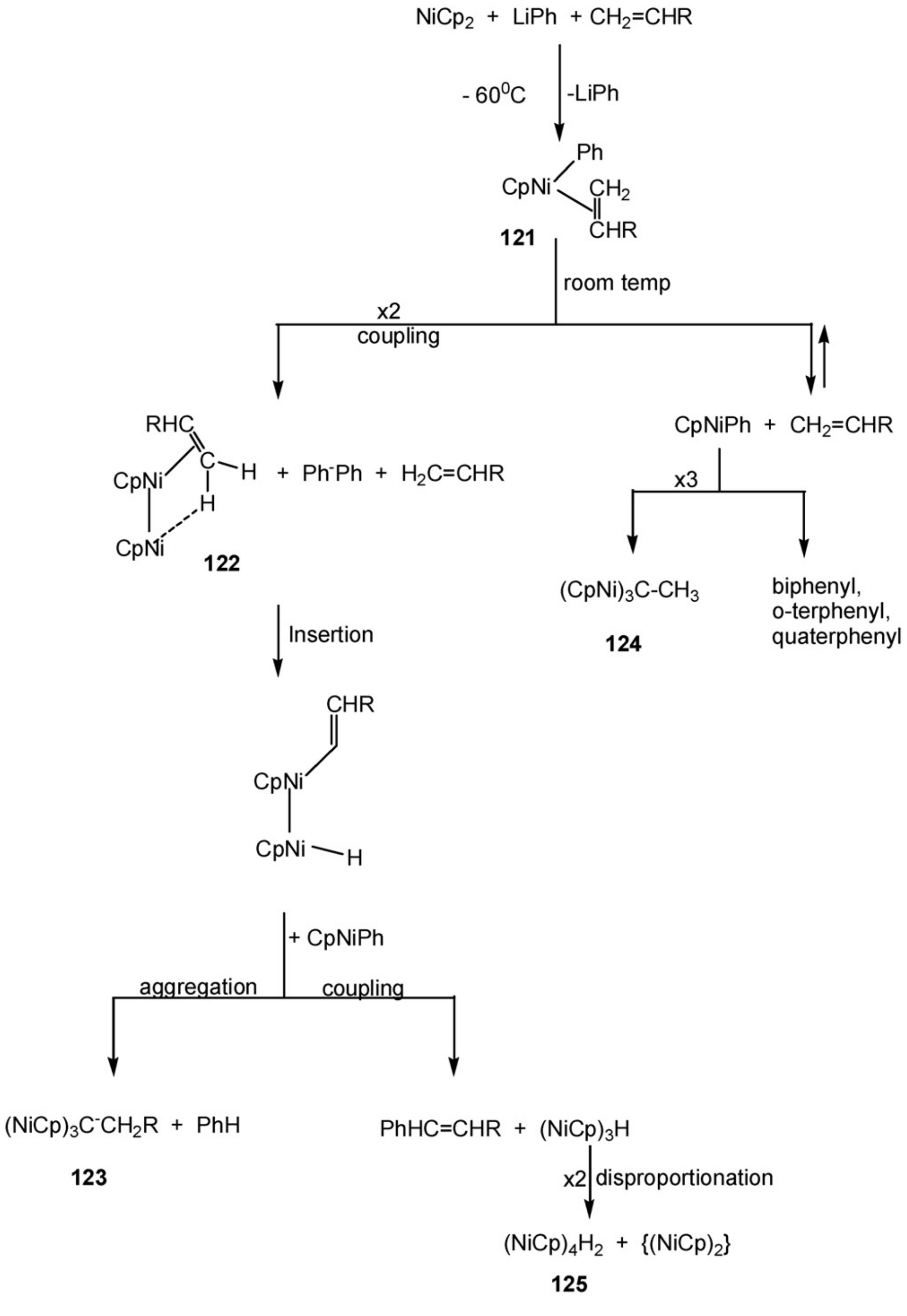
metal-catalyzed organic synthesis reactions [111]. The zerovalent complexes, particularly palladium(0) and nickel(0) complexes are commonly used as catalysts because of their high catalytic activity [112,113]. Highly active and short-lived metal-hydrocarbon intermediates are difficult to isolate to carry out further studies. Analogous platinum(0)–hydrocarbon complexes are usually more stable and amenable to study.

Pasynkiewicz and co-workers have demonstrated the activation of C–H bond in terminal olefins using cyclopentadienylnickel complexes [114]. They have shown how a reaction of nickelocene with phenyllithium in the presence of an α-olefin can yield a series of interesting nickel complexes as well as organic products as shown in Scheme 35.

At room temperature complex **121** can dissociate and exist in equilibrium with {CpNiPh} and the olefin. The complex **122** is formed by the coupling of the phenyl before dissociation of the olefin. Following activation of the C–H bond of the coordinated olefin caused by the presence of a coordinatively and electronically unsaturated dinickel centre, complex **122** can undergo aggregation or coupling followed by disproportionation to give complexes **123** and **125** (Scheme 35) [114].



Scheme 34.



Scheme 35.

3.2.2. *Chemical vapour deposition (CVD)*

Organometallic chemical vapour deposition (OMCVD) of thin film metallic conductors is an important technique used for the fabrication of microelectronic components. The technique involves the volatilization of an organometallic complex, which is the passed over a substrate and thermolysed to deposit a metal film [115,116,57]. Vapourization is performed under pressure and temperature conditions that allow a precursor vapour pressure adequate for film deposition is achieved. The complex is heated beyond its stability range, causing decomposition of the organometallic species and subsequently formation of metallic particles.

The key advantage of CVD over other deposition techniques is that pyrolysis temperature in OMCVD is hundreds of degrees lower [116]. Major applications of this method involves preparation of ohmic and Schottky diode contacts, diffusion barriers, coating for high temperature crucibles, microelectronics and the preparation of solid supported catalysts [116]. For instance, palladium films are of interest as potential replacement for gold as an electrical contact material in integrated circuits. This is due to its high electrical conductivity and resistance to oxidation [57].

Organometallic complexes bearing no heteroatom in ligand backbone are known to be relatively volatile and yield clean metal films and the synthesis of a platinum pent-4-en-yl complex is shown by Bergman and co-workers [35].

Complex **5** was found to be volatile, and the elemental composition on a copper substrate was consistently obtained as 65% Pt, 25% C and 10% Cu [35]. Other olefin and ally platinum precursors have also been reported [57]. A drawback with this method however, is formation of carbon contamination. The use of hydrogen as a carrier gas is known to minimize this.

4. Concluding remarks

It is clear from the review that a large number of Ni, Pd and Pt complexes with hydrocarbon ligands are known. These compounds range from mononuclear up to tetranuclear compounds. Although many complexes have π- bonded *n*-alkenes such as cycloalkenes, dienes and cyclopentadienes as ligands, there is a limited number of organometallic complexes with only σ-bonded metal–carbon bonds. It is also clear from the review that there are a large number of possible synthetic routes which give a range of different products, some of which are only isolated in low yields after separation. It is surprising to note the extent of the chemistry of nickelocenes and its derivatives that has been explored. Reactions of some of these compounds yield new complexes by ligand exchange, formation of new C–C bonds or intermolecular rearrangements, many of which are unexpected and occur via a variety of mechanisms. A number of spectacular advances have been made in the understanding of the bonding in metal-hydrocarbon complexes (M = Pt, Pd and Ni). Applications have been described for metal–hydrocarbon compounds including both as homogeneous and heterogeneous catalysis reactions as key intermediates, organic transformations and chemical vapour deposition studies.

Acknowledgement

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