

# Reactions of nickelocene with lithium and magnesium alkyls containing $\beta$ -hydrogen atoms<sup>1</sup>

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Received 22 January 1997

## Abstract

The reaction of nickelocene with  $\text{BrMgR}$ , where  $\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ ,  $\text{C}_2\text{H}_5$ ,  $(\text{CH}_2)_7\text{CH}_3$  and  $\text{CH}_2\text{CH}_2\text{CH}_3$ , have been studied. It was found that the presence of  $\beta$ -hydrogen in  $\text{R}$  did not cause the total splitting of the carbon–nickel bond but alkyldynetrinickel clusters were formed. It is the first example of the synthesis of alkyldynetrinickel clusters  $(\text{NiCp})_3\text{CR}'$  from the organonickel species possessing  $\beta$ -hydrogen. Besides trinickel clusters, the following compounds were always formed in all the studied reactions:  $(\text{NiCp})_4\text{H}_2$ ,  $(\text{NiCp})_6$ ,  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$  and  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$ . The structure of  $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{Ph}$  has been determined by a single-crystal X-ray diffraction study. © 1998 Elsevier Science S.A.

**Keywords:** Cyclopentadienylnickel clusters; Nickel;  $\beta$ -H elimination

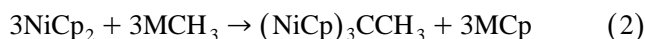
## 1. Introduction

Alkyldynetrinickel clusters of the general formula  $(\text{NiCp})_3\text{CR}$ , where  $\text{R} = \text{C}_6\text{H}_5$  [1],  $\text{C}(\text{CH}_3)_3$  and  $\text{Si}(\text{CH}_3)_3$  [2], have been previously obtained in the reactions of nickelocene with corresponding organolithium or -magnesium compounds (Eq. (1)).



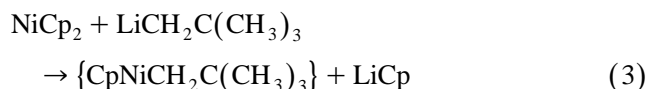
where  $\text{M} = \text{Li}, \text{MgBr}$ ;  $\text{R} = \text{C}_6\text{H}_5, \text{C}(\text{CH}_3)_3, \text{Si}(\text{CH}_3)_3$ .

Ethylidynetrinickel cluster  $(\text{NiCp})_3\text{CCH}_3$  [3] has also been obtained in the reactions of nickelocene with methyllithium or methylmagnesium bromide (Eq. (2)).

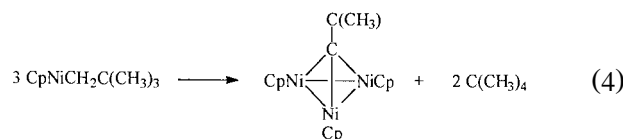


where  $\text{M} = \text{Li}, \text{MgBr}$ .

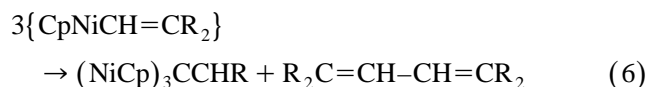
Because organolithium and -magnesium compounds were lacking  $\beta$ -hydrogen, the unstable organonickel compound formed in the reaction (Eq. (3)) did not undergo  $\beta$ -H elimination.



The elimination of consecutive  $\alpha$ -hydrogen atoms and reactions of unstable hydridometalcarbenes with  $\{\text{CpNiCH}_2\text{C}(\text{CH}_3)_3\}$  led to the formation of alkyldynetrinickel clusters and corresponding hydrocarbons (Eq. (4)).



Alkyldynetrinickel clusters can also be obtained from vinylnickel compounds if they possess  $\alpha$ -hydrogen atoms (Eqs. (5) and (6)) [3].

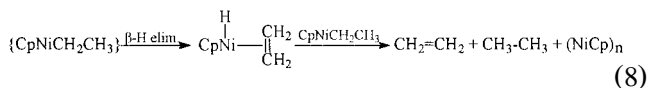


Alkyldynetrinickel clusters were not formed if alkylnickel compounds possessed  $\beta$ -hydrogen [2]. It has been reported that in the reaction of nickelocene with

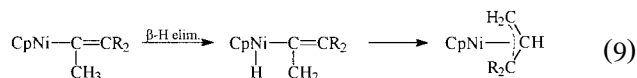
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<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday in recognition of his outstanding contributions to organometallic chemistry.

*n*-BuLi, 2-naphthyllithium, 2- and 4-picolylithium and prop-2-ynylmagnesium bromide no trinickel cluster is formed. It appears, according to Booth and Casey [2], that this method of synthesis is restricted to derivatives of benzyl lithium or benzylmagnesium halides and simple alkyl lithium or Grignard reagents which do not possess  $\beta$ -hydrogen. It has been presumed up to now that nickel-alkyl compounds decompose via a  $\beta$ -elimination with splitting of the Ni–C bond [4,5] (Eqs. (7) and (8)).

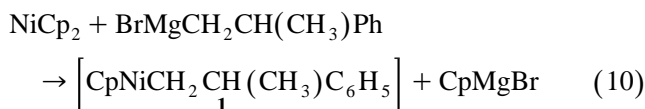


If vinylnickel compounds possess  $\beta$ -hydrogen then  $\pi$ -allylnickel complexes are formed as a result of  $\beta$ -H elimination [6,7] (Eq. (9)).



## 2. Results and discussion

In order to throw further light on  $\alpha$ - and  $\beta$ -H elimination reactions in cyclopentadienylalkylnickel compounds we have studied the reaction of nickelocene with  $\text{BrMgCH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  (Eq. (10)).



We have found that compound **1** reacts further to

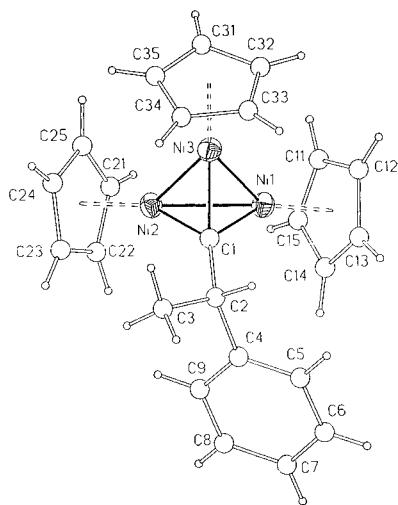


Fig. 1. The crystal structure of  $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{Ph}$ , **5**, with the atom numbering system.

Table 1  
Data collection and structure analysis parameters for **5**

Empirical formula	$\text{C}_24\text{H}_{24}\text{Ni}_3$
Formula weight	488.56
Crystal size ( $\text{mm}^3$ )	$0.4 \times 0.7 \times 0.1$
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
$a$ ( $\text{\AA}$ )	8.593(3)
$b$ ( $\text{\AA}$ )	20.610(5)
$c$ ( $\text{\AA}$ )	12.062(3)
$\beta$ (deg)	90.30(3)
Volume ( $\text{\AA}^3$ )	2136.2(7)
$Z$	4
Density (calc.) ( $\text{Mg m}^{-3}$ )	1.519
Temperature (K)	293(2)
Absorption coefficient ( $\text{mm}^{-1}$ )	2.622
Absorption correction	DIFABS procedure (0.8897–1.1793)
$F(000)$	1008
Radiation	Mo K $\alpha$ ( $\lambda = 0.71069 \text{\AA}$ ; graphite monochromator)
$\theta$ range for data collection (deg)	2 to 25
Scan type	$\omega$ -2 $\theta$
Scan ranges	$0 \leq h \leq 10, 0 \leq k \leq 23,$ $-14 \leq l \leq 14$
Measured reflections	3741
Observed reflections $I > 2\sigma(I)$	2654
Data/restraints/parameters	2654/30/245
Goodness-of-fit on $F^2$	1.107
Final $R$ indices [ $I > 2\sigma(I)$ ]	
$R = \sum( F_o  -  F_c ) / \sum( F_o )$	0.0318
$wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$	0.0452
Weighting scheme	$w = 1 / [\sigma^2(F_o^2)]$
Largest difference peak and hole ( $\text{e}^{-\text{\AA}^{-3}}$ )	0.369 and $-0.360$

form trinickel cluster **5**  $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{C}_6\text{H}_5$ . This means that the presence of the  $\beta$ -hydrogen atom and the possibility of  $\beta$ -H elimination does not always cause the splitting of the carbon–nickel bond. This is the first example of the synthesis of an alkylidynetrinickel cluster from an organonickel compound possessing  $\beta$ -hydrogen. The cluster **5** has been characterised spectroscopically and by the single-crystal X-ray technique. It crystallises in the monoclinic crystal system. The crystal structure is presented on Fig. 1. Data collection and structure analysis parameters are given in Table 1; fractional atomic coordinates, selected bond lengths and bond angles are listed in Tables 2–4 respectively. Ni–Ni distances are from 2.313 to 2.355  $\text{\AA}$ , and Ni–C<sub>alkylidyne</sub> are from 1.844 to 1.888  $\text{\AA}$ . Ni–Ni–Ni angles are about  $60^\circ$  and the Ni–C<sub>alkylidyne</sub>–Ni angles are about  $78^\circ$ . These data are comparable with the values published for similar cyclopentadienyltrinickel clusters [3,8].

Besides the trinickel cluster **5**, another cluster of the formula  $(\text{CpNi})_4\text{H}_2$  was also formed in the reaction studied. It was isolated chromatographically as a dia-

Table 2  
Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for **5**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Ni(1)	0.19524(6)	0.55103(2)	0.26771(4)	0.04043(13)
Ni(2)	-0.02494(6)	0.61486(3)	0.23110(4)	0.04113(13)
Ni(3)	0.18404(6)	0.61929(3)	0.11124(3)	0.04217(14)
C(1)	0.1765(5)	0.6422(2)	0.2589(3)	0.0410(10)
C(2)	0.2570(6)	0.6971(2)	0.3202(3)	0.0609(13)
C(3)	0.2089(11)	0.7631(3)	0.2926(5)	0.117(3)
C(11)	0.1991(9)	0.4454(3)	0.2665(6)	0.106(2)
C(12)	0.3572(10)	0.4733(3)	0.2537(5)	0.105(3)
C(13)	0.3838(7)	0.5087(3)	0.3505(4)	0.077(2)
C(14)	0.2610(7)	0.5039(3)	0.4176(4)	0.0747(15)
C(15)	0.1446(7)	0.4668(3)	0.3654(5)	0.079(2)
C(21)	-0.2306(6)	0.5602(3)	0.2516(5)	0.0801(15)
C(22)	-0.2198(6)	0.6107(3)	0.3332(5)	0.085(2)
C(23)	-0.2166(6)	0.6721(3)	0.2802(4)	0.0636(13)
C(24)	-0.2260(5)	0.6597(3)	0.1662(4)	0.0619(13)
C(25)	-0.2384(6)	0.5913(3)	0.1515(5)	0.073(2)
C(31)	0.1606(7)	0.5873(3)	-0.0571(4)	0.079(2)
C(32)	0.3154(7)	0.5841(3)	-0.0213(4)	0.076(2)
C(33)	0.3667(6)	0.6481(3)	0.0058(4)	0.084(2)
C(34)	0.2391(9)	0.6903(3)	-0.0083(4)	0.087(2)
C(35)	0.1172(7)	0.6517(3)	-0.0467(4)	0.079(2)
C(4)	0.2684(6)	0.6828(2)	0.4420(3)	0.0478(10)
C(5)	0.4096(6)	0.6667(2)	0.4854(4)	0.0642(12)
C(6)	0.4246(10)	0.6510(3)	0.5979(5)	0.090(2)
C(7)	0.2984(13)	0.6516(3)	0.6660(5)	0.116(3)
C(8)	0.1517(8)	0.6662(3)	0.6223(5)	0.090(2)
C(9)	0.1375(7)	0.6829(2)	0.5095(4)	0.06471(4)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j.$$

magnetic, black solid. The  $^1\text{H}$  NMR spectrum showed singlet at 5.35 ppm assigned to Cp protons and a singlet at -20.3 ppm assigned to hydrido protons. In the  $^{13}\text{C}$  NMR spectrum only one signal of the Cp carbon atoms at 82.6 ppm was observed. The highest ions observed in the mass spectrum appeared at  $m/e = 488-500$ . This is a result of overlapping of the molecular ion and other fragments formed by the abstraction of hydrogen atoms. It can be derived from the spectrum that the fragments have the isotopic pattern characteristic for four nickel atoms. The other ions observed were characteristic for the fragmentation of  $(\text{NiCp})_n$ -type clusters and were as follows: 362  $(\text{Ni}_4\text{Cp}_2)^+$ , 304  $(\text{Ni}_3\text{Cp}_2)^+$ , 246  $(\text{Ni}_2\text{Cp}_2)^+$  and 123  $(\text{NiCp})^+$ . The structure of the cluster was published earlier [9].

Traces of the higher cluster  $(\text{NiCp})_6$  [10] have also been isolated by means of column chromatography on neutral alumina ( $37 \times 2 \text{ cm}^2$ ) using toluene as an eluent. The mass spectrum shows the parent ion at  $m/e = 738$  and the following fragments:  $m/e = 550 (\text{Ni}_5\text{Cp}_4)^+$ ; 427  $(\text{Ni}_4\text{Cp}_3)^+$ ; 188  $(\text{NiCp}_2)^+$ ; 123  $(\text{NiCp})^+$ . Besides the above products, the presence of bis(cyclopentadienyl)( $\mu$ -cyclopentadiene) dinickel,  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$  [11], and  $(\eta^5\text{-cyclopentadienyl})(\eta^3\text{-cyclopentenyl})$  nickel,  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$  [11,12], was con-

Table 3  
Interatomic distances ( $\text{\AA}$ ), with estimated standard deviations in parentheses, of non-hydrogen atoms in **5**

Ni(2)–C(1)	1.849(4)	C(2)–C(4)	1.500(5)
Ni(2)–C(22)	2.085(5)	C(11)–C(15)	1.358(7)
Ni(2)–C(24)	2.107(5)	C(11)–C(12)	1.484(9)
Ni(2)–C(21)	2.112(5)	C(12)–C(13)	1.394(8)
Ni(2)–C(23)	2.113(4)	C(13)–C(14)	1.337(7)
Ni(2)–C(25)	2.123(5)	C(14)–C(15)	1.406(7)
Ni(2)–Ni(3)	2.313(1)	C(21)–C(25)	1.370(7)
Ni(2)–Ni(1)	2.344(1)	C(21)–C(22)	1.435(8)
Ni(1)–C(1)	1.888(4)	C(22)–C(23)	1.419(6)
Ni(1)–C(13)	2.090(5)	C(23)–C(24)	1.401(6)
Ni(1)–C(14)	2.126(5)	C(24)–C(25)	1.424(6)
Ni(1)–C(12)	2.129(6)	C(31)–C(35)	1.384(7)
Ni(1)–C(15)	2.144(5)	C(31)–C(32)	1.398(7)
Ni(1)–C(11)	2.178(6)	C(32)–C(33)	1.429(7)
Ni(1)–Ni(3)	2.355(1)	C(33)–C(34)	1.409(7)
Ni(3)–C(1)	1.844(4)	C(34)–C(35)	1.393(7)
Ni(3)–C(32)	2.092(4)	C(4)–C(5)	1.360(7)
Ni(3)–C(35)	2.096(5)	C(4)–C(9)	1.392(6)
Ni(3)–C(34)	2.110(5)	C(5)–C(6)	1.401(7)
Ni(3)–C(33)	2.111(4)	C(6)–C(7)	1.364(11)
Ni(3)–C(31)	2.143(5)	C(7)–C(8)	1.397(10)
C(1)–C(2)	1.517(5)	C(8)–C(9)	1.408(8)
C(2)–C(3)	1.461(8)		

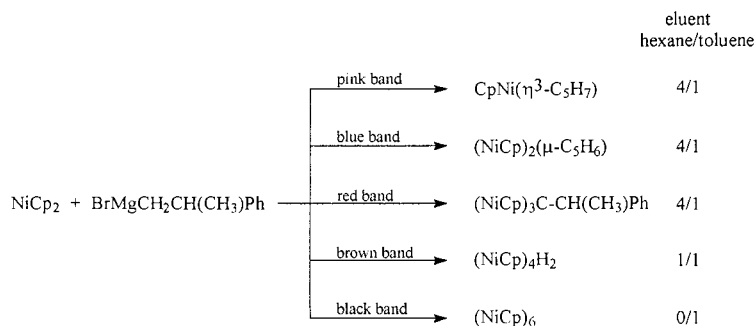
firmed. The above compounds were separated by column chromatography and identified by spectroscopic methods. They were formed at low yield as by-products. The composition of the products formed is presented in Scheme 1.

Cumene,  $\alpha$ -methylstyrene, 2,5-diphenylhexane and 2,5-diphenylhexene were detected by means of gas chromatography and mass spectrometry among organic products of the reaction of nickelocene with  $\text{BrMgCH}_2\text{CH}(\text{CH}_3)\text{Ph}$ .

After finding out that  $\{\text{CpNi}-\text{CH}_2\text{CH}(\text{CH}_3)\text{Ph}\}$  formed an alkylidynetrinickel cluster we studied other

Table 4  
Selected bond angles (deg) in **5**

Ni(3)–Ni(2)–Ni(1)	60.75(2)	C(2)–C(1)–Ni(3)	130.0(3)
Ni(2)–Ni(1)–Ni(3)	58.97(3)	C(2)–C(1)–Ni(2)	137.7(3)
Ni(2)–Ni(3)–Ni(1)	60.28(3)	C(2)–C(1)–Ni(1)	132.6(3)
Ni(3)–C(1)–Ni(2)	77.5(2)	C(3)–C(2)–C(4)	115.0(4)
Ni(3)–C(1)–Ni(1)	78.3(2)	C(3)–C(2)–C(1)	117.1(4)
Ni(2)–C(1)–Ni(1)	77.7(2)	C(4)–C(2)–C(1)	111.0(3)
C(1)–Ni(2)–Ni(3)	51.1(2)	C(5)–C(4)–C(2)	118.6(4)
C(1)–Ni(2)–Ni(1)	51.9(2)	C(9)–C(4)–C(2)	121.6(4)
C(1)–Ni(1)–Ni(2)	50.4(2)		
C(1)–Ni(1)–Ni(3)	50.1(2)	C(5)–C(4)–C(9)	119.8(4)
C(1)–Ni(3)–Ni(2)	51.3(2)	C(4)–C(5)–C(6)	120.5(5)
C(1)–Ni(3)–Ni(1)	51.7(2)	C(5)–C(6)–C(7)	120.8(7)
		C(6)–C(7)–C(8)	119.6(5)
		C(7)–C(8)–C(9)	119.4(5)
		C(4)–C(9)–C(8)	119.9(6)



Scheme 1.

alkylnickel compounds possessing β-hydrogen atoms (Eq. (11)).



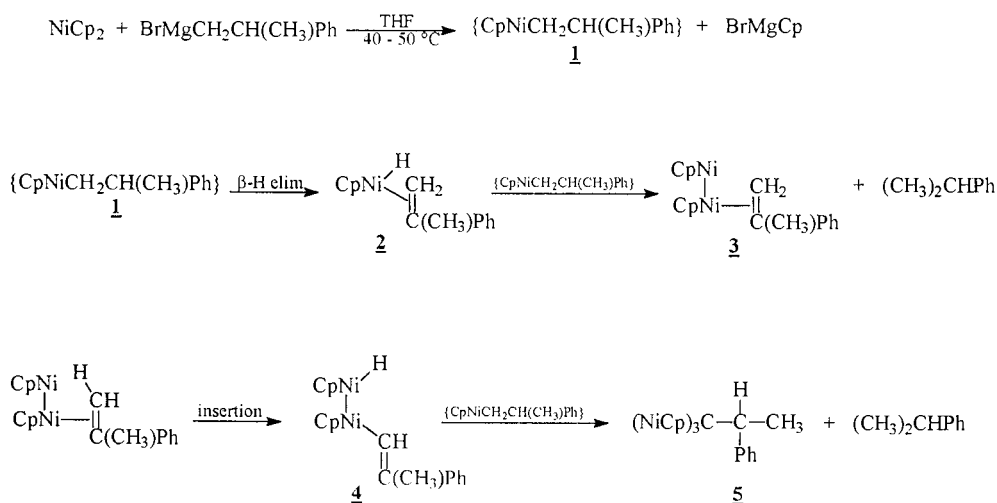
where R = C<sub>2</sub>H<sub>5</sub>; (CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>; CH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>.

The reaction of BrMgC<sub>2</sub>H<sub>5</sub> with nickelocene was carried out in THF at temperature 40–50 °C. The products were isolated by two methods. The first one consisted of hydrolysis of the formed BrMgCp with water followed by separation of the organic layer. The second method consisted of the extraction of organonickel and organic products with hexane–toluene = 10/1. In both methods the products were then separated by column chromatography on neutral alumina (eluent hexane and hexane–toluene). The products obtained by the two methods were identical. The ethylidynetrinickel cluster (NiCp<sub>3</sub>)CCH<sub>3</sub> (8% yield), fully characterised by us previously [3], was identified by means <sup>1</sup>H, <sup>13</sup>C NMR and mass spectroscopy. The other products were tetra(cyclopentadienylnickel)dihydride (NiCp)<sub>4</sub>H<sub>2</sub> [9] (18% yield), identified by means of spectroscopic methods, and hexa(cyclopentadienylnickel) (NiCp)<sub>6</sub> (14%

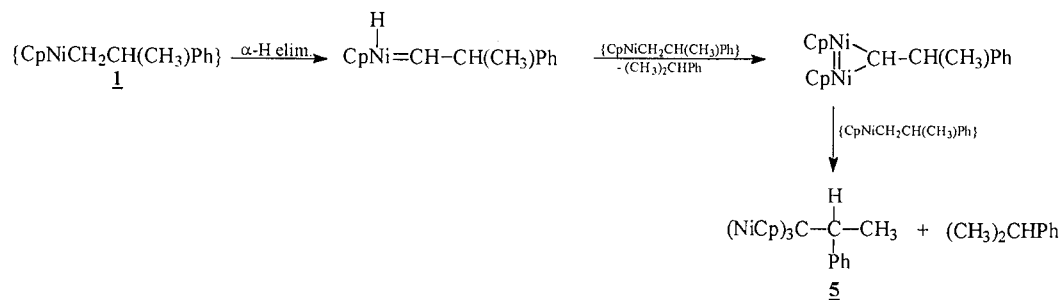
yield), characterised by NMR, IR and mass spectra [10]. Also, butylidynetrinickel cluster (NiCp)<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> was formed as a by-product. This was eluted together with (NiCp)<sub>3</sub>CCH<sub>3</sub> and its presence was confirmed by spectroscopic methods without isolation.

The reaction of nickelocene with octylmagnesium bromide was carried out at 40–50 °C; the reaction mixture was then hydrolysed and the products were separated by column chromatography. Three main bands were separated. The red band contained trinickel cluster (NiCp)<sub>3</sub>C(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub> (10% yield), characterised by <sup>1</sup>H, <sup>13</sup>C NMR and mass spectrometry. The brown band contained tetranickel cluster (NiCp)<sub>4</sub>H<sub>2</sub> [9] (26% yield), identified by spectroscopic methods. The last black-brown band contained hexanickel cluster (NiCp)<sub>6</sub> [10] (20% yield), also identified spectroscopically. The presence of small amounts of (NiCp)<sub>2</sub>(μ-C<sub>5</sub>H<sub>6</sub>) and CpNi(η<sup>3</sup>-C<sub>5</sub>H<sub>7</sub>) was also observed among products of this reaction.

The reaction of nickelocene with *n*-propylmagnesium bromide was carried out similarly to the reaction with octylmagnesium bromide. The following



Scheme 2.



Scheme 3.

products were isolated and identified:  $(\text{NiCp})_3\text{CCH}_2\text{CH}_3$  [3],  $(\text{NiCp})_4\text{H}_2$  [9] and  $(\text{NiCp})_6$  [10]. As in the reactions described above,  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$  and  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$  were also formed as by-products.

The above results show that in contrast to the previous opinions [2], the alkylnickel species  $\{\text{CpNiR}\}$ , with R possessing  $\beta$ -hydrogen, form trinickel clusters according to the Eq. (12).



where R =  $\text{CH}(\text{CH}_3)\text{Ph}$ ;  $\text{CH}_3$ ,  $n\text{-(CH}_2)_6\text{CH}_3$ ;  $\text{C}_2\text{H}_5$ ; M = Li, MgBr.

The presence of  $\beta$ -hydrogen does not cause the total splitting of the nickel–carbon bond with the formation of saturated and unsaturated hydrocarbons. This reaction can be regarded as the simplest method of the synthesis of alkyldynecyclopentadienyltrinickel clusters.

Because all the alkyl ligands studied by us possessed  $\alpha$ - and  $\beta$ -hydrogen it could be assumed that both  $\beta$ -H as well as  $\alpha$ -H elimination were possible. However, the literature data show that for ligands possessing  $\alpha$ - and  $\beta$ -H,  $\beta$ -H elimination proceeds more easily [4,5,13,14]. For the ligands lacking  $\beta$ -H, e.g.  $\text{CH}_3$ ,  $\text{CH}_2\text{C}(\text{CH}_3)_3$ ,  $\text{CH}_2\text{Si}(\text{CH}_3)_3$ , the hydrogen elimination proceeds less easily [5]. Considering the above statements, the possible course of reactions of nickelocene with 2-phenylpropylmagnesium bromide leading to the formation of

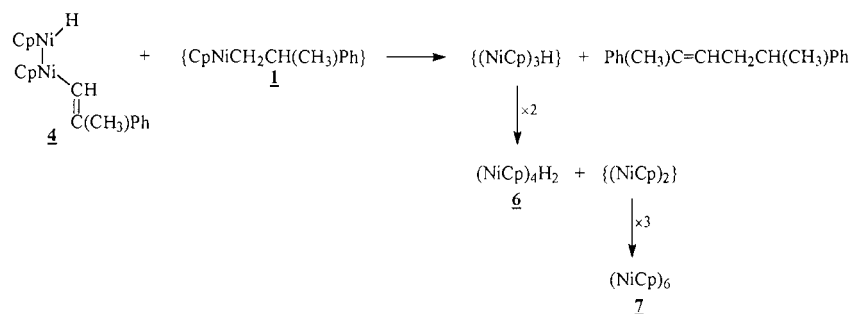
alkyldynetrinickel cluster is presented in Scheme 2. It can be assumed that reactions of nickelocene with other alkyllithium or alkylmagnesium compounds possessing  $\beta$ -hydrogen atoms proceed similarly.

Unstable compound **1** possesses  $\beta$ -H; therefore,  $\beta$ -H elimination can occur leading to the formation of a nickel hydride coordinated to the olefin. The hydridonickel  $\pi$ -complex **2** can react with the compound **1** to form complex **3** and cumene. The insertion of dinickel species into the C–H bond occurs in complex **3** leading to the formation of **4**. The latter reacts with another  $\{\text{CpNiCH}_2\text{C}(\text{CH}_3)\text{Ph}\}$  species to form the trinickel cluster **5**, the final product of the reaction. The activation of the terminal olefinic C–H bonds with the formation of trinickel clusters was proved by us in the reactions of nickelocene with phenyllithium in the presence of terminal olefins [9].

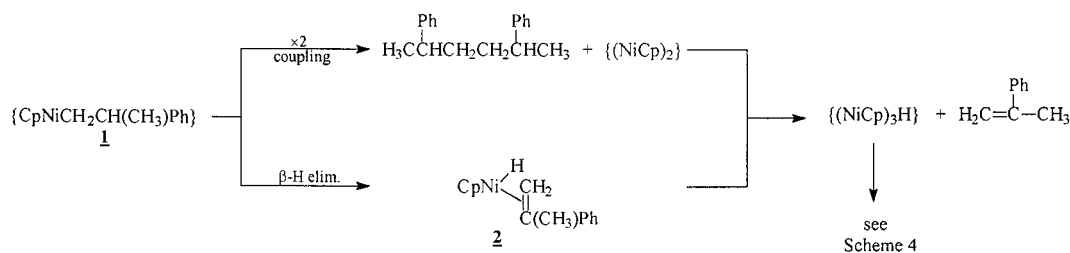
The formation of the trinickel cluster **5** could also be explained by  $\alpha$ -H elimination in compound **1** (Scheme 3), but in that case it would be difficult to explain the presence of  $\alpha$ -methylstyrene among the products. Therefore, it should be assumed that the cluster **5** is formed according to the  $\beta$ -H elimination pathway, or that both reactions of  $\beta$ -H and  $\alpha$ -H elimination proceed simultaneously.

A proposition of the reaction course leading to the formation of  $(\text{NiCp})_4\text{H}_2$  **6** and  $(\text{NiCp})_6$  **7** is presented in Scheme 4.

Compound **4**, the product of an insertion of a dinickel



Scheme 4.



Scheme 5.

species into the C–H bond of an olefin, can react with **1** to form a coupling product  $\text{Ph}(\text{CH}_3)\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{Ph}$  and  $\{(\text{NiCp})_3(\mu_3\text{-H})\}$ . A similar cluster  $\text{L}_n\text{Cr}_2\text{Cu}(\mu_3\text{-H})$  was prepared and fully characterised [15]. In the mass spectrum of  $(\text{NiCp})_3\text{C}(\text{CH}_2)_6\text{CH}_3$  an intensive ion at  $m/e = 370$  with the isotopic pattern characteristic for three nickel atoms was present. This ion corresponded to the cluster  $(\text{NiCp})_3(\mu_3\text{-H})$ . This cluster reacts further to form the stable tetranickel cluster  $(\text{NiCp})_4\text{H}_2$  and a very reactive species  $\{(\text{NiCp})_2\}$  (Scheme 4). These species can form a stable cluster **7** (Scheme 4) or react with  $\beta$ -H elimination product **2** to form  $(\text{NiCp})_3(\mu_3\text{-H})$  again (Scheme 5).

Besides the three main products of the reaction of nickelocene with alkylmagnesium compounds, small amounts of  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$  and  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$  were also formed. We have previously explained that they were formed as a result of hydrogenation of the cyclopentadienyl ring with  $\{\text{CpNiH}\}$  [11].

Besides isolated and characterised organonickel compounds, the organic products of the reactions of nickelocene with  $\text{BrMgCH}_2\text{CH}(\text{CH}_3)\text{Ph}$  were identified. They were: 2-phenylpropane (the course of the formation is shown in Scheme 2), 2,5-diphenylhexene (Scheme 4), 2,5-diphenylhexane and  $\alpha$ -methylstyrene (Scheme 5). The presence of the above compounds among the reaction products confirms our proposition of the reaction course. Analogous organonickel and organic compounds were formed in the reactions of nickelocene with other alkylmagnesium compounds studied.

### 3. Experimental details

All reactions were carried out under an atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. 1-Bromo-2-phenylpropane was prepared from allyl bromide and benzene according to Ref. [16].  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Varian VXR-300 instrument. Mass spectra were recorded on an AMD-604 mass spectrometer. GC/MS analyses were performed on a Hewlett Packard 5971 Series Mass Selective Detector with an HP 35 column (30 m  $\times$  0.25 mm).

#### 3.1. Reaction of nickelocene with 2-phenylpropylmagnesium bromide

To a solution of  $\text{NiCp}_2$  (0.62 g, 3.3 mmol) in 48 cm<sup>3</sup> THF a solution of 2-phenylpropylmagnesium bromide in THF (12 cm<sup>3</sup>, 3.6 mmol) was added within 1 h at 40 °C. Stirring was continued overnight, then the volatile substances were removed under reduced pressure; 5 cm<sup>3</sup> of THF and 50 cm<sup>3</sup> of hexane were added and the products were hydrolysed with 50 cm<sup>3</sup> of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was redissolved in toluene and chromatographed on  $\text{Al}_2\text{O}_3$  (37  $\times$  2 cm<sup>2</sup>, deactivated with 5% of water) using hexane or hexane–toluene as eluents. A small amount of pink  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$  was eluted with hexane. This was followed by a small amount of green  $\text{NiCp}_2$  (eluent: hexane). The next blue band containing  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$  [11] was collected (yield 4%; eluent: 10% toluene in hexane). This was characterised by  $^1\text{H}$  NMR:  $\delta(\text{ppm}) = 1.82$  (2H), 2.87 (2H), 5.07 (10H), 5.24 (2H). EIMS (70 eV)  $m/e = 312$  ( $\text{M}^+$ , 35%), 246 (98%), 188 (100%), 123 (43%), 58 (10%). The next brown-red band was eluted with 15% toluene in hexane. It was evaporated to dryness, redissolved in hexane and purified by additional column chromatography (eluent 2% THF in hexane). A brown-red solid was obtained. This was identified as  $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{Ph}$  (yield 16%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta(\text{ppm}) = 1.95$  (d, 3H,  $^3J_{\text{H-H}} = 6.94$  Hz,  $\text{CH}_3$ ), 4.71 (q, 1H,  $^3J_{\text{H-H}} = 7$  Hz, CH), 5.07 (s, 15H,  $\text{C}_5\text{H}_5$ ), 7.09–7.5 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta(\text{ppm}) = 296.4$  (C-alkylidyne), 149.53, 128.72, 126.16, (phenyl carbon atoms; one signal of the phenyl group carbon atoms overlapped with the solvent signals), 88.07 ( $\text{C}_5\text{H}_5$ ), 63.64 (CH), 28.44 ( $\text{CH}_3$ ). EIMS (70 eV)  $m/e$  (rel. intensity): 486 ( $\text{M}^+$ , 43%), 420 (100%), 380 (59%), 356 (34%), 304 (35%), 246 (29%), 188 (23%), 123 (17.5%). The crystal structure was determined by X-ray analysis (see Section 3.2). The next brown fraction was also collected (eluent 15% toluene in hexane). It was evaporated to dryness, redissolved in THF–hexane mixture and purified by additional column chromatography (eluent 3% THF in hexane). The brown solid obtained was identified as  $(\text{NiCp})_4\text{H}_2$  [9] (yield 20%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta(\text{ppm}) = -19.96$  (s, hydride), 5.35 (s,  $\text{C}_5\text{H}_5$ ).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta(\text{ppm}) = 82.70$  ( $\text{C}_5\text{H}_5$ ). The last brown fraction was eluted with toluene. A red-brown solid was obtained after evaporation of the solvent. This was identified as  $(\text{NiCp})_6$  (yield 15%) by means of mass spectrometry. EIMS (70 eV)  $m/e$ : 738 ( $\text{M}^+$ , 43%); 550 ( $\text{Ni}_5\text{Cp}_4$ ) $^+$ ; 427 ( $\text{Ni}_4\text{Cp}_3$ ) $^+$ ; 188 ( $\text{NiCp}_2$ ) $^+$ ; 123 ( $\text{NiCp}$ ) $^+$ .

The following organic compounds were also detected in the post-reaction mixture by GC/MS:  $\alpha$ -methylstyrene, 2-phenylpropane, 2,5 diphenylhexane and 2,5 diphenylhexene (spectra in agreement with DATABASE\NBS75K.L).

### 3.2. Crystal structure determination of $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{Ph}$

The crystal was sealed in a glass capillary under a nitrogen stream. Preliminary examination and intensity data collection were carried out on a Kuma KM-4 four-circle diffractometer [17] using graphite-monochromated  $\text{MoK}\alpha$  radiation (0.71069 Å). Intensities were collected with the  $\omega$ - $2\theta$  scan technique up to  $\theta = 25^\circ$ . After each group of 100 reflections, standard intensities were monitored and no evidence of crystal decay was observed. The recorded data were corrected for Lorentz and polarisation factors. An absorption correction following the DIFABS [18] procedure was applied. The structure was solved by direct methods (SHELXS86) [19] and refined by a full-matrix least squares program (SHELXL93) [20]. The carbon-bonded H-atoms were included in calculated positions. The C–C distances in cyclopentadienyl rings were restrained to the same length bonds using the SHELXL93 program procedure. The crystal structure with the atom numbering system is presented in Fig. 1. Data-collection and structure analysis parameters are given in Table 1; fractional atomic coordinates are in Table 2. Selected bond lengths and bond angles are listed in Tables 3 and 4.

Lists of bond lengths and angles, anisotropic thermal parameters and hydrogen atom parameters have been deposited at the Cambridge Crystallographic Data Centre.

### 3.3. Reaction of nickelocene with ethylmagnesium bromide

A solution of ethylmagnesium bromide in THF (9 cm<sup>3</sup>, 5.9 mmol) was added to a solution of  $\text{NiCp}_2$  (1.04 g, 5.5 mmol) in 87 cm<sup>3</sup> THF. The reaction was carried out as described in Section 3.1. The products were isolated by two methods. The first one consisted of hydrolysis of the formed  $\text{BrMgCp}$  with water followed by the separation of the organic layer. The second method consisted of the extraction of organon-

nickel and organic products with hexane–toluene = 10/1. In both methods the products were then separated by column chromatography on neutral alumina (eluents hexane and hexane–toluene). The products obtained by both methods were identical. The following compounds were obtained: small amounts of  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$ , small amounts of  $\text{NiCp}_2$ ,  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$  (yield 3%),  $(\text{NiCp})_3\text{C-CH}_3$  (yield 8%),  $(\text{NiCp})_4\text{H}_2$  (yield 18%), and  $(\text{NiCp})_6$  (yield 14%). The trinickel  $(\text{NiCp})_3\text{C-CH}_3$  [3] cluster was characterised by spectroscopic methods.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 5.14 (s, 15H,  $\text{C}_5\text{H}_5$ ); 3.70 (s, 3NH,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ (ppm) = 289.16 (C-methylidyne), 87.97 ( $\text{C}_5\text{H}_5$ ), 46.02 ( $\text{CH}_3$ ); EIMS (70 eV):  $m/e$  = 396 ( $\text{M}^+$ , 52%), 330 (100%), 264 (11%), 246 (22%), 188 (28%), 123 (23%).

### 3.4. Reaction of nickelocene with octylmagnesium bromide

A solution of octylmagnesium bromide in THF (11 cm<sup>3</sup>, 5 mmol) was added to a solution of  $\text{NiCp}_2$  (0.87 g, 4.6 mmol) in 73 cm<sup>3</sup> THF. The reaction was carried out as described in Section 3.1. The following compounds were obtained: small amounts of  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$ , small amounts of unreacted  $\text{NiCp}_2$ ,  $(\text{NiCp})(\mu\text{-C}_5\text{H}_6)$  (yield 3%),  $(\text{NiCp})_3\text{C-(CH}_2)_6\text{-CH}_3$  (yield 10%),  $(\text{NiCp})_4\text{H}_2$  (yield 26%) and  $(\text{NiCp})_6$  (yield 20%). The trinickel cluster was characterised by spectroscopic methods.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ (ppm) = 5.18 (s, 15H,  $\text{C}_5\text{H}_5$ ); 3.73 (t, 2H,  $-\text{CH}_2-$ ); 2.15 (t, 2H,  $-\text{CH}_2-$ ); 1.7–1.2 (m, 10H,  $-\text{CH}_2-$ ); 0.95 (t, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ (ppm) = 295.50 (C-methylidyne), 87.89 ( $\text{C}_5\text{H}_5$ ), 57.87, 36.05, 32.44, 30.43, 29.91, 23.15, (six signals of  $-\text{CH}_2$ -carbon atoms), 14.37 ( $-\text{CH}_3$ ). EIMS (70 eV):  $m/e$  = 480 ( $\text{M}^+$ , 98%), 410 (89%), 344 (65%), 304 (100%), 246 (49%), 188 (33%), 123 (15%).

### 3.5. Reaction of nickelocene with *n*-propyllithium

A solution of propyllithium in THF (16 cm<sup>3</sup>, 6.1 mmol) was added within 1 h at  $-30^\circ\text{C}$  to a solution of  $\text{NiCp}_2$  (1.05 g, 5.6 mmol) in 60 cm<sup>3</sup> THF. The reaction products were hydrolysed and separated as described in Section 3.1. The following compounds were isolated: small amounts of  $\text{CpNi}(\eta^3\text{-C}_5\text{H}_7)$ , small amounts of  $\text{NiCp}_2$ ,  $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$ ,  $(\text{NiCp})_3\text{C-C}_2\text{H}_5$ ,  $(\text{NiCp})_4\text{H}_2$  and  $(\text{NiCp})_6$ . The trinickel cluster was characterised by means of spectroscopic methods.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ (ppm) = 1.62 (t, 3H,  $-\text{CH}_3$ ); 3.6 (q, 2H,  $-\text{CH}_2-$ ); 5.15 (s, 15H,  $\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ (ppm) = 297.72 (C-alkylidyne), 87.77 ( $\text{C}_5\text{H}_5$ ); 52.02 ( $-\text{CH}_2-$ ); 20.00 ( $-\text{CH}_3$ ). EIMS (70 eV):  $m/e$  = 410 ( $\text{M}^+$ , 59%), 344 (62%), 304 (100%), 278 (5%), 246 (40%), 188 (20%); 123 (10%).

## Acknowledgements

The authors thank the State Committee for Scientific Research for financial support of this work (Grant no. 3 T09A 139 09).

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