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Coordination Chemistry Reviews 251 (2007) 1294–1308

COORDINATION CHEMISTRY REVIEWS

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Review

Transition metal-alkenyl complexes [$M–(CH_2)_nCH{=}CH_2$, $n \geq 2$]: Synthesis, structure, reactivity and applications

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Received 1 November 2006; accepted 7 December 2006

Contents

Abstract

A historical perspective is followed by an overview of methods used to synthesize transition metal-alkenyl complexes of the type $L_mM(CH_2)_n–CH{=}CH_2$ (where L_m = other ligands, M = transition metal and $n \geq 2$). Both mono- and bis(alkenyl) compounds are discussed. X-ray structures show that the alkenyl groups can coordinate either in an η^1- or an η^1,η^2-fashion. We have shown that reactivity patterns for these metal-alkenyl complexes can be different to those shown by metal-alkyl complexes and these differences are highlighted. For example bis(alkenyl) complexes can undergo ring closing metathesis (RCM) reactions to give metallacycloalkenes, as demonstrated recently by our research group. The intermediacy of transition metal-alkenyl species in ethylene oligomerization and other catalytic reactions is also discussed.

Keywords: Transition metal; Monoalkenyl complexes; Bis(alkenyl) complexes; Metallacycloalkenes

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Abbreviations: Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl or 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; dcpe, 1,2-bis(dicyclohexylphosphino)ethane; dmgH, dimethylglyoxime; py, pyridine; Tpy*, 4′-(4-*tert*-butylphenyl)-2,2′:6′,2″-terpyridine

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doi:10.1016/j.ccr.2006.12.004

1. Introduction

The main objective of this review is to survey the synthetic procedures, structural characterizations and the reactivity patterns of various metal-alkenyl compounds. To the best of our knowledge, this is the first direct review article on metal alkenyls. Transition metal-alkyl compounds of type **1** (Scheme 1) with a metal–carbon single bond have been known from the early days of organometallic chemistry [1] as key intermediates in many catalytic industrial processes and involved in fundamental organic transformations such as C–H bond activation and α- and β-hydride elimination [2]. However, little has been reported for the corresponding complexes where the alkyl moiety has a pendant double bond. The intermediacy of these species in catalytic cycles has spurred the development of metal-alkyl and metal-alkenyl chemistry.

Metal-alkyl compounds with a terminal functional group X are also important, e.g. $M–(CH_2)_nX$ (**2**) [3] (where X = halogen and OH). If the functional group X is a C=C double bond, several different types of compounds are possible depending on the position of the double bond relative to the metal. Thus, in $M–(CH_2)_nCH=CHR$ (where $n = 0$) we have M–CH=CHR (**3**) also called vinyl or alkenyl compounds [4] If $n = 1$, we have $M–CH_2–CH=CHR$ (**4**) which are η^1-allyl or σ-allyl compounds. These compounds are well known and their chemistry has been extensively studied [5]. In addition, allyl compounds have been used as catalyst precursors, e.g. tris(allyl)iridium and rhodium compounds have been prepared by Basset et al. as 'single site' catalysts consisting of a well-defined, metal-oxide surface bound catalytic systems for alkane metathesis and polyolefin depolymerization [6].

If there is a direct metal–carbon double bond, as in M=CHR (**5**), we have carbene complexes which are also very useful and well studied [7]. If $n = 2$ we have the σ-alkenyl compounds $M–CH_2–CH_2–CH=CHR$ (**6**), which are not well-known and have not yet been studied in detail (Scheme 1). This class of compounds has, however, been the focus of our research over the past few years and is the subject of this review. Broadly speaking, a metal-alkenyl complex can be defined as a ligand supported metal–carbon system in which the metal is σ-bonded to an aliphatic group containing at least two methylene units and a pendant terminal $–CH=CH_2$ group.

$L_mM\text{-}(CH_2)_nCH_2R$ **1** Metal Alkyls	$L_mM\text{-}(CH_2)_nX$ **2** Functionalised alkyl compounds
$L_mM\text{-}CH=CHR$ **3** Metal vinyls	$L_mM\text{-}CH_2CH=CH_2R$ **4** Metal allyls
$L_mM=CHR$ **5** metal carbenes	$L_mM\text{-}(CH_2)_nCH=CHR$ **6** $n \geq 2$ metal alkenyls

Scheme 1. L_m = other ligands; M = transition metal; $n \geq 2$; R = alkyl.

Transition metal-alkenyl complexes find widespread use in organic synthesis and some have been postulated as key intermediates in the Fischer–Tropsch process [8] or ethylene oligomerization reactions [48]. In addition, some bis(alkenyl)platinum(II) compounds have an important application in generating thin platinum films [9] for micro-electronic and catalytic applications [10] using the chemical vapour deposition (CVD) method [11]. Recent work from our laboratories has shown that these compounds show novel reactivity patterns and are indeed useful precursors for the preparation of other important classes of compounds particularly metallacycloalkanes [12,20].

These new results have prompted us to survey the topic of transition metal-alkenyl compounds of the type $M–(CH_2)_nCH=CHR$ (**6**) (where $n \geq 2$). We also include complexes where two such alkenyl groups are coordinated to a metal. Compounds that contain a heteroatom in the alkenyl chain have not been included but those with alkyl substituents are included.

Herein we discuss the synthesis, structure, reactivity and applications of these metal alkenyls which are emerging as an important class of organometallic compounds. We also describe how these are different from the analogous transition metal-alkyl compounds in reactivity. Finally we show how an improved understanding of the nature and reactivity of these metal alkenyls may be exploited to perform novel chemical transformations.

2. Synthesis and structure

Despite their significance and importance in organometallic chemistry and catalysis, metal-alkenyl compounds have proved remarkably difficult to isolate and characterize completely. Certain ligand systems can impart distinct reactivity to the metal alkenyls and provide access to more stable complexes, which are better amenable to reactivity studies and spectroscopic characterization. Some of the Pt-alkenyl complexes that we have prepared have been structurally characterized by X-ray crystallography. It appears that the most thermally sensitive metal-alkenyl complexes are, as expected, those with hydrogen atoms in the β-position. When the terminal alkene is close to the metal center, structural bond reorganization occurs. Firstly we summarize and assess key synthetic routes which have been used to prepare metal-alkenyl complexes.

2.1. Monoalkenyl compounds

Thus far, the most frequently reported metal-alkenyl complexes are those containing the metals such as Fe [13–17,32,33], Pt [18–20] and Ti [21–24], with only a few reports of complexes based on other metals such as Ni [25], Hf [26], Rh [27], Mo

[28,29], Co [30,31], Pd [34], Ru [35] and Zr [36] (Scheme 2). The main methods used for the synthesis of these complexes are (i) the anion route, (ii) the Grignard route, with only a few reports on synthesis, (iii) from dienes and (iv) by oxidative addition of a haloalkene to a transition metal.

2.1.1. *Anion route*

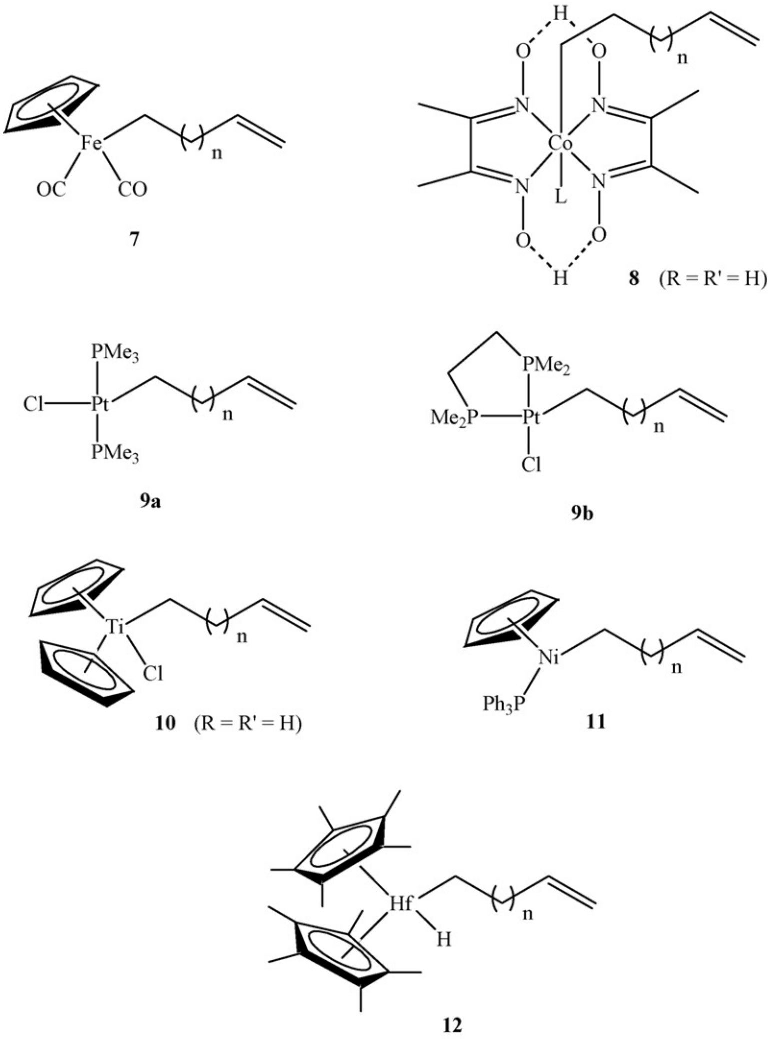
The first report of the synthesis of a metal-alkenyl complex we found in the literature was that of the iron-butenyl complex, $CpFe(CO)_2(CH_2CH_2CH{=}CH_2)$ (**7**), by Green and Smith [13] which was later also reported by others [14,15] The synthesis of a series of these iron-alkenyl complexes, using the anion method, was reported by Roustan et al. [32] who also reported on the reactivity of the complexes. Iron-alkenyl complexes of this type have also been investigated by Mapolie and co-workers who prepared a series of these complexes with varying alkenyl chain lengths, as well as the analogous pentamethylcyclopentadienyl complexes, viz. $(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nCH{=}CH_2\}$ (R = H, Me; n = 2–4, 6) [16,17].

In addition, a number of cobaloxime, bis(dimethylglyoximato)pyridinecobalt, complexes with alkenyl ligands $py(dmgH)_2Co(CH_2CHRCR'{=}CH_2)$ (**8**) (R = H, Me, Ph; R′ = H, Me; py = pyridine and dmgH = dimethylglyoxime) have been reported using this route [30,31].

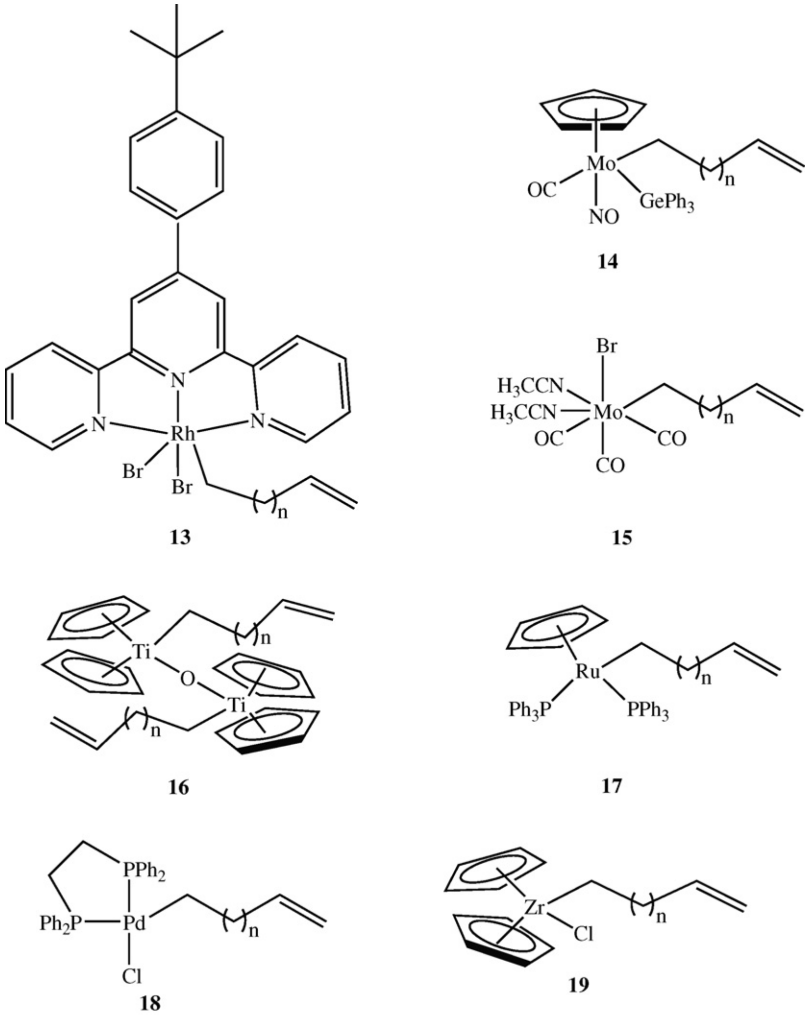
2.1.2. *Transmetalation reactions*

The Grignard method has so far been the most widely employed route in the preparation of metal-alkenyl complexes of Pt [18–20] (**9**), Ti [21] (**10**), Ni [25] (**11**), Pd [34] (**18**), Ru [35] (**17**) and Zr [36] (**19**). The platinum-alkenyl complexes of type (**9**) have been prepared by the reaction of $PtCl_2(COD)$ with the appropriate Grignard reagent to give the bis(alkenyl) product followed by cleavage of one of the Pt–C bonds using HCl to give the monoalkenyl products. In contrast, the alkylation of $Pd(dppe)Cl_2$ was reported to give only the monoalkenyl product, $PdCl(dppe)\{(CH_2)_2CH{=}CH_2\}$ [34].

Titanium-alkenyl complexes of type (**10**) have been synthesized from Cp_2TiCl_2 and the appropriate organomagnesium halides to give the products $Cp_2TiCl\{(CH_2)_2CHRCR'{=}CH_2\}$ (R = H, Ph; R′ = H, CH_3) in varying yields [20]. In a similar way, the synthesis of nickel-alkenyl complexes [25] of type (**11**), $CpNi(PPh_3)\{(CH_2)_2CH{=}CH_2\}$ and ruthenium-alkenyl complexes [35] of the type $CpRu(PPh_3)_2\{(CH_2)_nCR{=}CH_2\}$ (n = 2, R = H; n = 3, R = Me) was reported. Denner and Alt recently



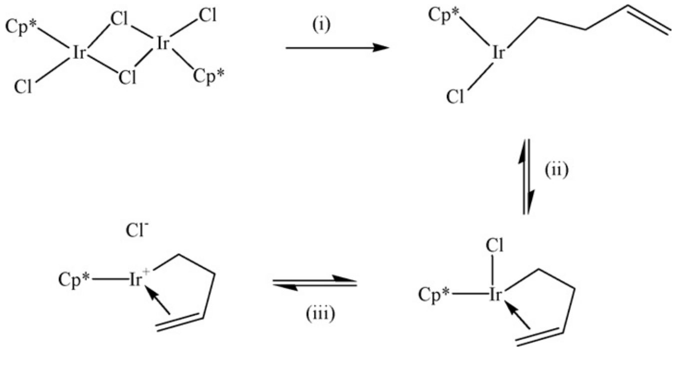
Scheme 2.



Scheme 2 (*Continued*).

reported the synthesis of zirconium-alkenyl complexes of the type $Cp_2ZrCl\{(CH_2)_nCH{=}CH_2\}$ ($n = 2, 3$) [39].

We have synthesized $PtCl(dppp)\{(CH_2)_3CH{=}CH_2\}$ from $PtCl_2(dppp)$ with 1 mol of the corresponding Grignard reagent and the expected product was obtained in a moderate yield [41]. Our experiments also revealed that reactions of $Cp^*IrCl_2(PPh_3)$ with various 1-alkenyl Grignard reagents yielded the expected monoalkenyl complexes. These products are sensitive to light, heat and the solvent system (Scheme 3).



Scheme 3. (i) Et_2O, $BrMgCH_2CH_2CHCH_2$; (ii) C_6H_6; (iii) $CHCl_3$ or CH_2Cl_2.

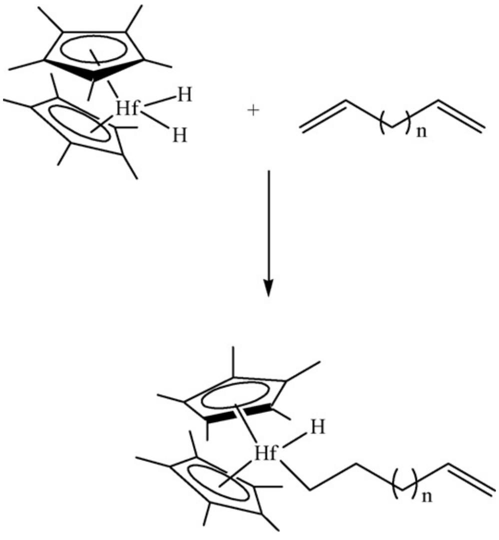
2.1.3. *From dienes*

The synthesis of hafnium-alkenyl complexes of type (**12**), $Cp^*_2(H)Hf(CH_2)_nCH{=}CH_2$ ($n = 3$–5) prepared by the reaction of $Cp^*_2HfH_2$ and the corresponding α,ω-diene, has been reported by Bercaw and Moss [26]. The hafnium-alkenyl hydride complex $Cp^*_2(H)Hf(CH_2)_3CH{=}CH_2$ was observed spectroscopically (Scheme 4) at low temperatures but not isolated, and on warming to 20 °C converts to a mixture of the five-membered hafnacycle and the binuclear alkanediyl derivative as shown in Scheme 12.

Similarly, reaction of $Cp^*_2HfH_2$ with 1,5-hexadiene gave a mixture of the hafnium-alkenyl hydride complex and α,ω-dihafnaalkanediyl complex, and also rearranges on standing at room temperature over 4 days to the six-membered hafnacycle. In contrast, the hafnium-alkenyl complex formed from the longer chain 1,6-heptadiene is stable and cyclization to the seven-membered hafnacycle did not occur. No other metal-alkenyl complexes have been reported using this route.

2.1.4. *Oxidative addition route*

Frühauf and co-workers [27] recently reported the synthesis of a series of rhodium-alkenyl complexes of type (**13**) $[(Tpy^*)Rh(Br)_2\{(CH_2)_nCH{=}CH_2\}]$ ($Tpy^* = 4'$-(4-



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Scheme 4. $n = 3$–5.

tert-butylphenyl)-2,2′:6′,2″-terpyridine; $n = 2$–4, 6, 9). These complexes were prepared by the oxidative addition of an excess of the appropriate ω-bromo-1-alkene to [RhBr(Tpy*)] to give a single product in almost quantitative yield.

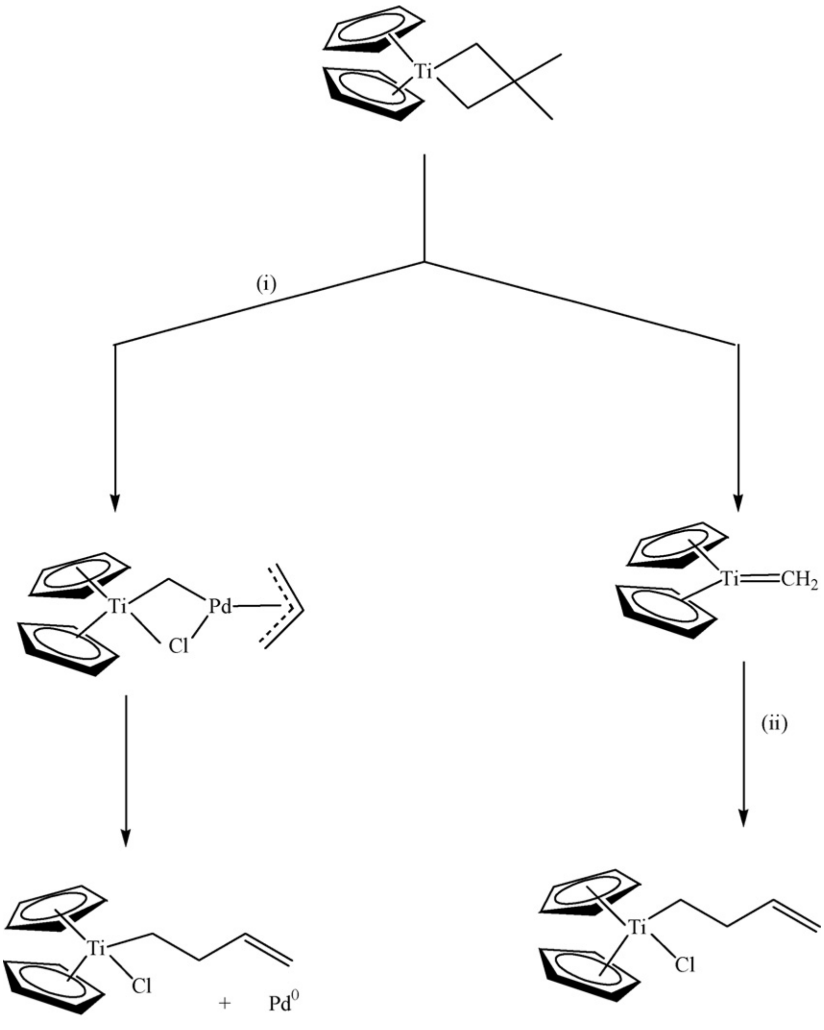
The molybdenum-butenyl complex [CpMo(NO)(CO)(GePh$_3$){(CH$_2$)$_2$CH=CH$_2$}] (**14**) was prepared by the reaction of [CpMo(NO)(CO)(GePh$_3$)]$^-$ with 4-iodo-1-alkene and obtained in good yield [28].

The seven-coordinate molybdenum-butenyl complex [Mo(CO)$_3$(CH$_3$CN)$_2$(Br){(CH$_2$)$_2$CH=CH$_2$}] (**15**) has also been reported by the reaction of Mo(CO)$_6$ with 4-bromo-1-butene in refluxing acetonitrile [29].

2.1.5. Other methods

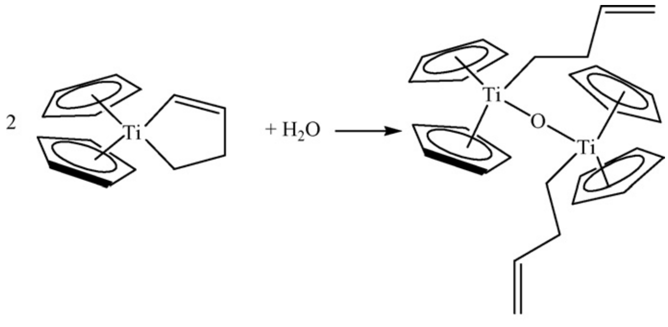
Grubbs and co-workers have reported the synthesis of a titanium-butenyl complex, Cp$_2$Ti(Cl){(CH$_2$)$_2$CH=CH$_2$} (**10**) from the titanacyclobutane complex using two different methods as shown in Scheme 5 [22,23].

The reaction of $Cp_2\overline{TiCH_2C(CH_3)_2CH_2}$ with [(η^3-allyl)PdCl]$_2$ produced a titanium complex which the authors tentatively iden-



10 **10**

Scheme 5. (i) [(η^3-Allyl)PdCl$_2$]; (ii) allylic chloride (1.1 equiv.), room temperature, benzene, 12 h.



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Scheme 6.

tified as the titanium-butenyl complex. This complex has also been prepared by the reaction of the titanacyclobutene complex with allylic chloride via a titanium-methylene complex.

The synthesis of a binuclear titanium-butenyl complex has been reported by Alt and Hermann, from the reaction of the titanacyclopentene complex (**16**) with water, as shown in Scheme 6 below [24a].

In addition, the α,ω-butenyl complexes $\mathrm{Tp^{Br3}Ir(H)(\eta^1{:}\eta^2\text{-}CH_2CH_2CH{=}CH_2)}$ ($\mathrm{Tp^{Br3}}$ = trispyrazolylborate ligand) have been prepared by thermolysis of the vinyl-ethylene complex $\mathrm{Tp^{Br3}Ir(H)(\eta^1\text{-}CH{=}CH_2)(\eta^2\text{-}CH_2{=}CH_2)}$ and $\mathrm{M(\eta^1{:}\eta^2\text{-}CH_2CPhRCH{=}CH_2)}$ (M = Ir, R = H; M = Rh, R = Ph) from the highly strained phenyl substituted methylenecyclopropane at room temperature [24b,c]. The rhodium-butenyl complex $\mathrm{[CnRh(\eta^1\text{-}CH{=}CH_2)(\eta^1\text{-}CH_2CH_2CH{=}CH_2)]^+}$ (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) has also been proposed as an intermediate in the formation of π-allylic complex $\mathrm{[CnRh(\eta^1\text{-}CH{=}CH_2)(\eta^3\text{-}CH_2CHCHCH_3)]^+}$ [24d]. Diosmacyclobutane is reported to react with butadiene to afford the binuclear 1,2-adduct $\mathrm{Os_2(CO)_8[\mu\text{-}CH_2CH(CH{=}CH_2)]}$ in which the butenyl ligand bridges both metal centres [24e].

The yields obtained via the above synthetic procedures are generally low for most of the metal-alkenyl complexes partly because of the unstable M–C bonds and also because of the reactive terminal alkene moiety. These difficulties may be part of the reason for the gap between the early work and more recent reports in this field.

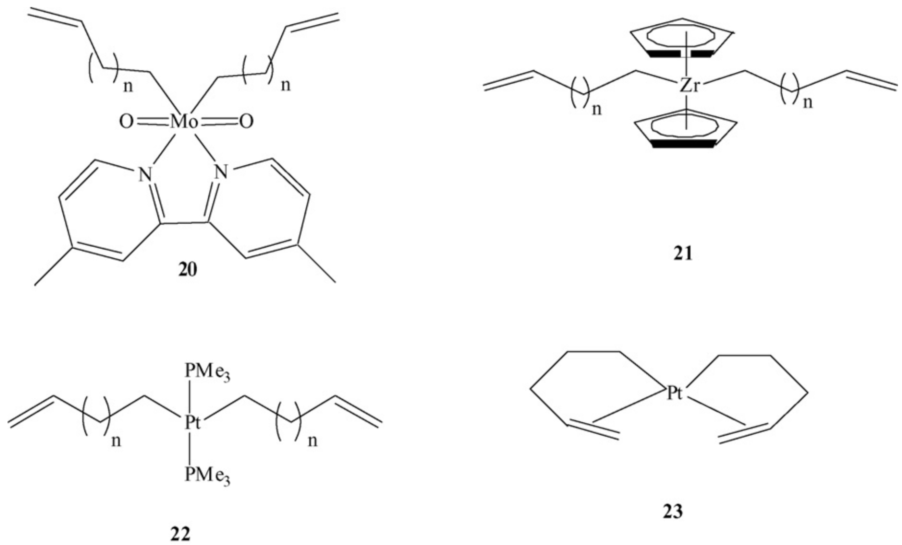
2.2. *Bis(alkenyl) compounds*

While there are a number of reports on monoalkenyl complexes prepared using the various synthetic methods described above, the known bis(alkenyl) complexes are limited to platinum [37,38], molybdenum [28,29] and zirconium [36], and have been prepared exclusively by reaction of a metal halide with a Grignard reagent. No other methods are known for the synthesis of alkenyl complexes of these metals (Scheme 7).

The bis(alkenyl)platinum(II) complex $\mathrm{Pt(PMe_3)_2\{(CH_2)_3C(CH_3){=}CH_2\}_2}$ (**22**) was prepared by the alkylation of $\mathrm{Pt(COD)Cl_2}$ with the corresponding Grignard reagent in the presence of $\mathrm{PMe_3}$. In a similar way, Benn et al. [38] have synthesized the bis(alkenyl) complexes $\mathrm{L_2Pt\{(CH_2)_2CH{=}CH_2\}_2}$ (where $\mathrm{L_2}$ = dmpe, dcpe, dppe). In contrast, Tagge et al. have shown that reacting $\mathrm{Pt(COD)Cl_2}$ with pent-4-en-1-ylmagnesium bromide gives *cis*-bis(η^1,η^2-pent-4-en-1-yl)platinum (**23**), a complex in which the alkenyl ligand is bound to the metal in a η^1,η^2-fashion [37]. The complex $\mathrm{Pt\{(CH_2)_3CH{=}CH_2\}_2}$ (**23**) is air and moisture stable, but thermally sensitive in the solid state, decomposing within 2 weeks at room temperature.

The molybdenum bis(alkenyl) complex $\mathrm{L_2Mo(O)_2\{(CH_2)_4CH{=}CH_2\}_2}$ (**20**) (where $\mathrm{L_2}$ = 4,4′-dimethyl-2,2′-dipyridyl) was prepared by the reaction of $\mathrm{L_2Mo(O)_2Br_2}$ with the corresponding Grignard reagent, followed by aerobic oxidation of the reaction mixture to give the stable product in low yield [36].

The zirconium bis(alkenyl) complexes, $\mathrm{Cp_2Zr\{(CH_2)_\mathit{n}CH{=}CH_2\}_2}$ (**21**) (n = 1, 2), were prepared in moderate yields by reaction of $\mathrm{Cp_2ZrCl_2}$ with 2 mol equiv. of the appropriate Grignard reagent [39].



20 **21** **22** **23**

Scheme 7.

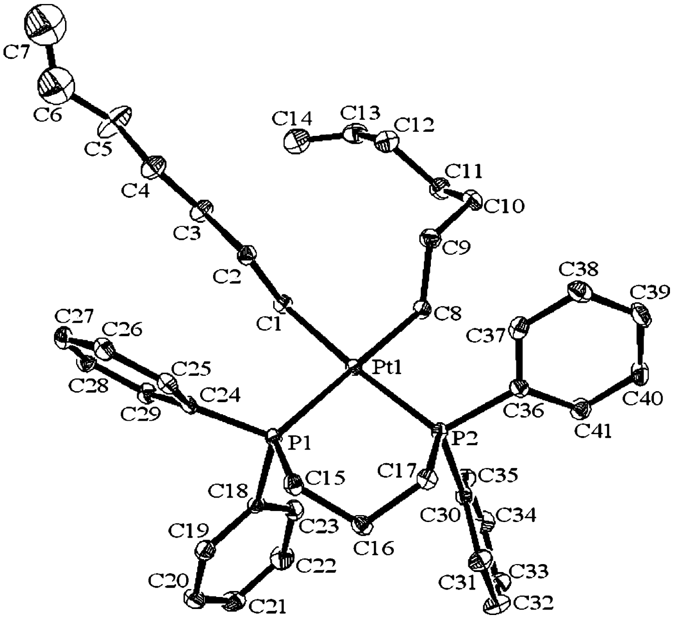
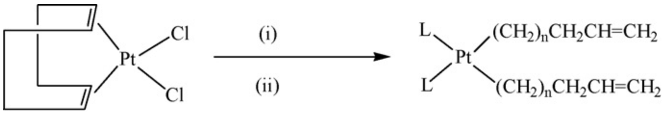


Fig. 1. Molecular structure of (dppp)Pt{$(CH_2)_5CH{=}CH_2$}$_2$; selected bond lengths (Å): Pt(1)–P(1) 2.2923(7), Pt(1)–P(2) 2.2777(7), Pt(1)–C(1) 2.120(3), Pt(1)–C(8) 2.118(3) [41].



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Scheme 8. (i) $BrMg(CH_2)_nCH_2CH{=}CH_2$, Et_2O, −78 °C; (ii) L = PPh_3, $^tBu_3P$, dppe, dppp; n = 1–4 and 7.

We have recently prepared [40] a series of bis(alkenyl)platinum(II) complexes $L_2Pt\{(CH_2)_nCH{=}CH_2\}_2$ (**24**) (L = PPh_3; L_2 = dppe, dppp; n = 2, 3, 4, 5, 8) in high yields using the Grignard route (Scheme 8). The X-ray crystal structures of two bis(alkenyl)platinum(II) complexes of different chain lengths (n = 5 and n = 2) have been determined (Figs. 1 and 2, respectively). These structures clearly show that the alkenyl groups are bonded in an η^1-mode with pendant alkene double bonds. Furthermore, we have found that the dppe or dppp containing metal-alkenyl complexes are crystalline solids and thermally stable up to about 100 °C, even though they have hydrogen atoms in the β-position.

3. Chemical reactivity

Metal-alkenyl complexes can show three distinct reaction pathways: (i) reaction at the M–C bond, (ii) reaction at the C=C bond and (iii) coordination of the pendant alkene. Clearly the pathways (ii) and (iii) are not accessible to metal-alkyl complexes. We believe that these special features impart novel chemistry on these complexes.

The interaction of metal alkenyls with electrophilic reagents such as acids and halogens gives the corresponding hydro-

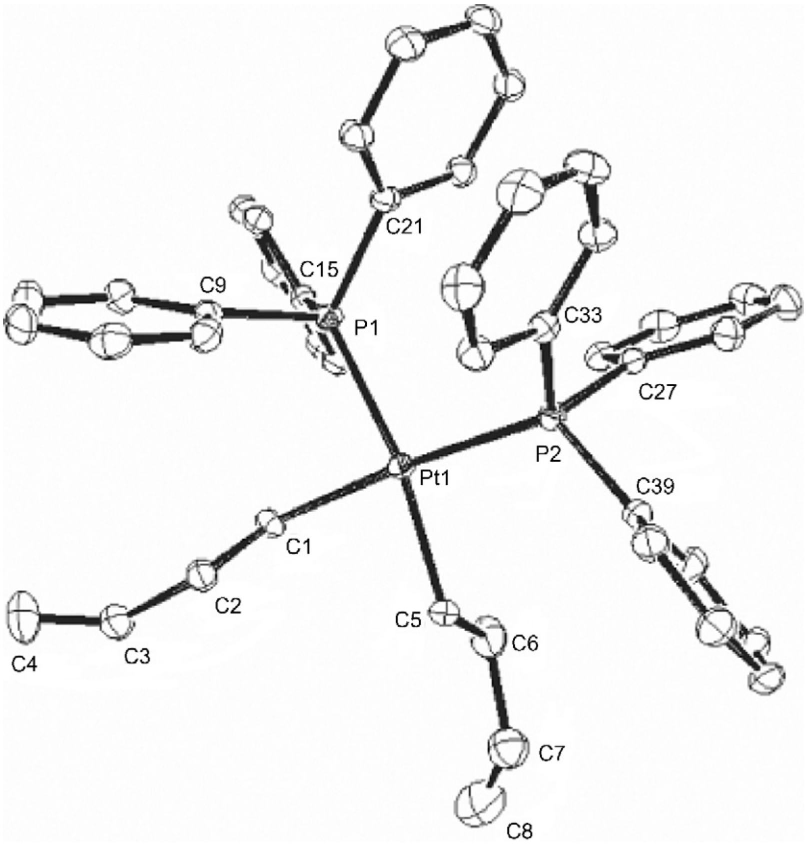


Fig. 2. Molecular structure of $(PPh_3)_2Pt\{(CH_2)_2CH{=}CH_2\}_2$; selected bond lengths (Å): Pt(1)–P(1) 2.300(9), Pt(1)–P(2) 2.304(9), Pt(1)–C(1) 2.127(2), Pt(1)–C(5) 2.095(3), C(3)–C(4) 1.304(4) [20].

carbons or 1-haloalkenes resulting from the cleavage of metal–carbon bonds. Some of these reactions may have obvious potential in organic synthesis, since they provide a method for the formation of new C–C bond by reductive elimination reaction or formation of C–X bonds. The following sections deal first with the reactivity patterns of monoalkenyl complexes followed by the reactivity of bis(alkenyl) metal complexes.

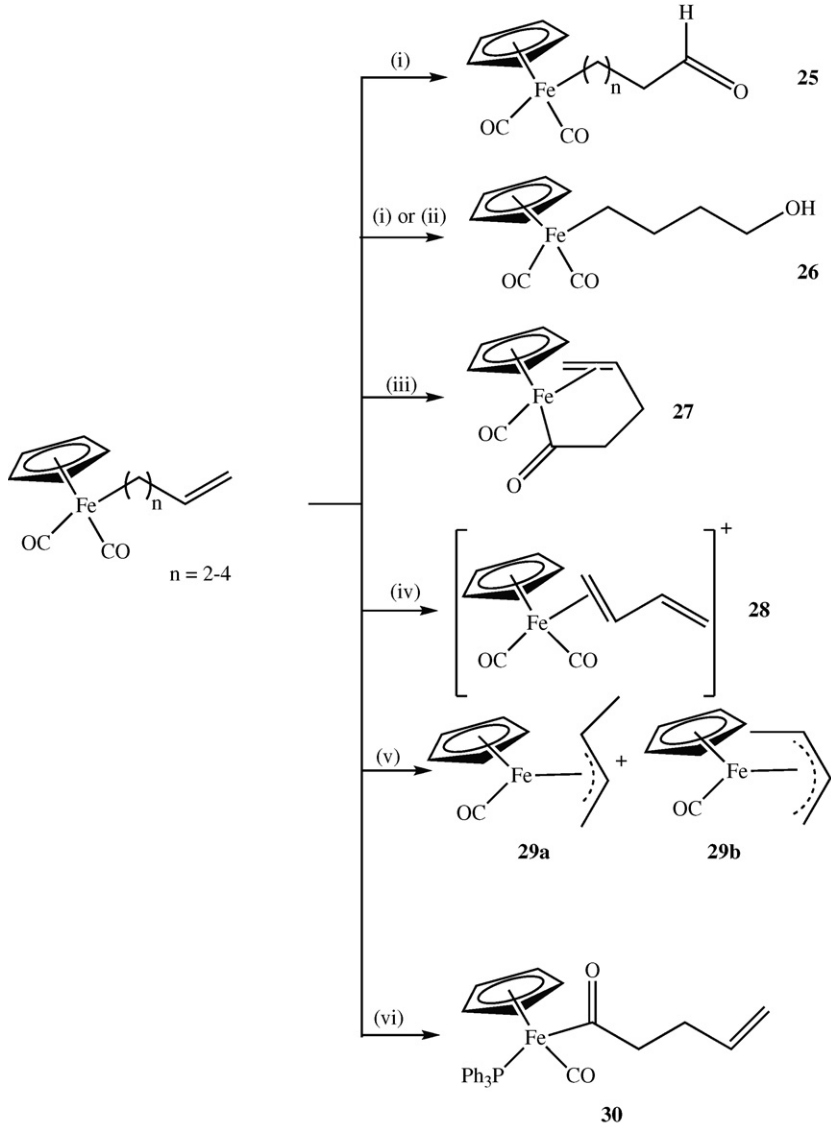
3.1. Monoalkenyl complexes

The reactivity of the iron-alkenyl complexes has been investigated in detail including hydrogenation and hydroformylation reactions as well as the reaction with the Lewis acid $TiCl_4$ [13,14,16,17]. In some of these cases, the C=C double bond undergoes an addition reaction to yield a functionalized metal-alkyl complex. Similar to metal alkyls, the reactivity with the trityl salt Ph_3CBF_4 has been reported by Baird and co-workers to cause β-hydride elimination giving rise a new metal–olefin bond [14]. Details of these various reaction pathways are shown in Scheme 9.

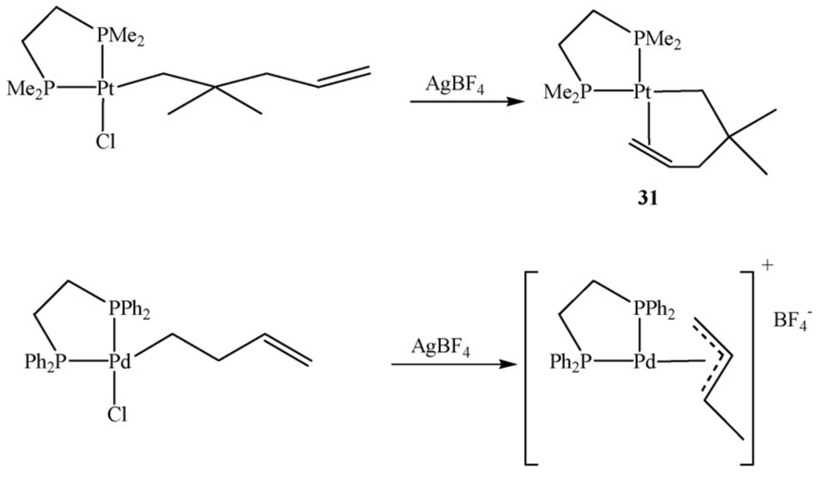
The iron-alkenyl complexes $CpFe(CO)_2\{(CH_2)_nCH{=}CH_2\}$ ($n = 2$, 3) were hydrogenated in the presence of Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, to yield the corresponding iron-alkyl complexes $CpFe(CO)_2\{(CH_2)_{n+1}CH_3\}$. The iron-alkenyl complexes ($n = 2$, 3) were also reacted with synthesis gas ($CO:H_2$; 1:1) in the presence of the hydroformylation catalyst $HRh(CO)(PPh_3)_3$, to give a mixture of the ω-hydroxyalkyl (**26**) complex and the aldehyde (**25**). It is also reported that the iron-butenyl complex reacts with $TiCl_4$ to undergo carbonyl insertion to form complex (**27**) where the pendant alkene is coordinated to the iron in an η^1,η^2-fashion [17].

This product (**27**) has also been reported to form when the iron-butenyl complex is heated in CH_3NO_2. This sort of reactivity is not observed with the longer chain iron-pentenyl complex.

Roustan et al. [32] found that photolysis of the iron-butenyl complex gave an isomeric mixture of two η^3-methylallyl complexes (**29a** and **29b**) as shown in Scheme 9.



Scheme 9. (i) $HRh(CO)(PPh_3)_3/H_2/CO$/THF/1 atm; (ii) BH_3•THF/H_2O_2/NaOH; (iii) $TiCl_4$ or Δ; (iv) Ph_3CBF_4; (v) *hν*; (vi) (1) PPh_3, *hν*, (2) –CO.



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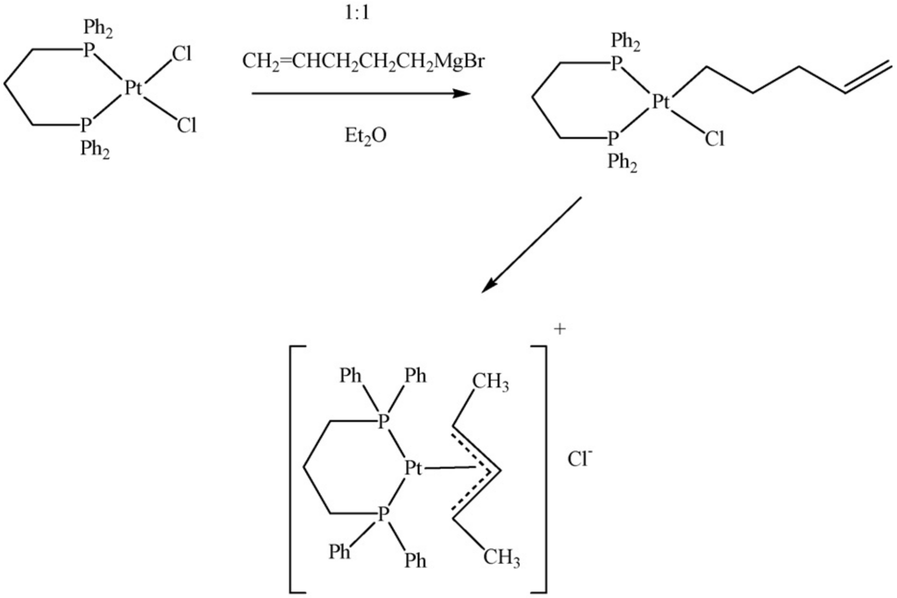
Scheme 10.

The iron-alkenyl complexes $CpFe(CO)_2\{(CH_2)_nCH{=}CH_2\}$ ($n = 2$–4) are also reported to react with PPh_3 to give the acyl complexes (**30**). However, photolysis of the iron-alkenyl complexes in the presence of PPh_3 gives the PPh_3 substituted alkenyl complexes and carbonyl insertion did not occur.

The irradiation of the iron-butenyl complex resulted in the evolution of carbon monoxide and formation of the η^3-methylallyl derivative (**29**) whereas an analogue of compound (**27**) is obtained if the original alkenyl ligand is disubstituted at the β-carbon. In contrast, thermolysis of the iron-butenyl complex results in the formation of (**27**), as shown in Scheme 9 [13].

Treatment of the platinum-alkenyl complex $PtCl(dmpe)(CH_2C(CH_3)_2CH_2CH{=}CH_2)$ with $AgBF_4$ results in the formation of an η^1,η^2-compound (**31**) where the pendant alkenyl becomes coordinated to Pt [19]. The palladium-alkenyl complex, $PdCl(dppe)\{(CH_2)_2CH{=}CH_2\}$ however, is reported to react with $AgBF_4$ to give the cationic η^3-1-methylallyl complex (**32**) in high yield as shown in Scheme 10.

Recent results have shown that the $PtCl(dppp)\{(CH_2)_3CH{=}CH_2\}$ complex undergoes an irreversible rearrangement to the η^3-1,3-dimethylallyl cationic complex (**33**, Scheme 11), depending on the experimental conditions [42]. The new monoalkenyl complex, $PtCl(dppp)\{(CH_2)_3CH{=}CH_2\}$ is sensitive to solvent, temperature and light. Attempts were also made to prepare monoalkenyl complexes of the Group 9 metals (M = Ir, Rh), but these products readily rearrange to the allylic isomers, in



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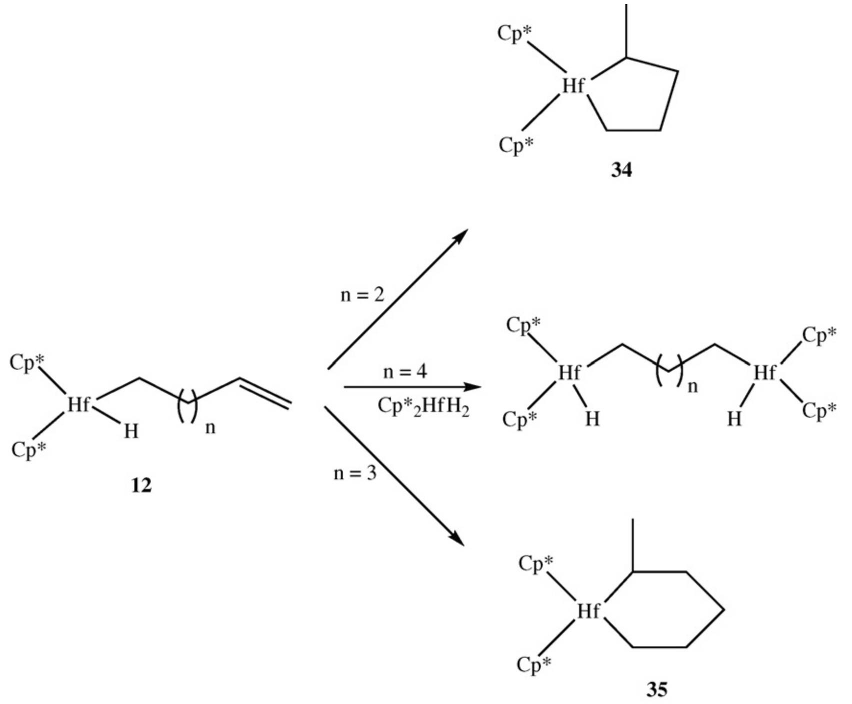
Scheme 11.



Scheme 12.

a similar way to their platinum analogues. The halide ligands in these complexes are strong nucleophiles, and accelerate the rate of rearrangement ($I^- > Br^- > Cl^-$) [41].

The hafnium-alkenyl hydride complexes $Cp^*_2(H)Hf(CH_2)_nCH{=}CH_2$ (**12**, $n = 2$, 3) which form at low temperature, converts, upon warming to RT, to the metallacyclic hafnamethylcyclopentane (**34**) and hafnamethylcyclohexane (**35**) complexes, respectively (Scheme 12) [26]. However, the longer chain alkenyl complex ($n = 4$) does not cyclize but slowly converts to the bimetallic $Cp^*_2(H)Hf(CH_2)_7Hf(H)Cp^*_2$ in the presence of $Cp^*_2HfH_2$.

Corriu and co-workers [28] investigated the thermal reactivity of the molybdenum-alkenyl complexes $[CpMo(NO)(CO)(GePh_3)\{(CH_2)_nCH{=}CH_2\}]$ ($n = 2$, 4) (**14**) (Scheme 13). When refluxed in THF solution, CO is rapidly evolved with conversion of the alkenyl ligand to give the η^3-allyl complex (**36**). The structure of complex (**36**) ($R = C_3H_7$) has been confirmed by X-ray crystallography.

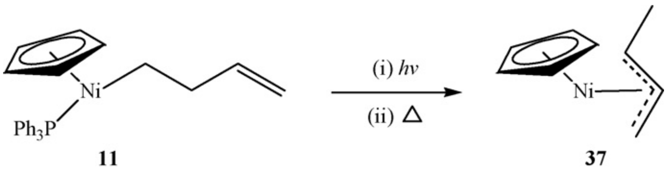
The nickel-butenyl complex, $CpNi(PPh_3)\{(CH_2)_2CH{=}CH_2\}$ (**11**), behaves in a similar manner (Scheme 14) [25]. Thermolysis or photolysis of this complex in benzene leads to the displacement of the PPh_3 ligand to give the η^3-methylallyl complex as the product (**37**).

3.2. *Bis(alkenyl) compounds*

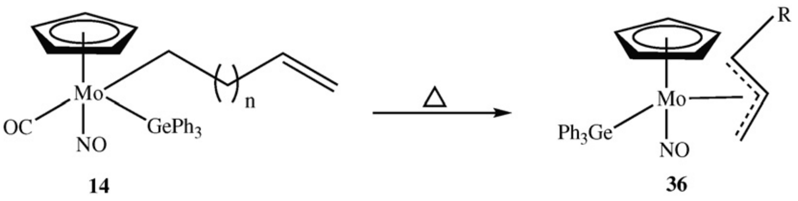
In addition to the three reaction pathways shown by monoalkenyl complexes, further reaction pathways are open to bis(alkenyl) complexes. These include the ring closing metathesis reaction.

3.2.1. *Ring closing metathesis (RCM)*

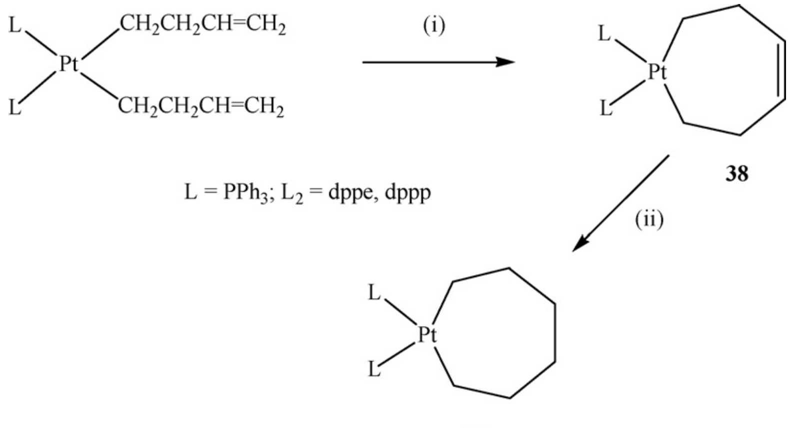
We have recently shown [20,40] that some bis(alkenyl) metal complexes are able to undergo a ring closing metathesis reaction (RCM) with Grubbs' catalyst to yield corresponding metallacycloalkenes. Thus for example platinacycloheptene (**38**) as shown in Scheme 15 can be prepared in good yield using this method. We have used the same synthetic procedure to successfully convert a range of other metal bis(alkenyl) com-



Scheme 14.



Scheme 13. $n = 1$, $R = CH_3$; $n = 3$, $R = C_3H_7$.



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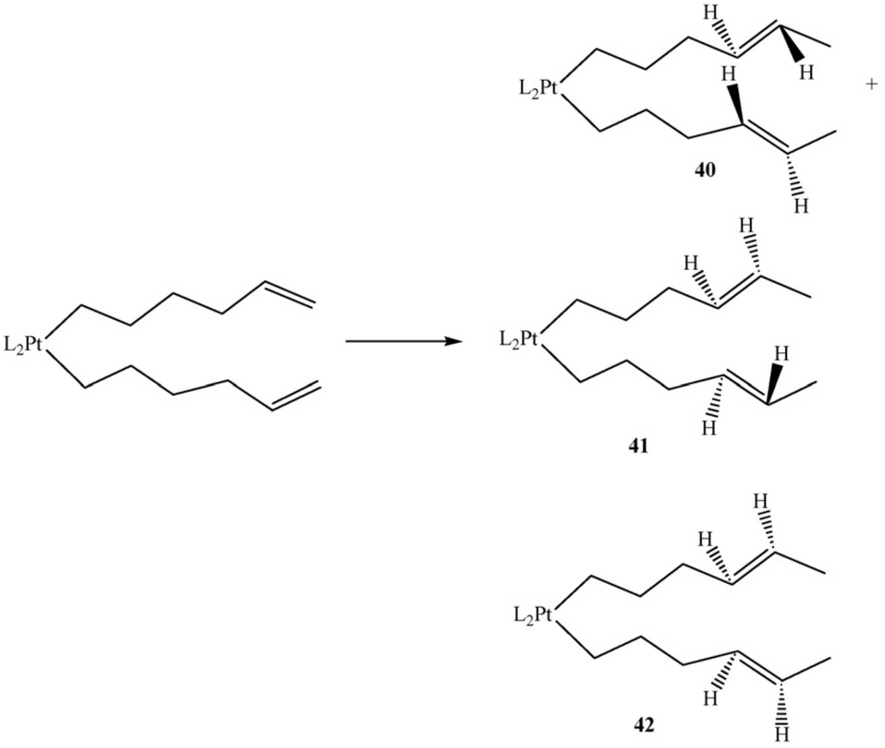
Scheme 15. (i) Grubbs catalyst generation 1, CH_2Cl_2 reflux 1 h; (ii) H_2, Pd/C, CH_2Cl_2.

plexes to the corresponding metallacycloalkenes [40]. These metallacycloalkenes can then be converted to metallacycloalkanes (e.g. **39**) in good yield after catalytic hydrogenation with palladium on carbon. Currently, other metallacycloalkane complexes bearing a wide variety of ligand systems with different ring sizes (M = Pt, Pd, Rh, Ir, Cr, Zr, Fe, Ru, Os and others) are being investigated by our research group [42].

3.2.2. Isomerization

Recently we have found that the bis(alkenyl) complexes $L_2Pt(CH_2CH_2CH_2CH_2CH{=}CH_2)_2$ undergo a quantitative isomerization to yield corresponding internal alkene complexes and their isomers (**40–42**) (Scheme 16) [41]. These reactions are quite dependent on the nature of the tertiary phosphine ligand system. These products were isolated and fully characterized. The monoalkenyl complexes of Pt, Ir and Rh react in a similar manner. One of the key characteristics of these transition metal-alkenyl compounds is that the nature of the other ligands as well as the length of the alkenyl ligand can influence the structure and reactivity. Thus, in the case of (diphos)platinum(II) complexes, the rate of isomerization increases with an increase in the alkenyl chain length. In contrast, with other ligands such as PPh_3 and P^tBu_3, the complexes decompose even at moderate temperatures prior to the isomerization [41]. The isomerization is favoured rather than the expected β-hydrogen elimination reactions in



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Scheme 16. Benzene, 100 °C and L_2 = dppe, dppp.

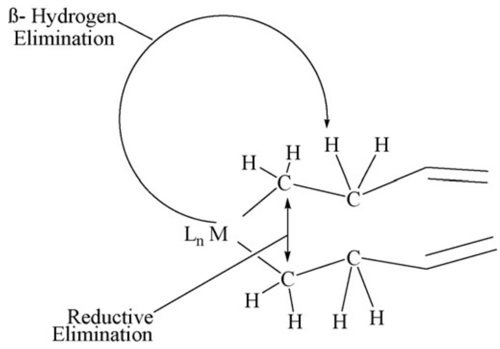


Fig. 3. Possible decomposition pathways for metal bis(alkenyl) compounds.

platinum(II)-alkenyl complexes under these experimental conditions [41].

3.2.3. Thermal decomposition and rearrangement reactions

The thermal stability of the metal-alkenyl complexes appears to be largely dependent on the solvent system, thus halogenated solvents readily cleave the M–C bond to form metal halides irrespective of the ligand system [40]. Bis(alkenyl) metal complexes could give various products on decomposition—these include (i) long chain dienes by reductive elimination, (ii) diene and 1-alkene by β-hydride elimination followed by reductive elimination (see Fig. 3) and (iii) isomerization or rearrangement of the coordinated alkenyl ligand. A particularly important step in the mechanism of a catalytic or stoichiometric reaction, involving a metal-alkyl or metal-alkenyl species, is its decomposition to give the desired organic products. Although thermal decomposition pathways of metal-alkenyl complexes may be similar to those of metallacycles or metal-alkyl complexes, the formation of products can differ considerably because of the pendant alkene functionality [40].

Vetter and Sen [36] investigated the anaerobic and aerobic decomposition of a molybdenum(VI) dioxo bis(alkenyl) complex (Eq. (1)). Under anaerobic conditions, thermal decomposition of $L_2Mo(O)_2\{(CH_2)_4CH{=}CH_2)\}_2$ (**20**) led to the formation of 1-hexene, 1,5-hexadiene, methylcyclopentane and methylenecyclopentane. The aerobic decomposition gave the same mixture of products but in addition, cyclopentylformaldehyde was also formed.

Tagge et al. [37] reported the thermal decomposition studies on *cis*-bis(η^1,η^2-pent-4-ene-1-yl)platinum(II) (**23**) as shown in Eq. (2) to give a complex mixture of C_5 products which presumably arise from β-elimination or hydrogen abstraction reactions. No products were observed that could have been derived from the reductive elimination of the two alkenyl fragments.

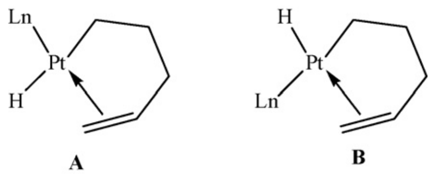
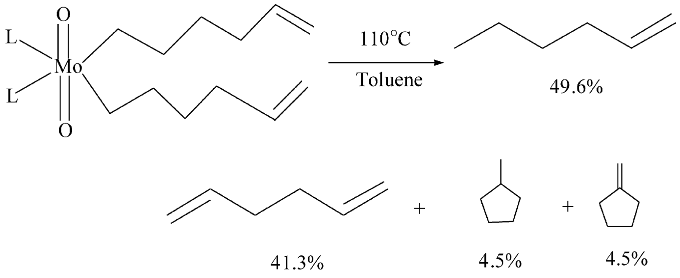
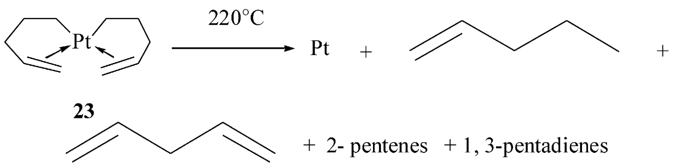


Fig. 4. Proposed intermediates in the decomposition reactions of metallacycloalkanes.



(1)

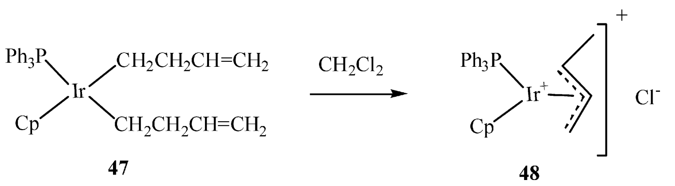


(2)

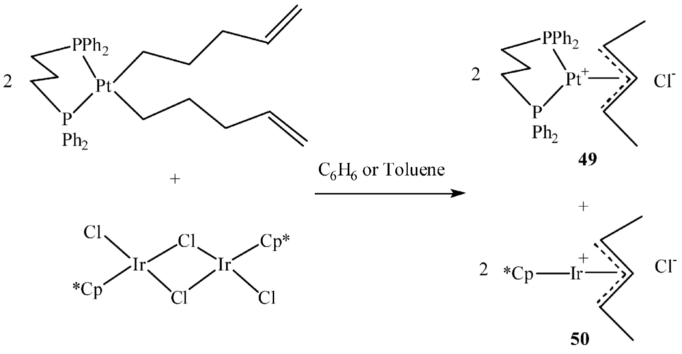
Our experiments revealed that there are particular effects exerted by the nature of the ligands and their donor atoms such as oxygen, nitrogen, phosphorus in relation to the stability and reactivity of metal-alkenyl compounds in solutions [40,42]. Thus the triphenylphosphine complexes, $Pt(PPh_3)_2\{(CH_2)_nCH{=}CH_2\}_2$ decompose to yield an intense red colour which we believe to be due to $Pt_n(PPh_3)_m$ clusters. In contrast, the $PtL_2\{(CH_2)_3CH{=}CH_2\}_2$ complexes (where L_2 = dppp or dppe) were quite stable up to 100 °C without decomposition. The diphosphine ligands have generally been found to increase the thermal stability of the complexes significantly.

It is also believed [43] that metal-alkenyl species may be important intermediates in the decomposition of metallacycloalkanes through β-hydride elimination. The proposed intermediate is an alkenyl hydride (**A** or **B**) which then can decompose further to give a 1-alkene (Fig. 4).

The decomposition pathway of Group 9 metal-alkenyl complexes of the type $Cp^*M(PPh_3)(CH_2CH_2CH{=}CH_2)_2$, where M = Rh or Ir is considerably more complex than that of their platinum analogues. Thermolysis of the bis(alkenyl)iridium complex (**47**) above room temperature yielded [42] a stable η^3-1-methylallyl cationic complex (**48**) (Eq. (3)). These allylic complexes are thermally stable up to about 100 °C. Transmetalation reaction of the bis(pentenyl)platinum(II) complex with the $[Cp^*IrCl_2]_2$ dimer yielded stoichiometric amounts of M-(1,3-dimethylallyl) derivatives (M = Pt, Ir) (**49**, **50**) as shown in Eq. (4) [42].



(3)



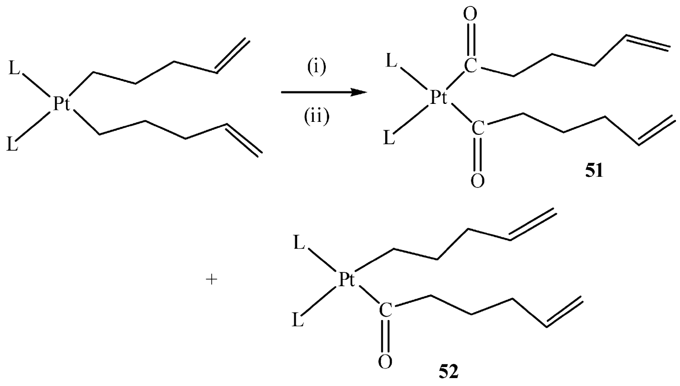
(4)

3.2.4. Oxidative addition

The oxidative addition reactions of methyl iodide to some organoplatinum(II) complexes of the type PtL_2R_2 have been reported in the literature. The bis(alkenyl)platinum(II) complexes also undergo [42] oxidative addition reactions with methyl iodide to yield different products, depending on the experimental conditions (Scheme 17). The reaction proceeds to give (**43**) or (**44**) through the formation of hexacoordinate platinum(IV) species by oxidative addition as reported earlier [44]. The organic products were 1-alkenes, 2-alkenes and α,ω-dienes. Attempts to isolate these intermediate hexacoordinate platinum(IV) species have so far been unsuccessful.

3.2.5. Carbonylation

The reaction of carbon monoxide with the bis(pentenyl)platinum(II) complex $L_2Pt\{(CH_2)_3CH{=}CH_2\}_2$ (L_2 = dppe) afforded the expected mono(acyl) and di(acyl) inserted products (**51**, **52**) (Eq. (5)) while the reactions with other bis(pentenyl) complexes either gave unidentified products (L_2 = COD) or led to the formation of unstable products (L = PPh_3) [42].

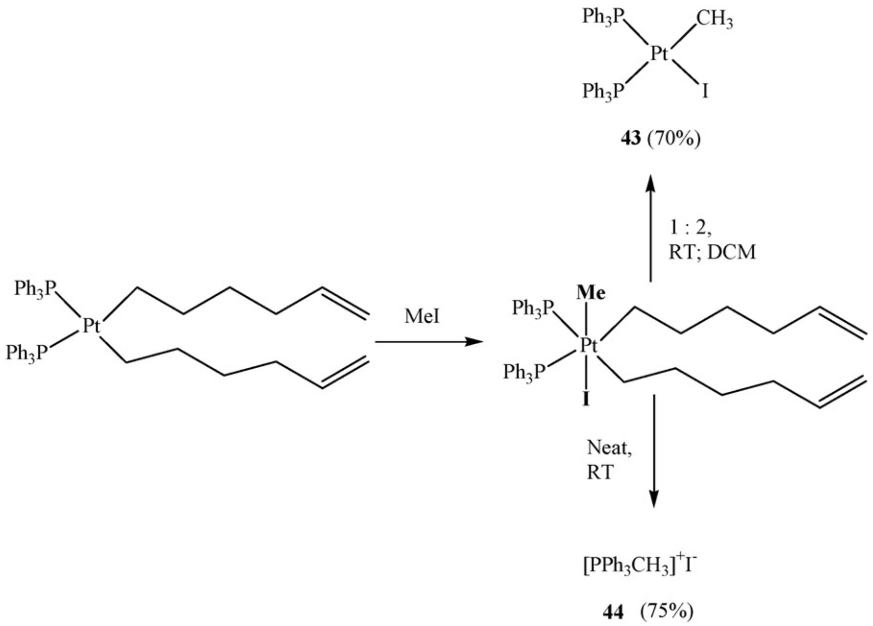


(i) CO ; (ii) Benzene or Toluene

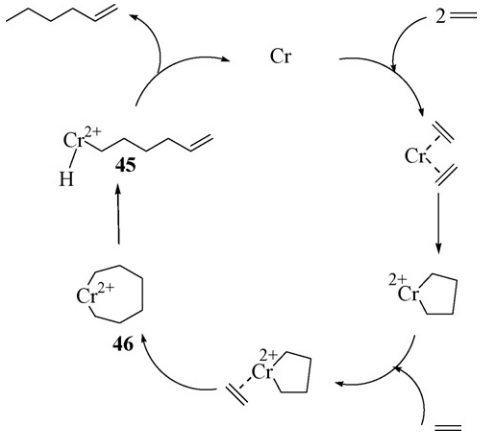
(5)

4. Catalytic reactivity of metal alkenyls and their involvement in catalytic reactions

Chromium-catalyzed trimerization of ethylene to 1-hexene is proposed to proceed via the formation of a chromium seven-membered metallacycle (**46**) (Scheme 18) [45–47]. The involvement of large ring metallacycles in this catalytic cycle is supported by analyzing the isotopomer distributions of ethylene trimerization when the reaction is performed in a 1:1 mixture of C_2D_4 and C_2H_4 [46,47]. The mechanism proceeds by fast insertion of ethylene into chromacyclopentane to form chroma-



Scheme 17.



Scheme 18.

cycloheptane which undergoes ring opening β-H elimination to generate the chromium-hexenyl hydride (**45**). Reductive elimination of (**45**) gives the 1-hexene product and the active catalytic species [48,49]. Although the proposed chromium-alkenyl intermediate has not been isolated, it is expected to result from the β-H elimination of (**46**). Further credence for this intermediate is supported by the reported crystal structure of chromium alkyl hydride species [50]. Recently a new chromium catalyst has been developed for the selective trimerization and tetramerization of ethylene to 1-octene with high selectivity [48,50]. The authors propose that this reaction also proceeds via a metallacycle mechanism and this implies the existence of a nine-membered chromium metallacycle which likely decomposes to the respective chromium-octenyl hydride intermediate [51].

Some zirconocene mono- and bis(alkenyl) complexes of the type Cp_2ZrClR and Cp_2ZrR_2 (where R = alkenyl) have been prepared and shown to be precursors to alkene polymerization catalysts on addition of methylaluminoxane (MAO) [39].

5. Concluding remarks and future prospects

From this review we can see that a range of metal-alkenyl complexes have been made with one or more alkenyl groups by various researchers following different procedures. The active pendant alkene moiety provides additional reaction opportunities which are not shown by metal-alkyl compounds. The pendant bis(1-alkenyl)platinum(II) complexes underwent irreversible isomerization to give bis(2-alkenyl)platinum(II) complexes as the major product, depending on the nature of the ligand system. The formation of η^3-allyl-metal complexes from M–C σ bonds was observed as a result of rapid rearrangement depending on the experimental conditions. Reactions of these metal-allyl complexes with soft donor ligands afford a variety of adducts all containing σ-alkenyl groups. The increased reactivity of M–C bond (especially Ir–C bond) in these products could be useful for the preparation of bis(alkenyl) metal moieties bonded to metal-oxide surfaces. The increased thermal and redox stability of these supported organometallic centers may lead to useful catalytic properties for hydrocarbon functionalization reactions.

The formation and use of metal-alkenyl complexes may extend the scope of applications in synthetic organic chemistry. The potential of these complexes has been exploited in the synthesis of interesting medium to large size metallacycloalkenes and metallacycloalkanes, which are important catalytic intermediates.

New and interesting chemistry of these metal-alkenyl complexes can be expected in the future.

Acknowledgements

We thank Prinessa Chellan for assistance in putting this manuscript together and the DST Centre for Excellence in Catalysis (C*change), Anglo Platinum Corporation, National Research Foundation (NRF), Johnson Matthey and the University of Cape Town for support.

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