STEREOCHEMICAL FACTORS OF γ-H ELIMINATION IN CYCLOPENTADIENYLVINYLNICKEL COMPOUNDS

Antoni PIETRZYKOWSKI[1], Stanislaw PASYNKIEWICZ[2] and Piotr BUCHALSKI[3]

Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland;
e-mail: [1] anpietr@ch.pw.edu.pl, [2] pasyn@ch.pw.edu.pl, [3] pjb@ch.pw.edu.pl

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday in recognition of his outstanding contributions to a development of organometallic chemistry.

The reactions of nickelocene with *cis*-1,2-diphenylpropylmagnesium bromide and with *trans*-1,2-diphenylpropenyllithium had been studied. It was found that *cis*-1,2-diphenylpropenylcyclopentadienylnickel underwent γ-H elimination to form a mixture of (η^5-cyclopentadienyl)[η^3-1,2-(*anti*)-diphenylpropenyl]nickel and (η^5-cyclopentadienyl)[η^3-1,2-(*syn*)-diphenylpropenyl]nickel as the main products. The mechanism of this reaction has been discussed. Dihydrotetra(cyclopentadienylnickel) cluster $(NiCp)_4H_2$ was the main organometallic product of the reaction of nickelocene with *trans*-1,2-diphenylpropenyllithium. There was no γ-H elimination products formed in this reaction. It has been concluded that γ-H elimination in cyclopentadienylvinylnickel compounds is stereochemically controlled process and can occur only if a distance of γ-hydrogen from the nickel atom is relatively small.

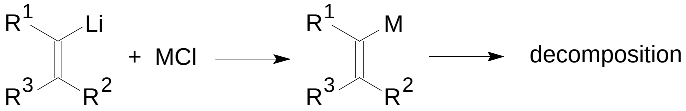
Key words: Hydrogen elimination; π-Allyl complexes; Nickel.

The best recognized pathway of thermal decomposition of metal σ-hydrocarbyls is β-H elimination. It may be represented by the general equation (*1*).

$$LM–CH_2–CH_2R \rightleftharpoons LMH + CH_2{=}CHR \qquad (1)$$

For simple alkyls this process is believed to be predominant and it requires migration of a β-hydrogen from carbon to the metal with the formation of an alkene[1,2]. Recognition of the above process and the growing number of isolable transition metal alkyl compounds with alkyls lacking a β-hydrogen caused the role of β-hydrogen elimination to be often overemphasized. An α-H elimination process had also been recognized and generally accepted[3,4]. γ-H elimination is also known, although it was much less extensively studied[5–10].

The thermal decomposition of η^1-vinyliridium(I) and -rhodium(I) complexes was studied by Schwartz et al.[11] in the following reaction (Eq. (*2*)).



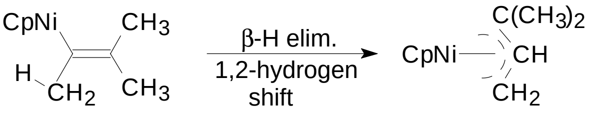
(*2*)

They have found that decomposition proceeds only *via cis*-β-vinylic H elimination ($R^2 = H$) or β-allylic H elimination ($R^1 = CH_3$). Neither α-H ($R^1 = H$) nor γ-H elimination ($R^2 = CH_3$) have been observed.

We have studied a series of reactions of cyclopentadienylvinylnickel compounds of the general formula $CpNiCR^1{=}CR^2R^3$ (refs[12–14]). They are formed in the reactions of nickelocene with corresponding vinyllithium or -magnesium compounds[12,14] or in the reactions of nickelocene with methyllithium in the presence of alkynes[13]. The cyclopentadienylvinylnickel compounds are unstable and they undergo further reactions to form various products. We have shown that depending on the kind of the R substituents all three decomposition pathways, *i.e.* α-, β- and γ-H elimination are possible.
If $R^1 = H$, then regardless of the kind of R^2 and R^3 an α-H elimination takes place with formation of tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters[12] (Eq.(*3*)).

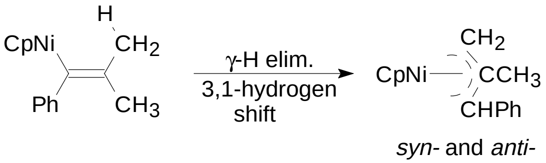
$$3\ \{CpNi{-}CH{=}CR^2R^3\} \rightarrow (NiCp)_3C{-}CHR^2R^3 + R^2R^3C{=}CH{-}CH{=}CR^2CR^3 \qquad (3)$$

If $R^1 = CH_3$, then β-H elimination occurs to form (η^3-allyl)(η^5-cyclopentadienyl)-nickel[13] (Eq. (*4*)).



(*4*)

If cyclopentadienylvinylnickel does not posses neither α- nor β-hydrogen ($R^1 = C_6H_5$; $R^2 = R^3 = CH_3$), then γ-H elimination occurs with formation of two isomers of (η^5-cyclopentadienyl)(η^3-1-phenyl-2-methylallyl)nickel[14] (Eq. (*5*)).



(*5*)

The purpose of this work was to establish whether the γ-H elimination in cyclopentadienylvinylnickel compounds is stereochemically controlled, *i.e.* whether the position of CH_3 group (*cis* or *trans* to the metal) affects the reaction course.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer. Mass spectra were recorded on an AMD 604 spectrometer. GC/MS analyses were performed on a Hewlett–Packard 5971 Series Mass Selective Detector with a HP 35 column (30 m × 25 mm). The reported yields of crude products (*i.e.* after the first column chromatography) were based on the starting amount of nickelocene. All manipulations were carried out under dry argon. All solvents were thoroughtly dried and deoxygenated over a benzophenone radical anion and distilled before use. Chromatography was carried out on neutral alumina (Merck 90, 0.063–0.200 mm, deactivated with 5% of water).

cis-1-Bromo-1,2-diphenylpropene[15], *cis*-1,2-diphenylpropenylmagnesium bromide[16] and *trans*-1,2-diphenylpropenyllithium[16] were prepared according to reported methods, as indicated.

Reaction of Nickelocene with *cis*-1,2-Diphenylpropenylmagnesium Bromide

A solution of *cis*-1,2-diphenylpropenylmagnesium bromide (9.7 mmol) in THF (45 cm^3) was added dropwise to a boiling solution of nickelocene (1.66 g, 8.8 mmol) in THF (80 cm^3). After stirring the mixture for 24 h at room temperature, the solvent was removed, and toluene (80 cm^3) and deoxygenated water (100 cm^3) were added. The mixture was filtered through a bed of alumina. The organic layer was separated, concentrated to about 10 cm^3 and chromatographed on alumina with hexane and hexane–toluene mixture as eluents, to give nickelocene (0.21 g) and a mixture of (η^5-cyclopentadienyl)[η^3-1,2-(*anti*)-diphenylpropenyl]nickel and (η^5-cyclopentadienyl)[η^3-1,2-(*syn*)-diphenylpropenyl]nickel as a deep green oil (1.25 g, 3.9 mmol; 44%). The compounds were characterized by ^{1}H and ^{13}C NMR in C_6D_6. The NMR results are presented in Tables I and II, respectively. Based on the integration of ^{1}H NMR signals it was found that the mixture contained 78% of the *anti* and 22% of *syn* isomer. Mass spectrum (EIMS 70 eV) showed a molecular ion at *m/z* 316 ($C_{20}H_{18}Ni^+$, calculated for ^{58}Ni; the isotopic pattern was characteristic for one nickel atom; relative intensity 52%). The other fragments were at *m/z* = 250 $(M - C_5H_6)^+$ (100%); 194 $C_{15}H_{14}^{\ddagger}$ (46%); 191 $C_{15}H_{11}^{\ddagger}$ (42%); 115 $C_9H_7^{\ddagger}$(27%); 77 $C_6H_5^{\ddagger}$ (11%); $^{58}Ni^+$ (7%). The residue eluted from the column was a mixture of unidentified products.

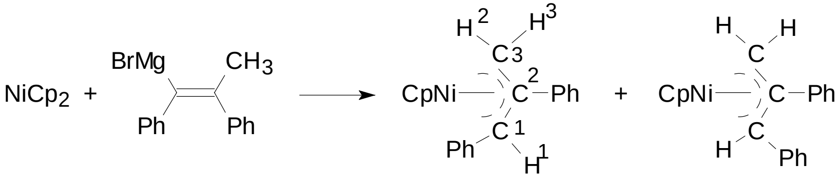
Reaction of Nickelocene with *trans*-1,2-Diphenylpropenyllithium

A solution of *trans*-1,2-diphenylpropenyllithium (8.9 mmol) in THF (45 cm^3) was added dropwise to a solution of nickelocene (1.53 g, 8.1 mmol) in THF (80 cm^3) at room temperature. After stirring for 24 h, the solvent was removed, and toluene (100 cm^3) and deoxygenated water (100 cm^3) were added. The mixture was filtered through a bed of alumina. The organic layer was separated, concentrated to about 10 cm^3 and chromatographed on alumina with hexane and hexane–toluene mixture as eluents. Organic products, eluted with hexane before the first organometallic band, were collected and subjected to GC/MS analyses. α-Methylstilbene was identified (spectra in agreement with DATABASE\NBS75K.L) and obtained as white crystals after a recrystallization from hexane (1.21 g, 6.2 mmol). ^{1}H NMR confirmed it as *trans*-α-methylstilbene. The first organometallic fraction contained traces of unreacted nickelocene. The second brown fraction (eluted with hexane–toluene 1 : 1) was collected. The solvents were evaporated to dryness, yielding a black solid. Recrystallization from hexane–THF gave black crystals of $(NiCp)_4H_2$ (0.60 g, 1.2 mmol; 59%); no melting was observed up to 350 °C. The identification was based on ^{1}H NMR spectrum (C_6D_6; δ, ppm): 5.35 s, 20 H (Cp); –20.01 s, 2 H (hydride protons) and ^{13}C NMR spectrum (C_6D_6; δ, ppm): 82.67 d, ^1J(C,H) = 173 Hz (Cp). These data agreed well with reported ones[17]. EIMS (70 eV): M^+ overlapped with fragments appearing at *m/z* 488–504. The other fragments at *m/z* = 428, 426, 424, 374, 306, 246, 188, 123 were consistent with the literature[17]. The other products eluted were not identified. However, the careful check showed that π-allylcyclopentadienylnickel complexes were not formed during the reaction.

RESULTS AND DISCUSSION

Noltes *et al.*[16] have proved that *cis*-1-bromo-1,2-diphenylpropene isomerises during the reaction with lithium to form *trans*-1,2-diphenylpropenyllithium, while the reaction of *cis*-1-bromo-1,2-diphenylpropene with magnesium leads to formation of *cis*-1,2-diphenylpropenylmagnesium bromide. We have reacted these two compounds with nickelocene to find out whether the *cis* or *trans* position of the methyl group in relation to the nickel atom affects γ-H elimination in cyclopentadienylvinylnickel compounds.

Nickelocene reacts with *cis*-1,2-diphenylpropenylmagnesium bromide to form a mixture of (η^5-cyclopentadienyl)[η^3-1,2-(*anti*)-diphenylpropenyl]nickel (**1a**) and (η^5-cyclopentadienyl)[η^3-1,2-(*syn*)-diphenylpropenyl]nickel (**1b**) as the main products (Eq. (*6*)).



1a *anti-* **1b** *syn-*

(*6*)

The reaction was carried out in boiling THF. The reaction mixture was then treated with water. The organic layer was dried, concentrated and products were separated by column chromatography (neutral alumina + 5% H_2O, eluents: hexane and hexane–toluene). The first light green fraction contained a small amount of unreacted nickelocene. The second main fraction was collected, the solvents were partially evaporated and the residue was chromatographed again. Dark green oil (purple-red in an electric bulb light) was obtained after solvents evaporation.

^{1}H, ^{13}C NMR and mass spectra showed that the product was a mixture of two isomers of the compound **1**. The molecular peak at *m/z* = 316 (calculated for ^{58}Ni with the isotopic pattern characteristic for one nickel atom; relative intensity 52%) was observed in the mass spectrum of compound **1**. ^{1}H and ^{13}C NMR spectra of the compounds **1a** and **1b** are shown in Tables I and II (atom numbering scheme in Eq. (*6*)). Based on the integration of ^{1}H NMR signals, the product consisted of 78% of the *anti* isomer (**1a**) and 22% of the *syn* isomer (**1b**).

The reaction of nickelocene with *trans*-1,2-diphenylpropenyllithium was carried out in THF at room temperature. The reaction mixture was then treated with water to hydrolyse LiCp. The organic layer was dried, concentrated and products were separated by column chromatography (neutral alumina + 5% H_2O, eluent hexane and hexane–toluene). α-Methylstilbene was identified among organic products. The first organometallic fraction contained traces of unreacted nickelocene. The main product of the reaction was isolated from the second brown fraction. It was identified as dihydridotetra(cyclopentadienylnickel) cluster[17] $(NiCp)_4H_2$. The identification was based on ^{1}H, ^{13}C NMR and mass spectra and their comparison with literature data[17]. There were neither (η^5-cyclopentadienyl)(η^3-1,2-diphenylpropenyl)nickel (**1**) nor other γ-H elimination products formed in the reaction.

The results of the above reactions clearly show that π-allyl cyclopentadienylnickel complexes are formed in the reaction of nickelocene with *cis*-1,2-diphenylpropenylmagnesium bromide but not in that with *trans*-1,2-diphenylpropenyllithium.

cis and *trans* Isomers of the unstable compound {CpNi–C(C_6H_5)=C(CH_3)Ph} are formed in the initial steps of these reactions respectively.

TABLE I
^{1}H NMR spectra of compounds **1a** and **1b**

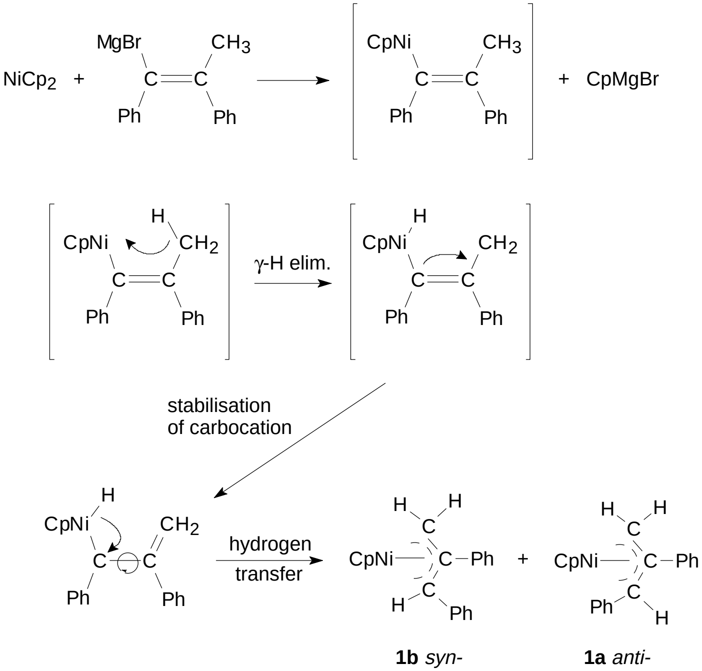
Compound	δ, ppm				
	H^1	H^2	H^3	Cp	Ph
1a[a]	5.37 s	2.44 s	3.43 s	5.09 s	6.91–7.41 m
1b[b]	2.72 s	1.60 s	2.98 s	5.14 s	6.91–7.41 m

[a] $J(H^1,H^3)$ not observed. [b] $J(H^1,H^2)$ not observed.

TABLE II
^{13}C NMR spectra of compounds **1a** and **1b**

Compound	δ, ppm				
	C^1	C^2	C^3	Cp	Ph
1a	59.1	102.4	43.3	90.4	125.0–142.8
1b	61.1	105.4	42.0	90.5	125.0–142.8

The *cis* isomer of {CpNi–C(C_6H_5)=C(CH_3)Ph} does not possess neither α- nor β-hydrogen, so the formation of π-allyl complexes **1a** and **1b** can be explained by a γ-H elimination process. The course of the reaction (*6*) is proposed on Scheme 1. A driving force of this reaction is the anxiety of the nickel atom to achieve 18-electron configuration. γ-H elimination occurs, leading to the formation of an ustable nickel hydride in an oxidative addition step. The shift of double bond from C^1–C^2 to C^2–C^3 stabilizes the carbocation. Due to the free rotation around C^1–C^2 bond, the transfer of the hydrogen from nickel to C^1 in an intramolecular reductive elimination step leads to the formation of *anti* and *syn* isomers of π-allyl complex. The *anti* isomer is predominant probably due to the steric reasons. The whole process can be described as a nickel mediated 3,1-hydrogen shift.



SCHEME 1

The *trans* isomer of {CpNi–C(C_6H_5)=C(CH_3)Ph} does not possess neither α- nor β-hydrogen either, it possesses γ-hydrogen atoms, but in that case we have not observed the formation of π-allyl complexes. The main product isolated from the reaction mixture was dihydridotetra(cyclopentadienylnickel) cluster $(NiCp)_4H_2$. This compound has been formed in several reactions of nickelocene with organolithium or -magnesium compounds[17,18]. Our previous studies showed that it was always formed during decomposition of cyclopentadienyl(phenyl)nickel, *i.e.* in the case when substituent σ-bonded to nickel does not possess neither α-, β- nor γ-hydrogen atoms, undergoing facile hydrogen abstraction. We have shown that the solvent (THF) is the source of the hydrogen necessary for the formation of $(NiCp)_4H_2$ (ref.[18]). From the point of view of the possibility of α-, β- or γ-hydrogen abstraction, the *trans* isomer of $\{CpNi–C(C_6H_5)=C(CH_3)Ph\}$ is similar to the phenyl group. There is a lack of α- and β-hydrogen atoms, and γ-hydrogen atoms are further apart from the nickel than in the *cis* isomer. The long distance disables γ-H elimination and π-allyl complexes cannot be formed. We presume that a decomposition of {*trans*-$CpNi–C(C_6H_5)=C(CH_3)Ph$} proceeds similarly to that of {CpNiPh} and that $(NiCp)_4H_2$ is formed like described previously[18].

The following conclusions can be drawn: γ-H elimination in cyclopentadienylvinylnickel compounds leads to the formation of π-allyl complexes. This process is possible only if the distance of the γ-hydrogen from the nickel atom is relatively small (γ-H bearing group is *cis* situated in the relation to the nickel atom) what indicates that stereochemical factors play a key role in γ-H elimination. If γ-hydrogen atoms are in the CH_3 group *trans* to the nickel, then γ-H elimination does not proceed and π-allyl complexes cannot be formed. This result also proves that 3,1-hydrogen shift leading to the formation of an allyl group is not direct but proceeds with a mediation of the nickel atom.

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REFERENCES

1. Whitesides G. M., Gaarch J. F., Stedronsky E. R.: J. Am. Chem. Soc. *94*, 5258 (1972).
2. Reger D. L., Culbertson E. C.: J. Am. Chem. Soc. *98*, 2789 (1976).
3. Green M. L. H.: Coord. Chem. *21*, 127 (1980).
4. Brookhart M., Green M. L. H.: J. Organomet. Chem. *250*, 395 (1983).
5. Andersen R. A., Jones R. A., Wilkinson G.: J. Chem. Soc., Dalton Trans. *1978*, 446.
6. Jones R. A., Wilkinson G.: J. Chem. Soc., Dalton Trans. *1979*, 472.
7. Foley P., DiCosimo R., Whitesides G. M.: J. Am. Chem. Soc. *102*, 6713 (1980).
8. Tulip T. H., Thorn D. L.: J. Am. Chem. Soc. *103*, 2448 (1981).
9. Behling T., Girolami G. S., Wilkinson G.: J. Chem. Soc., Dalton Trans. *1984*, 877.
10. Whitesides G. M., Hackett M., Brainard R. L., Lavalleye J. P. M., Sowinski A. F., Izumi A. N., Moore S. S., Brown D. W., Staudt E. M.: Organometallics *4*, 1819 (1985).
11. Schwartz J., Hart D. W., MacGiffert B.: J. Am. Chem. Soc. *96*, 5613 (1974).
12. Lehmkuhl H., Krüger C., Pasynkiewicz S., Poplawska J.: Organometallics *7*, 2038 (1988).
13. Pasynkiewicz S., Pietrzykowski A., Poplawska M.: J. Organomet. Chem. *443*, 131 (1993).
14. Pasynkiewicz S., Pietrzykowski A., Buchowicz W., Poplawska M.: J. Organomet. Chem. *463*, 235 (1993).
15. Kelly J. M., Trautman R. J.: J. Chem. Soc., Dalton Trans. *1984*, 913.
16. Ten Hoedt R. W. M., van Koten G., Noltes J. G.: J. Organomet. Chem. *170*, 131 (1979).
17. Pasynkiewicz S., Buchowicz W., Pietrzykowski A., Glowiak T.: J. Organomet. Chem., in press.
18. Pasynkiewicz S., Buchowicz W., Pietrzykowski A.: J. Organomet. Chem., in press.