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Invited review

Hydrogen elimination in cyclopentadienylnickel compounds as a route to organonickel and organic compounds

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Abstract

Reactions of α-, β- and γ-hydrogen elimination in cyclopentadienylnickel compounds formed in the reactions of nickelocene with lithium or magnesium compounds are discussed. Elimination of α-hydrogen from CpNiR where R is CH_3, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, CH_2Ph or $CH{=}C(CH_3)_2$ leads to the formation of trinickel clusters $(CpNi)_3CR'$, bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel and (η^5-cyclopentadienyl)(η^3-cyclopentenyl)nickel. β-Hydrogen and γ-hydrogen elimination in vinylnickel compounds not posessing α-hydrogen have been studied. Elimination and transfer of hydrogen forms (η^3-allyl)(η^5-cyclopentadienyl)nickel compounds. The mechanisms of these reactions are discussed.

Keywords: Hydrogen-elimination; Nickel; Cyclopentadienyl; Reaction mechanism

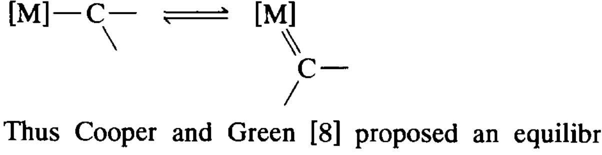
1. Introduction

The thermal decomposition of the σ transition metal–carbon bond most often occurs by β-H elimination reaction and with formation of thermodynamically stable products: alkenes and alkanes. The mechanism of this reaction is well documented for dialkylplatinum(II) complexes [1]. Thermal decomposition of PtR_2L_2 results in the clean disproportionation liberating the alkane RH and the alkene R(–H) in a 1 : 1 ratio:

$$PtR_2L_2 \longrightarrow RH + R(-H) + Pt^{(0)}\text{ complexes} \qquad (1)$$

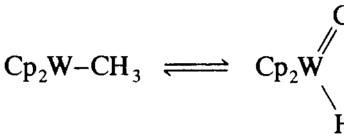
Whitesides et al. [2] proposed a dissociative mechanism for the decomposition of $Pt(^nBu)_2(PPh_3)_2$ and Yamamoto and coworkers [3] investigated the disproportionation of *trans*-$PdEt_2L_2$ [3].

For compounds having only one alkyl group bearing β-hydrogen bonded to the metal, the β-H elimination reaction has been less studied [4,5]. An α-H elimination process has also been described and generally accepted [6,7]. Equilibrium has been assumed:



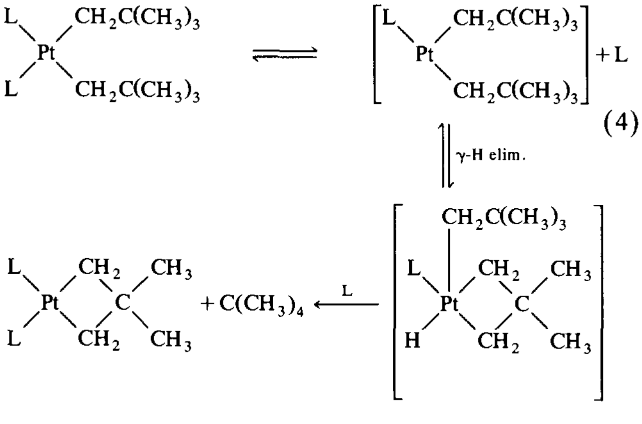
$$[M]-\overset{H}{C}\!\!< \;\rightleftharpoons\; \overset{H}{[M]}{=}C\!< \qquad (2)$$

Thus Cooper and Green [8] proposed an equilibrium between an intermediate 16-electron cation and the 18-electron carbene-hydride:



$$Cp_2W{-}CH_3 \rightleftharpoons Cp_2W(=CH_2)(H) \qquad (3)$$

A γ-H elimination is also known. It was found by Wilkinson and coworkers [9,10] that alkylation of $Ru_2Cl(O_2CMe)_4$ with $Mg(CH_2SiMe_3)_2$ or $Mg(CH_2CMe_3)_2$ did not give dialkyls, but instead metallocyclobutane complexes together with one equivalent of alkane. Further studies led to the suggestion of the γ-H elimination mechanism for the formation of metallacycles [11–14]:



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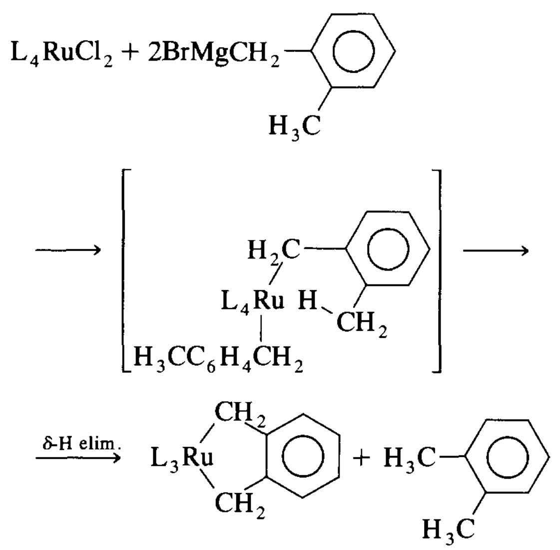
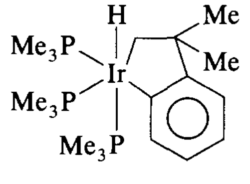
The δ-H elimination reaction has been studied least of all. (Chappel and Cole-Hamilton [15] reported the formation of bis(*o*-methylbenzyl) complexes of platinum occurs via hydrogen elimination from the δ-carbon atom of one alkyl group to form 2,3-benzoplatinacyclopentene complexes. A similar reaction was observed for the ruthenium complex [16]:



(5)

Tulip and Thorn [12] observed a facile insertion at the aryl δ(*ortho*) position of the neophyl (CH_2CMe_2Ph) ligand. Thus a 1 : 1 mixture of complex $[Ir(PMe_3)_4]Cl$ and $LiCH_2CMe_2Ph$ in hexane rapidly yields the benzoirydacyclopentene complex:



2. α-H elimination

We have found that the tris(η^5-cyclopentadienyl)(μ_3-ethylidyne)trinickel cluster (**1**) is formed in the reaction of methyllithium with nickelocene [17]:

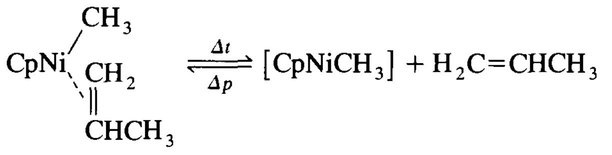
$$NiCp_2 + LiCH_3 \longrightarrow \underset{\mathbf{1}}{(NiCp)_3(\mu_3\text{-}CCH_3)} \qquad (6)$$

The reaction was carried out in tetrahydrofuran (THF) at 0–20°C, and the products were separated by column chromatography on neutral alumina. Cluster **1** is extremely stable, it sublimes at 60°C (0.001 Torr), melts without decomposition at 158–160°C and is not hydrolysed by water but is readily oxidized in air.

In the first step of reaction (6), one cyclopentadienyl and a methyl ligand are exchanged between Ni and Li to form the labile species $CpNiCH_3$:

$$NiCp_2 + LiCH_3 \longrightarrow \underset{\mathbf{2}}{[NiCpCH_3]} + LiCp \qquad (7)$$

This 16-electron intermediate **2** can be trapped by coordination to propene and isolated as the η^2-propene complex $CpNi(\eta^2\text{-}CH_2{=}CHCH_3)CH_3$ (**3**) [18,19]. Complex **3** decomposes above −20°C to regenerate propene and $CpNiCH_3$:



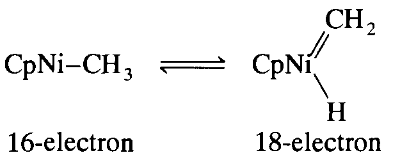
$$CpNi(CH_3)(\eta^2\text{-}CH_2{=}CHCH_3) \underset{\Delta p}{\overset{\Delta t}{\rightleftharpoons}} [CpNiCH_3] + H_2C{=}CHCH_3$$

3

(8)

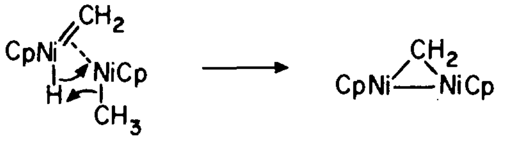
Thus reaction (8) is reversible, and in the presence of an excess and at elevated pressure of propene no decomposition of **3** occurs at room temperature. Thermal decomposition of **3** gives propene, methane and a small amount of ethane.

Complex **2** is a coordinatively unsaturated 16-electron species. α-H elimination results in an increase in the number of valence electrons to 18:



$$CpNi{-}CH_3 \rightleftharpoons CpNi(=CH_2)H \qquad (9)$$

The cyclopentadienyl)(methylidene)nickel hydride is very unstable [20] and immediately reacts with another molecule of $CpNiCH_3$ to give the dinickel complex:



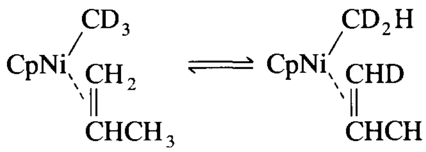
(10)

Further α-H elimination and reaction of the products with $CpNiCH_3$ leads to the formation of (η^5-cyclopentadienyl)(μ_3-methylidyne)trinickel cluster, which has not been isolated:

$$\{(NiCp)_2CH_2\} + CH_3NiCp \longrightarrow \{(NiCp)_3C{-}H\} + CH_4 \qquad (11)$$

The additional reactions of the cluster leading to exchange of a hydrogen atom for the methyl group to give the isolated and fully characterized (η^5-cyclopentadienyl)(μ_3-ethylidyne)trinickel cluster $(NiCp)_3C{-}CH_3$ [17] were not explained. It can be assumed, on the basis of the products formed (clusters $(NiCp)_6C_2$, $(NiCp)_6C$, $(NiCp)_5CCH_3$ and $(NiCp)_4CCH_3$), that it proceeds by an aggregation of {NiCp} with a trinickel cluster already present, simultaneous evolution of methane and ethane [21,22].

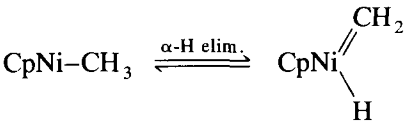
We had previously observed that exchange of deuterium for hydrogen also proceeds by α-D elimination [23]:



$$CpNi(CD_3)(CH_2{=}CHCH_3) \rightleftharpoons CpNi(CD_2H)(CHD{=}CHCH_3) \qquad (12)$$

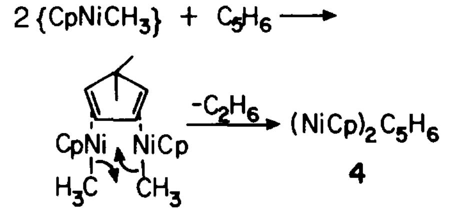
The transfer of deuterium from CD_3 to the olefin probably proceeds via formation of an unstable nickel deuteride.

It was found that, in addition to trinickel and higher clusters, bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel ($(NiCp)_2\mu\text{-}C_5H_6$) (**4**) and ($\eta^5$-cyclopentadienyl)($\eta^3$-cyclopentenyl)nickel ($CpNi(\eta^3\text{-}C_5H_7)$) (**5**) are formed in the reaction of nickelocene with methyllithium [24]. Complex **4** can be formed only as a result of initial reduction of cyclopentadienyl ring bonded to nickel by hydrogen of the methyl group:



$$CpNi{-}CH_3 \underset{}{\overset{\alpha\text{-H elim.}}{\rightleftharpoons}} CpNi(=CH_2)H \longrightarrow CpH + Ni + \text{organic product} \qquad (13)$$

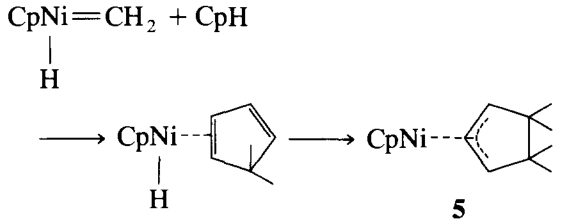
Subsequently the cyclopentadiene reacts with $CpNiCH_3$ to give $(CpNiCH_3)_2{-}C_5H_6$, which undergoes ethane elimination:



(14)

Complex **4** has been fully characterized spectroscopically and by determination of its X-ray structure [24].

A small amount of the π-allyl complex **5** is also formed in the reaction of nickelocene with methyllithium. This can be attributed to further hydrogenation of cyclopentadiene, formed in the reaction shown in Eq. (13), by the nickel hydride:



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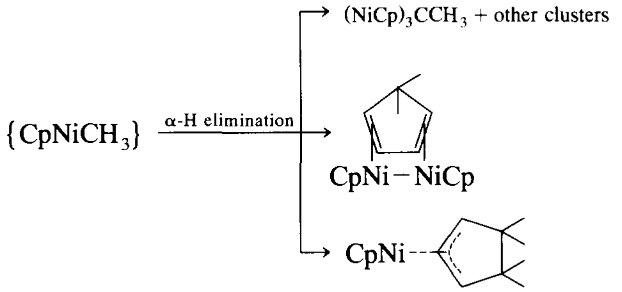


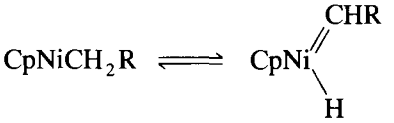
Scheme 1.

As shown above, α-H elimination from $CpNiCH_3$ leads to the formation of several organonickel compounds (Scheme 1) and to deuterium–hydrogen exchange (Eq. (12)).

Groups without β-hydrogen, e.g. $CH_2C_6H_5$, $CH_2C(CH_3)_3$ and $CH_2Si(CH_3)_3$, react in the same way as the methyl group. The corresponding trinickel clusters are formed in the reactions of nickelocene with organolithium or magnesium compounds:

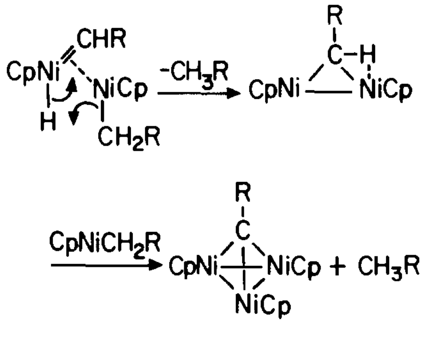
$$NiCp_2 + MCH_2R \longrightarrow (NiCp)_3C{-}R + MCp \qquad (16)$$

where $R = C_6H_5$ [25], $C(CH_3)_3$ or $Si(CH_3)_3$ [26] and M = Li or MgX. The unstable 16-electron compound $\{CpNiCH_2R\}$ undergoes α-H elimination to form the reactive nickel hydride:



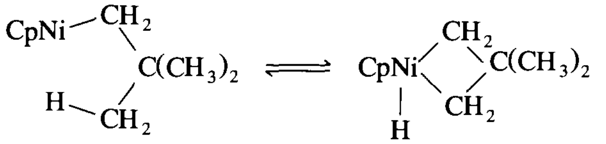
$$CpNiCH_2R \rightleftharpoons CpNi(=CHR)H \qquad (17)$$

The further reactions of the formed hydrides with the starting compounds give trinickel clusters:



(18)

We showed that the clusters formed are thermally very stable and do not react with water but readily undergo oxidation. Toluene, $C(CH_3)_4$ and $Si(CH_3)_4$ respectively have been detected in the product mixtures arising from reactions (16). It should be stressed that for nickel, contrary to the observations by Wilkinson and coworkers [9,10] and Whitesides and coworkers [11,14] on Ru, Pt and Os complexes, $CH_2C(CH_3)_3$ and $CH_2Si(CH_3)_3$ groups do not undergo γ-H elimination but only α-H elimination. This is due to the thermodynamic instability of the γ-H elimination products:



(19)

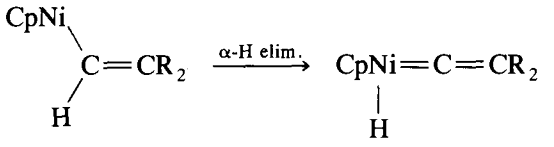
We subsequently studied vinylnickel compounds **6** of general formula CpNi–CH=CR$_2$, where R = H or CH$_3$ [17]. They were obtained from the reactions of nickelocene with vinyllithium or magnesium compounds **6**:

$$\text{NiCp}_2 + \text{M–CH=CR}_2 \longrightarrow \{\text{CpNi–CH=CR}_2\} + \text{MCp} \qquad (20)$$

where M = Li or MgX. All the vinylnickel compounds examined gave tris(η^5-cyclopentadienyl)(μ$_3$-alkylidyne)trinickel clusters (NiCp)$_3$C–CHR$_2$):

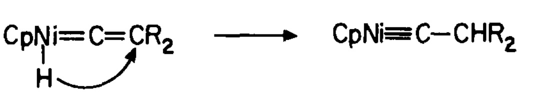
$$3\{\text{CpNi–CH=CR}_2\} \longrightarrow \underset{\mathbf{7}}{(\text{NiCp})_3\text{C–CHR}_2} + \text{R}_2\text{C=CH–CH=CR}_2 \qquad (21)$$

The formation of trinickel clusters **7** proceeds via a 2,3-hydrogen transfer mediated by nickel. In the first step, α-H elimination takes place:



(22)

Then 1,3-hydrogen transfer by an intramolecular or intermolecular process gives carbyne-type unstable species:

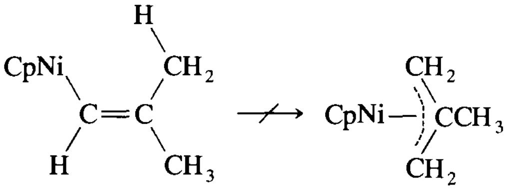


(23)

The carbyne species reacts immediately with (NiCp)$_2$ (formed in a coupling reaction) to give the trinickel cluster:

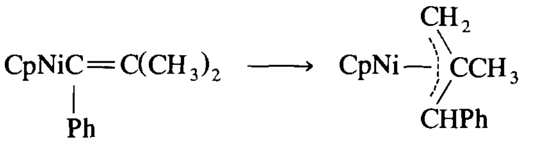
$$2\,\text{CpNi–CH=CR}_2 \longrightarrow (\text{NiCp})_2 + \text{R}_2\text{C=CH–CH=CR}_2$$
$$\text{CpNi}\equiv\text{C–CHR}_2 \longrightarrow (\text{NiCp})_3\text{C–CHR}_2 \qquad (24)$$

Butadiene or its methyl derivatives have been identified in the product mixtures. Vinylnickel compounds possessing α- and γ-hydrogen atoms do not give γ-H elimination products, i.e. π-allyl compounds:



(25)

As previously shown, substitution of the α-hydrogen by a phenyl group induces of γ-H elimination and formation of π-allyl compound [27]:

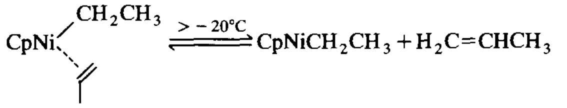


(26)

The above results show that in vinylnickel compounds **6** possessing α-hydrogen, its elimination proceeds more readily that that of a γ-H. The reactions of nickelocene with vinyllithium or magnesium compounds provide new and easy methods for synthesis of trinickel clusters **7** with any R. For none of the reactions reported up to now can formation of free {CpNiH} be postulated, but it must be assumed that hydrogen transfer proceeds intramolecularly and the driving force of this process is the formation of thermodynamically stable products.

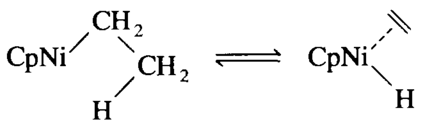
3. β-H elimination

The thermal decomposition of compounds containing a nickel–carbon σ bond has not previously studied in detail. Et$_2$Ni(dipy) decomposes at 110°C under reduced pressure and ethane, ethene and *n*-butane were formed as gaseous products [28]. The thermal decomposition of R$_2$Ni(PPh$_3$)$_2$ with R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$ or ^{i}C$_4$H$_9$ has also been studied [29]. Thermal decomposition of Et$_2$NiL$_2$ results in disproportionation to liberate ethane, ethene and higher alkanes. The monoalkylnickel compounds CpNi(PPh$_3$)R containing a β-hydrogen were shown to decompose through a β-H elimination to give alkanes and alkenes [30,31]; no nickel-containing products were isolated. Thermal decomposition of the above complexes requires a higher temperature (60–160°C), and alkylnickel compounds of lower thermal stability (CpNiR(η^2-CH$_2$=CHCH$_3$) (R-CH$_3$, CD$_3$, C$_2$H$_5$, C$_3$H$_7$ or CH$_2$Si(CH$_3$)$_3$) were chosen for our studies [23]. The thermolysis of the ethyl complex begins with dissociation of the coordinated propene molecule:

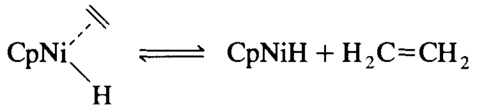


(27)

The unstable $CpNiCH_2CH_3$ complex undergoes β-H elimination:


(28)

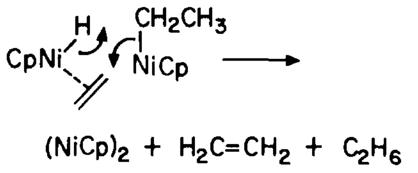
The next step of the reaction is still not clear: it could involve dissociation of the complexed olefin according to


(29)

and an attack of free CpNiH on $CpNiCH_2CH_3$ according to

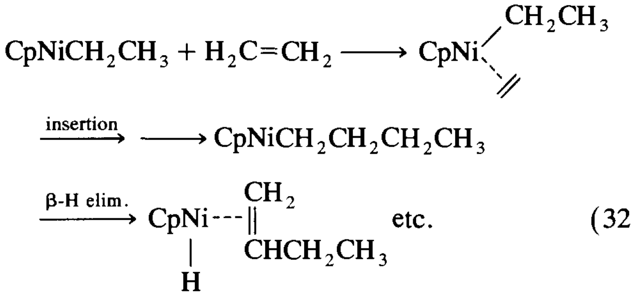
$$CpNiH + CpNiCH_2CH_3 \longrightarrow (NiCp)_2 + C_2H_6 \quad (30)$$

or alternatively it could involve a concerted process:


(31)

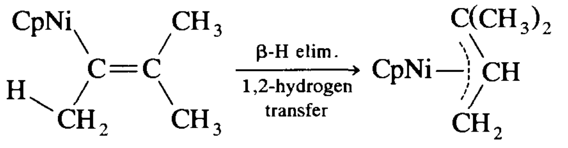
An absence of factors stabilizing CpNiH and its extremely high reactivity, favour the reaction shown in Eq. (31).

The clusters $(NiCp)_4$ and $(NiCp)_6$ were found in product mixture. They are formed by the aggregation of unstable $\{(NiCp)_2\}$. Gaseous products of the reaction are ethylene and ethane, an almost equimolar amount, together with about 5% of 1-butene which indicates that about 5% of the $CpNiCH_2CH_3$ reacts with ethylene to give the latter:


(32)

The absence of butane in the gaseous products indicates that the compounds containing β-hydrogen do not undergo coupling.

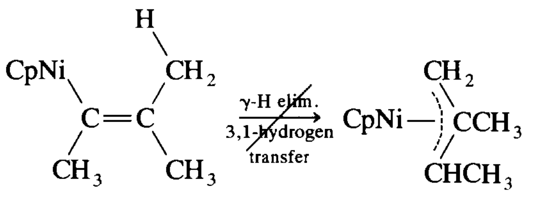
Nickelocene reacts with 1,2-dimethylpropenyllithium to give $CpNi–C(CH_3)=C(CH_3)_2$ [27,32]. This complex has no α-H but possesses β- and γ-H. As a result of a hydrogen transfer from β- to α-carbon stable (η^3-allyl)(η^5-cyclopentadienyl)nickel is formed **8**:



(33)

10 **8**

If γ-H elimination reaction occurred, then **9** should be formed:



(34)

10 **9**

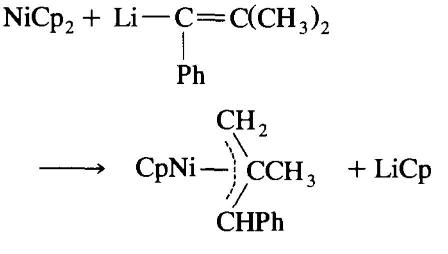
The presence of this complex was not detected among the products. It appears that with CpNi(vinyl) complexes possessing both β- and γ-hydrogen atoms only β-H elimination occurs. The decisive factor is probably the shorter distance of β-hydrogen than of γ-hydrogen from the nickel atom in **10**.

The reactions of nickelocene with vinyllithium or magnesium compounds provide a convenient method for making π-allylnickel complexes.

4. γ-H elimination

γ-H elimination was studied for complexes of Ru, Os, Pt etc. having two $CH_2(CH_3)_3$ or $CH_2Si(CH_3)_3$ groups bonded to the metal [9–11,14]. It was found that such compounds underwent γ-H elimination to give metallacyclobutane complexes and one equivalent of alkane.

We chose cyclopentadienylnickel compounds not containing α- and β-hydrogen, for a study of γ-H elimination reactions. The reaction of nickelocene with 1-phenyl-2-methylpropenyllithium gives $CpNi–CPh=C(CH_3)_2$, (η^5 = cyclopentadienyl)[η^3-1-(*anti*)-phenyl-2-methylallyl]nickel and (η^5-cyclopentadienyl)[η^3-1-(*syn*)-phenyl-2-methylallyl]nickel [27,32]:

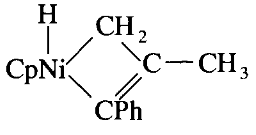

(35)

anti **11** and *syn* **12**

The unstable compound CpNi–C(Ph)=C(CH_3)$_2$ does not posses α- and β-hydrogen; so the formation of allyl compounds **11** and **12** can be attributed to γ-H elimination. The course of the reaction shown in Eq. (35) is depicted in Scheme 2. The driving force of the γ-H elimination is the preference of the nickel atom to achieve an 18-electron configuration, as in the case of β- and α-elimination.

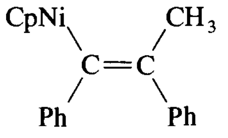
The shift of the double bond from C(1)–C(2) to C(2)–C(3) results in stabilization of the carbocation. Owing to the free rotation around the C(1)–C(2) bond, the attack of hydrogen bonded to nickel on C(1) can take place from two sides resulting in formation of *anti* and *syn* isomers of the π-allyl complex.

If an intermediate complex **13** were be formed as a result of γ-H elimination, then *syn* and *anti* isomers could not be obtained:

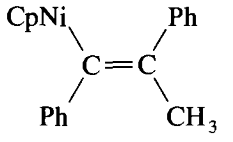


13

To find out whether the distance of the γ-hydrogen from the nickel atom has the influence on γ-H elimination reaction, we prepared *cis* and *trans* isomers **14** and **15** of cyclopentadienylvinylnickel [33]:

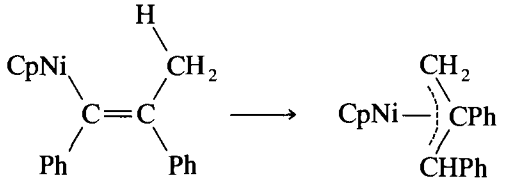


14



15

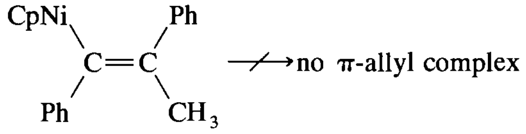
The distance of γ-hydrogen from the nickel atom in **14** is short and γ-hydrogen elimination reaction occurs readily, to give the π-allyl complexes **16** and **17**:



(36)

14 *syn* **16** and *anti* **17**

The *cis* isomer of CpNi–C($SiMe_3$)=C(CH_3)$SiMe_3$ reacts analogously to form π-allyl compounds [34]. Compound **15** (the *trans* isomer) does not form π-allyl complexes because of the long distance of γ-hydrogen from the nickel atom:



(37)

15

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