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(η^3-Allyl)(η^5-cyclopentadienyl)nickel complexes

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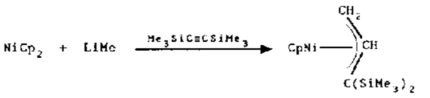
Abstract

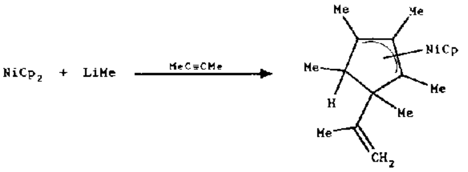
Unstable CpNi(vinyl) compounds of the type $CpNi{-}CR'{=}CR_2$ ($R' = CH_3$, C_6H_5, $R = CH_3$) are formed in the reaction of nickelocene with vinyllithium or -magnesium compounds. CpNi(vinyl) reacts further to form π-allyl complexes and other compounds not yet fully characterized. For $R' = CH_3$, π-allyl complex **1** is formed and for $R' = C_6H_5$ two π-allyl isomers *anti*-**2a** and *syn*-**2b** are formed. The mechanisms of α-, β-, γ- and η-H elimination and of hydrogen transfer reactions are discussed.

1. Introduction

(η^3-Allyl)(η^5-cyclopentadienyl)nickel complexes can be prepared by reacting nickelocene with 2-alkenyl Grignard reagents [1,2]. We have shown that (η^3-allyl)(η^5-cyclopentadienyl)nickel complexes can also be prepared by reacting nickelocene with methyllithium in the presence of bis(trimethylsilyl)acetylene (eqn. (1)) or 2-butyne (eqn. (2)) [3,4].



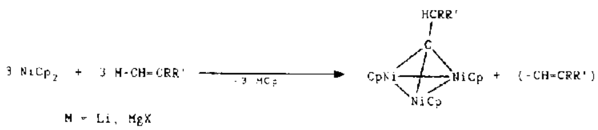
(1)



(2)

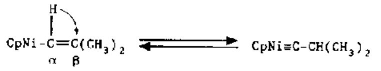
Unstable CpNi(vinyl) compounds of the type $CpNi{-}C(R'){=}CRR'$ ($R = CH_3$; $R' = CH_3$ or $Si(CH_3)_3$) are formed as intermediates in both of these reactions.

If α-hydrogen is present in the CpNi(vinyl) compound, then (η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters are formed (eqn. (3)) [5].



(3)

The formation of (η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters is conditioned by the hydrogen transfer from C_α to C_β (eqn. (4)).

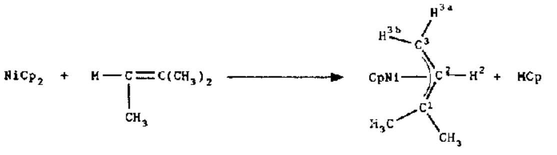


(4)

The purpose of this work was to study the reactions of CpNi(vinyl) compounds possessing a CH_3 or C_6H_5 group bonded to C_α to find out whether the transfer of these groups from C_α to C_β with the formation of corresponding clusters occurred or whether the reactions proceeded via β- or γ-H elimination with the formation of other products.

2. Results

Nickelocene reacts with 1,2-dimethylpropenyllithium or -magnesium bromide to form (η^3-1,1-dimethylallyl)(η^5-cyclopentadienyl)nickel (**1**) as the main product (eqn. (5)).



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(5)

The reaction products were hydrolyzed, compound **1** was isolated by column chromatography and then purified by distillation at room temperature under reduced pressure (10^{-3} Torr). Purple-red viscous liquid was obtained. Its ^1H NMR spectrum showed a singlet of

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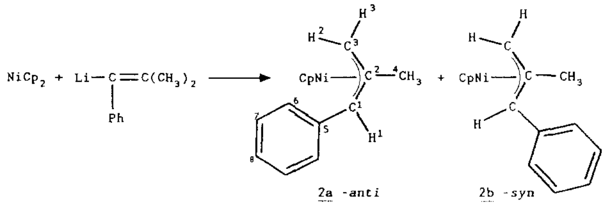
cyclopentadienyl protons at 5.17 ppm, a doublet of doublets of H(2) at 4.96 ppm ($J = 11.0$; 6.6 Hz), a doublet of H(3a) at 2.67 ppm ($J = 6.6$ Hz), a doublet of H(3b) at 1.63 ppm ($J = 11.0$ Hz) and two singlets of methyl protons at 1.16 and 0.75 ppm (integration ratio: found, 4.8 : 1.0 : 1.0 : 1.1 : 2.8 : 3.1, calc., 5 : 1 : 1 : 1 : 3 : 3). The ^{13}C NMR spectrum showed one signal of cyclopentadienyl carbons at 89.4 ppm, two signals of methyl carbons at 30.3 and 20.6 ppm, a signal of C(3) at 35.5 ppm and a signal of C(2) at 91.4 ppm. A signal of C(1) was not observed. The mass spectrum showed the molecular peak at $m/e = 192$ and other fragments characteristic for cyclopentadienylallyl nickel compounds (124, $NiC_5H_6^+$; 99, $NiC_3H_5^+$; 58, Ni^+; 39, $C_3H_3^+$).

Nickelocene reacts with 1-phenyl-2-methylpropenyllithium to form (η^5-cyclopentadienyl)[η^3-1-(*anti*)-(phenyl)-2-(methyl)allyl]nickel (**2a**) and (η^5-cyclopentadienyl)[η^3-1-(*syn*)-(phenyl)-2-(methyl)allyl]nickel (**2b**). The reaction was carried out at room temperature in diethyl ether. The reaction mixture was then treated with water to hydrolyze LiCp, dried and the products were separated by column chromatography (neutral alumina + 1.5% H_2O, eluent heptane). The first light green fraction was collected, the solvents were evaporated and the residue was distilled at 45–50°C under reduced pressure (10^{-3} Torr). Dark green oil (purple-red in the light of an electric bulb) was obtained (eqn. (6)).



(6)

^{1}H, ^{13}C NMR spectra show that the two π-allyl isomers, *syn* and *anti*, of compound **2** are formed in the reaction (6). There was no methyl group transfer from β-carbon at α-carbon observed in the reaction products as it took place in the case of the trimethylsilyl group [3]. The molecular peak at $m/e = 254$ and other fragments characteristic for cyclopentadienyl nickel compounds (188, $NiCp_2^+$; 123, $NiCp^+$; 58, Ni^+) were observed in the mass spectrum of compound **2**. ^{1}H, ^{13}C NMR spectral data of compounds **2a** and **2b** are shown in Tables 1 and 2.

TABLE 1. ^{1}H NMR spectra of compounds **2a** and **2b**

Compound	Chemical shifts δ (ppm), J (Hz)						
	H^1	H^2	H^3	CH_3	Cp	Ph	$J(H^1H^3)$
2a	4.99d	2.19s	3.08d	2.15s	5.16d	6.94–6.97m	1.6
2b	2.63s	1.29s	2.94s	2.29s	5.20d	7.15–7.17m	$J(H^1H^2)$ [a]

[a] Not observed.

The molar ratio of the isomers formed, **2a**/**2b**, was variable. Based on the integration of ^{1}H NMR signals, it was found that in different experiments, isomer **2a** was formed with 24–55% yield and isomer **2b** with 75–54% yield, respectively. We presume that the various molar ratio of isomers is the result of differences in chromatographic separation of the product. The influence of different reaction conditions also cannot be excluded.

3. Discussion

The compound {CpNi–C(CH_3)═C(CH_3)$_2$} does not possess α-H but possesses β-H, so β-H elimination with the formation of π-allyl proceeds easily (eqn. (5)). The course of the reaction (5) is shown in Scheme 1. The driving force of β-H migration to the nickel is the increase in the number of nickel electrons from 16 to 18. The second step of the reaction is the stabilization of carbocation by the shift of Ni–C_α to Ni–C_β. The migration of the hydride anion to a positively charged carbon atom leads to the formation of π-allyl complex. Besides the reaction (5), an oligomerization of unstable {CpNi–C(CH_3)═C(CH_3)$_2$} with the formation of a tetramer also occurs. This reaction has been described previously [8].

The results of our studies confirm that unstable compounds {CpNi–C(CH_3)═C(CH_3)$_2$} and {CpNi–C(C_6H_5)═C(CH_3)$_2$} do not form (μ_3-alkylidyne)trinickel clusters. Thus, the migration of methyl and phenyl groups from α-carbon to β-carbon does not

TABLE 2. ^{13}C NMR spectra of compounds **2a** and **2b**

Compound	Chemical shifts δ (ppm), (^1J(CH) (Hz))								
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	Cp
2a	62.5d (151)	103.2s	45.3t (158)	25.6q – [b]	143.4s	128.5d (165)	128.7d (158)	124.9d (160)	90.13d (173)
2b	64.1d (152)	– [a]	40.1t (156)	19.6q (129)	130.9s	128.7d (160)	129.9d (159)	126.2d (160)	90.18d (173)

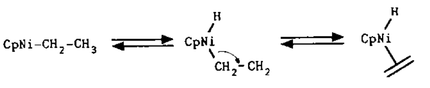
[a] Not observed. [b] Signal overlapping with THF.

occur. These observations show that the key step in the formation of a (μ_3-alkylidyne)trinickel cluster from {CpNi-CH=C(CH$_3$)$_2$} [5] is α-hydrogen elimination, its migration to nickel [6] and further transfer to β-carbon. Nickel plays an intermediate role in hydrogen transfer from C_α to C_β. Because nickel does not mediate in the transfer of methyl or phenyl groups [7], (μ_3-alkylidyne)trinickel clusters do not form.

The unstable compound {CpNi-C(C$_6$H$_5$)=C(CH$_3$)$_2$} does not possess α- and β-hydrogen, so the formation of allyl compounds **2a** and **2b** can be explained by the γ-H elimination process. The course of the reaction (6) is shown in Scheme 2. The driving force of γ-H elimination is the anxiety of the nickel atom to achieve 18-electron configuration similar to the cases of β- and α-H elimination. The shift of the double bond from C^1–C^2 to C^2–C^3 stabilizes the carbocation. Due to the free rotation around the C^1–C^2 bond, the attack of hydrogen bonded to nickel on C^1 can occur from two sides leading to the formation of *anti* and *syn* isomers of π-allyl.

To our knowledge, the γ-H elimination reaction has not been previously described for organonickel compounds. If the σ-bonded ligand possesses β- or α-hydrogen, then β-H or α-H elimination occurs first. Furthermore, for alkyl ligands without α- or β-hydrogen, γ-H elimination does not lead to the stabilization of the system (eqn. (7)), as happens in the case of β-H elimination (the formation of the olefinic complex) (eqn. (8)).

(7)

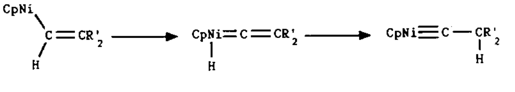


(8)

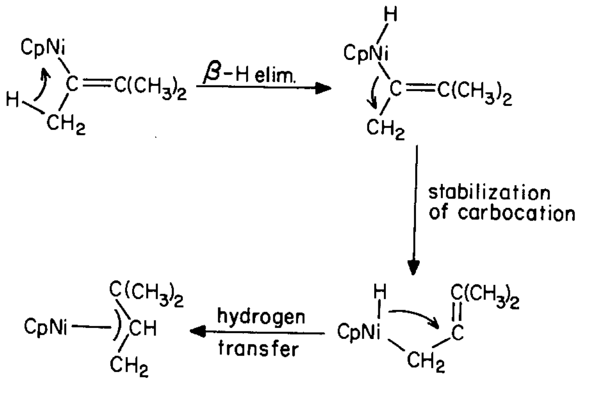
Unstable (η^5-cyclopentadienyl)vinylnickel is initially formed in the reaction of nickelocene with vinyllithium compounds (eqn. (9)).

$$\mathrm{NiCp_2 + Li{-}CR{=}CR'_2 \longrightarrow CpNi{-}CR{=}CR'_2 + LiCp} \qquad (9)$$

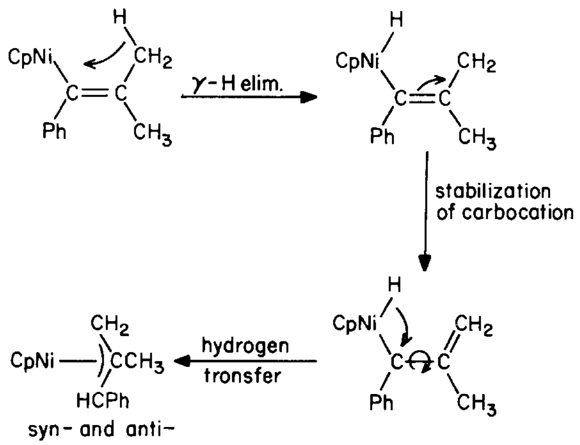
The course of H-elimination depends on the kind of R. For R = H, α-H elimination occurs. Nickel plays a mediator's role in the 1,2-hydrogen shift process (eqn. 10). The mechanism of the reaction (10) will be the subject of a future publication.



$$\mathrm{CpNi(H)C{=}CR'_2 \longrightarrow \underset{\displaystyle H}{\underset{|}{CpNi}}{=}C{=}CR'_2 \longrightarrow CpNi{\equiv}C{-}\underset{\displaystyle H}{\underset{|}{CR'_2}}} \qquad (10)$$



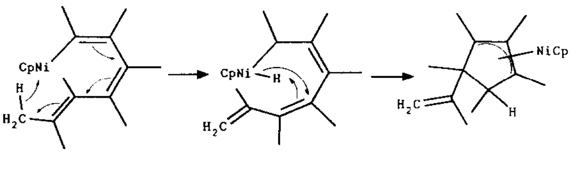
Scheme 1.



Scheme 2.

For R = CH$_3$, β-H elimination occurs; 2,1-hydrogen shift is observed in this reaction and the nickel atom also plays a mediator's role (Scheme 1). Besides the hydrogen transfer, the splitting of Ni–C$_\alpha$ with the formation of a Ni–C$_\beta$ bond occurs. It is a precondition for the formation of a stable π-allyl compound. For R = C$_6$H$_5$, γ-H elimination with 3,1-hydrogen shift occurs (Scheme 2).

We have previously found that π-allyl complex was formed in the reaction of nickelocene with methyllithium in the presence of an excess of 2-butyne, in addition to other products (eqn. (2)) [4]. The formation of this complex (eqn. (11)) can be explained by a η-H elimination process. The reaction course was analogous to the reaction of β-H (Scheme 1) and γ-H elimination (Scheme 2).



(11)

Unstable (η^5-cyclopentadienyl)vinylnickel compounds formed in the reaction (9), in addition to the formation of π-allyl compounds, undergo other reactions with the formation of μ_3-alkylidynetrinickel clusters, tetramers $[CpNi{-}C(CH_3){=}C(CH_3)_2]_4$ [8] and other compounds not yet fully characterized. All the compounds $\{CpNi{-}CR{=}CR'_2\}$ obtained undergo coupling reactions to form butadiene derivatives and active $(CpNi)_n$ species (eqn. (12)).

$$2\ NiCp{-}CR{=}CR'_2 \longrightarrow R'_2C{=}CR{-}CR{=}CR'_2 + (NiCp)_2 \qquad (12)$$

Butadiene derivatives were isolated from the reaction products and fully characterized.

The following conclusions can be made:

(1) Anxiety of the nickel atom to achieve 18e configuration is the reason for α-, β-, γ- and η-H elimination and further for 1,2-, 2,1-, 3,1-, 1,4- and 7,4-hydrogen shift.

(2) 1,2-, 2,1-, 3,1-, 1,4- and 7,4-hydrogen transfer is mediated by the nickel atom.

(3) Unstable nickel hydrides undergo further reactions to form thermodynamically stable compounds (methylidynetrinickel clusters and π-allyl complexes).

(4) The Ni–C bond in (η^5-cyclopentadienyl)vinylnickel compounds does not split in α-, γ- and η-H elimination processes. In the case of β-H elimination, Ni–C_α breaks and Ni–C_β is formed simultaneously with 2,1-hydrogen shift.

(5) The migration of hydrogen from carbon to nickel is not accompanied by the formation of free {CpNiH} and its further attack on the organic fragment of the molecule.

4. Experimental details

All manipulations were carried out under dry argon. Solvents were dried and distilled over the benzophenone radical anion and deoxygenated prior to use. Chromatography was carried out on neutral alumina (Merck 90, 0.063–0.200 mm, deactivated with 2% of water). The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer. Syntheses of 1,2-dimethylpropenyllithium and 1-phenyl-2-methylpropenyllithium were carried out according to the literature methods [9,10].

4.1. *Reaction of $NiCp_2$ with 1,2-dimethylpropenyllithium*

An etheral solution of 1,2-dimethylpropenyllithium (10.6 mmol) was added to a solution of nickelocene (1 g, 5.3 mmol) in 30 cm^3 of THF. The mixture was stirred at room temperature. After 24 h, the solvents were evaporated *in vacuo*. Deoxygenated water (10 cm^3) and hexane (50 cm^3) were added to the residue and stirred for 1 h. The organic layer was separated, washed, dried with molecular sieves and concentrated. The residue was chromatographed on alumina using hexane as an eluent. The first, deep red fraction contained allyl compound **1**, the second fraction contained unreacted nickelocene. The residue from the column was a mixture of unidentified compounds. The yield of allyl compound **1** was 12–16%.

4.2. *Reaction of $NiCp_2$ with 1-phenyl-2-methylpropenyllithium*

An etheral solution of 1-phenyl-2-methylpropenyllithium (12.6 mmol) was added drop by drop to a solution of nickelocene (2.18 g, 11.5 mmol) in 120 cm^3 of diethyl ether. The mixture was stirred at room temperature for 24 h, deoxygenated water (70 cm^3) was added and stirred for further 1 h. The mixture was filtered through a bed of alumina (2 cm high), the etheral layer was separated and dried over molecular sieves. The solvent was evaporated under reduced pressure. The residue was dried *in vacuo* (10^{-1} Torr) at room temperature for 3–4 h. Sublimation of small amounts of $NiCp_2$ was observed. Viscous, brown oil was obtained. Hexane (20 cm^3) was added, a black solid was filtered off and the filtrate was concentrated and chromatographed on alumina using heptane as eluent. The first green fraction was separated. The solvent was evaporated under reduced pressure and the residue was distilled at 45–50°C *in vacuo* (10^{-3} Torr). Deep green oil (purple-red in the light of an electric bulb) was obtained. It was identified as a mixture of isomers **2a** and **2b** based on its ^1H, ^{13}C NMR and mass spectra.

Acknowledgements

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