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The activation of C–H bonds in internal alkenes and dienes by {NiCp} species formed in the reaction of nickelocene with alkali metals

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday in recognition of his outstanding contributions to organometallic chemistry

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Abstract

Reactions of nickelocene with metallic sodium in the presence of internal alkenes: *trans*-3-hexene, *cis*-2-heptene and 2,3-dimethyl-2-butene have been studied. It was found that {NiCp} species generated in the reaction of nickelocene with sodium dehydrogenate internal alkenes to alkynes. The latter form then complexes with tri(cyclopentadienylnickel) $(NiCp)_3RC{\equiv}CR$ and with di(cyclopentadienylnickel) $(NiCp)_2RC{\equiv}CR$. If the methyl group is adjacent to the alkene double bond, the activation of the C–H bonds of this group leads to the formation of alkylidyne tri(cyclopentadienylnickel) clusters. In the reaction of nickelocene with lithium in the presence of 1,5-hexadiene, alkylidyne tri(cyclopentadienylnickel) cluster $(NiCp)_3CCH_2CH_2CH_2CH{=}CH_2$ and intramolecularly stabilised complex $Cp\,\overline{NiCH(CH_3)CH_2CH_2CH{=}}CH_2$ were formed. In all the reactions studied di-, $(NiCp)_2CpH$, and tetra(cyclopentadienylnickel), $(NiCp)_4H_x$, compounds were formed besides the other products.

Keywords: Nickel; Alkali metals; Clusters; Cyclopentadienyl; Alkene activation; C–H bond activation

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1. Introduction

We have previously found that electronically and coordinately unsaturated nickel atoms in $\{(NiCp)_2\}$ or {NiCp} species formed in the reactions of nickelocene with phenyllithium [1,2] or with sodium [3] activate sp^2 C–H bonds of terminal olefins. The aim of this work was to find out whether C–H bond in internal alkenes could be activated in such reaction.

2. Results

Reactions of nickelocene with metallic sodium and alkene (molar ratio 1:1.4:2.5) in THF were carried out at −30 °C for 3 h and then overnight at room temperature. Solvent and unreacted alkenes were evaporated and the residue was extracted with toluene to separate nickel clusters from NaCp formed in the reaction. A mixture of nickel clusters was chromatographed on neutral alumina (deactivated with 5% of water) using hexane and hexane–toluene as eluents.

We have studied reactions of nickelocene with sodium in the presence of *trans*-3-hexene, *cis*-2-heptene and 2,3-dimethyl-2-butene. Finally we have studied the reaction of nickelocene with lithium and 1,5-hexadiene. In each case two products resulting from stabilisation of {NiCp}

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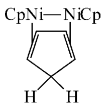
species were formed: $(NiCp)_2CpH$ **2** [4] and $(NiCp)_4H_x$ **4** [2,5].



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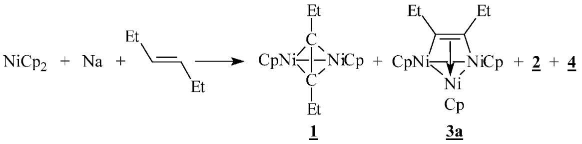
Other products in each reaction were formed due to activation of an appropriate alkene.

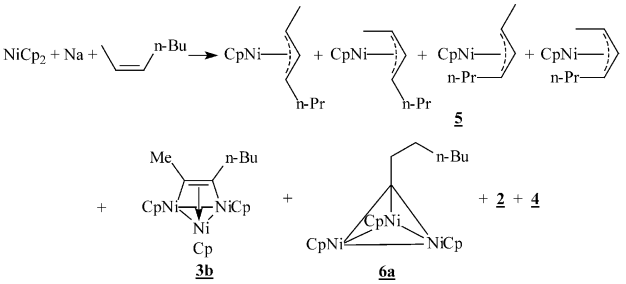
In the reaction with *trans*-3-hexene two complexes with alkyne (di- **1** and trinickel **3a**) were isolated (Eq. (1)).



(1)

Formation of these compounds proceeds via dehydrogenation of an alkene molecule to alkyne. The compound **1** was identified on the basis of ^{1}H and ^{13}C-NMR and MS spectra. MS spectrum of **1** revealed the parent ion at *m/e* 328 (^{58}Ni calc.) with an isotopic pattern characteristic for two nickel atoms in a molecule. MS spectrum of **3a** revealed the parent ion at *m/e* 451 (^{58}Ni calc.) with an isotopic pattern characteristic for three nickel atoms in a molecule. Because of paramagnetic properties of this compound there were no observable signals in ^{1}H-NMR spectrum. Crystals appropriate for X-ray diffraction studies were obtained from hexane solution. It crystallises in orthorhombic crystal system with 12 molecules in a unit cell. Due to bad quality of the crystal (high mosaicity, small number of reflections collected) only Ni atoms were refined with anisotropic displacement parameters. Carbon atoms were refined isotropically. Analysis of structural parameters shows that the structure of **3a** is analogous to the trinickel complex with 2-butyne, the structure of which we have published previously [6]. Corresponding bond lengths of these two compounds differ by less than 0.04 Å. It allows us to conclude that in both compounds alkyne ligand is bonded to three nickel atoms via two σ and one π bonds ($2\sigma+\pi$ or μ_3-η^2) [7].

In case of *cis*-2-heptene two different pathways of reaction were observed. The first one was similar to this for *trans*-3-butene-dehydrogenation of an alkene to alkyne with the formation of trinickel cluster **3b**. MS spectrum of **3b** revealed the parent ion at *m/e* 465 (^{58}Ni calc.) with an isotopic pattern characteristic for three nickel atoms in a molecule. The second pathway of this reaction was activation of the C–H bond in the methylene and methyl groups next to the double bond. In that case π-allyl complex **5** and the alkylidyne tri(cyclopentadienyl)nickel cluster **6a** were formed, respectively (Eq. (2)).

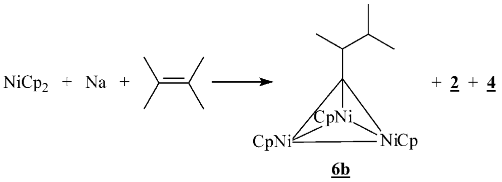


(2)

MS spectrum of **5** revealed the parent ion at *m/e* 220 (^{58}Ni calc.) with an isotopic pattern characteristic for one nickel atom in a molecule. The compound **5** exists as a mixture of isomers, therefore, its ^{1}H-NMR spectrum is complicated. It shows signal of Cp groups at 5.2–5.3 ppm, signals of allyl protons in the range 2–5 ppm and signals of alkyl protons in the range 0.75–1.5 ppm.

In the MS spectrum of **6a** the parent ion at *m/e* 466 (^{58}Ni calc.) was present with an isotopic pattern characteristic for three nickel atoms in a molecule. ^{1}H-NMR spectrum of **6a** revealed a singlet of protons of cyclopentadienyl groups at δ 5.18 ppm, triplet of protons of CH_2 group bonded to alkylidyne carbon atom at 3.71 ppm and three multiplets and a triplet of the remaining protons of the alkyl chain in the range between 1.0 and 2.1 ppm. ^{13}C-NMR spectrum showed a signal at δ 295.21 ppm characteristic for alkylidyne carbon atom, signal at 87.97 ppm of carbon atoms of cyclopentadienyl ring and six signals from 13.88 to 57.93 ppm of carbon atoms of alkyl chain.

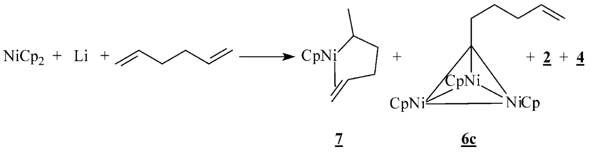
The only pathway of the reaction with 2,3-dimethyl-2-butene was activation of the methyl group, resulting in the formation of alkylidyne trinickel cluster **6b** (Eq. (3)).



(3)

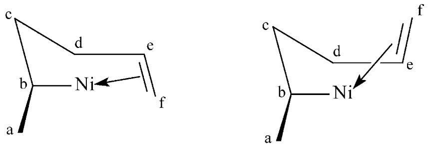
MS spectrum of **6b** revealed the parent ion at *m/e* 452 (^{58}Ni calc.) with an isotopic pattern characteristic for three nickel atoms in a molecule. ^{1}H-NMR spectrum of **6b** revealed a singlet of protons of cyclopentadienyl groups at δ 5.14 ppm, two multiplets of protons of CH groups at 3.44 and 2.62 ppm and three dublets of protons of methyl groups at 1.49, 1.21 and 1.06 ppm (terminal methyl groups are diastereotopic having different chemical shifts). ^{13}C-NMR spectrum showed a signal at δ 302.19 ppm characteristic for alkylidyne carbon atom, signal at 88.09 ppm of carbon atoms of cyclopentadienyl ring and five signals from 17.38 to 63.01 ppm of carbon atoms of the alkyl chain.

The final reaction we have examined was carried out in the presence of 1,5-hexadiene. In this case {NiCp} activated alkene in two ways: by intramolecular stabilisation **7** or by formation of alkylidyne trinickel cluster **6c** (Eq. (4)).



(4)

In the mass spectrum of the complex **7**, the parent ion at *m*/*e* 206 (^{58}Ni calc.) was in agreement with the isotopic pattern for one nickel atom. NMR spectra of **7** exhibit two sets of signals corresponding to two diastereomers formed at the molar ratio of ca. 3:1 (based on integration of methyl group signals in the ^{1}H-NMR spectrum). The values of chemical shifts in the ^{1}H- and ^{13}C-NMR spectra are given in Tables 1 and 2.



7

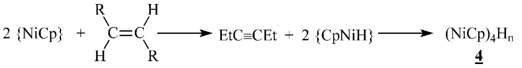
In the mass spectrum of **6c** the parent ion at *m*/*e* 450 (^{58}Ni calc.) was present with an isotopic pattern characteristic for three nickel atoms in a molecule. ^{1}H-NMR spectrum of **6c** revealed a singlet of protons of cyclopentadienyl groups at δ 5.15 ppm, multiplets of protons at the double bond at 5.99 and at 5.15 ppm and a triplet (3.67 ppm), a quartet (2.37 ppm) and multiplet (2.18 ppm) of the remaining protons of alkyl chain. ^{13}C-NMR spectrum showed a signal at δ 294.41 ppm characteristic for alkylidyne carbon atom, signal at 87.91 ppm of carbon atoms of cyclopentadienyl ring, two signals carbon atoms at the double bond at 139.31 and 114.93 ppm and three signals from 34.53 to 57.15 ppm of carbon atoms of alkyl chain.

3. Discussion

Electronically and co-ordinately unsaturated {NiCp} species, formed in the reaction of nickelocene with alkali metals (Eq. (5)), activate C–H bonds in internal alkenes, forming many cyclopentadienylnickel complexes and clusters.

$$\mathrm{NiCp_2} + \underset{\mathrm{M=Na,Li}}{\mathrm{M}} \rightarrow \{\mathrm{NiCp}\} + \mathrm{MCp} \qquad (5)$$

The main pathways of {NiCp} reactions with internal alkenes appeared to be an abstraction of both olefinic hydrogen atoms with the formation of an alkyne (Eq. (6)), or/and a hydrogen abstraction from the methyl or methylene group adjacent to a double bond what led mainly to the formation of alkylidynetri(cyclopentadienylnickel) clusters and π-allyl complexes (Eq. (7))



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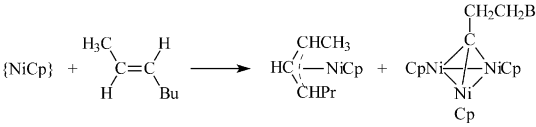
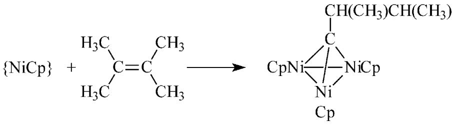


(7)

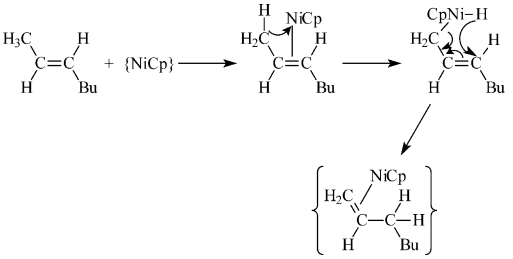
The alkyne generated in the reaction (6) formed di- and tri(cyclopentadienylnickel) complexes **1** and **3** [6,8].

In case of 2,3-dimethyl-2-butene only hydrogen abstraction from the methyl group occurred, due to the lack of olefinic hydrogen atoms. It led to the formation of alkylidynetri(cyclopentadienylnickel) cluster (Eq. (8))



(8)

The formation of alkylidynetri(cyclopentadienylnickel) clusters has a complex character. We presume that initially an isomerisation of an internal alkene to the terminal one via nickel mediated 1,3-hydrogen transfer proceeds (Eq. (9)).



(9)

The formation of alkylidynetri(cyclopentadienylnickel) clusters from terminal alkenes has been observed by us previously [3,9].

The new reaction is also the formation of π-allyl(cyclopentadienylnickel) complexes from nickelocene and

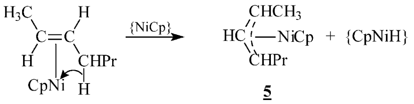
Table 1
^{1}H-NMR spectrum of **7**

Diastereomer	H_{Cp}	H_a	H_b	H_c	H_d	H_e	H_f
a δ (ppm)	5.03 (s)	0.82 (dd)	2.63 (m)	0.38 (m) 0.74 (m)	1.78 (m) 1.85 (m)	4.63 (m)	2.78 (dd) 2.50 (dt)
b δ (ppm)	5.03 (s)	0.89 (dt)	1.94 (m)	0.31 (m) 1.26 (m)	2.15 (m) 1.69 (m)	4.75 (m)	2.77 (dd) 2.63 (m)

Table 2
^{13}C-NMR spectrum of **7**

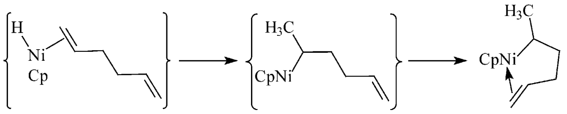
Diastereomer	C_{Cp}	C_a	C_b	C_c	C_d	C_e	C_f
a δ (ppm)	93.05 (d)	28.71 (q)	26.65 (d)	34.38 (t)	31.85 (t)	77.83 (d)	45.29 (t)
b δ (ppm)	93.33 (d)	29.53 (q)	27.66 (d)	37.28 (t)	30.08 (t)	78.09 (d)	47.28 (t)

internal alkenes. These complexes have been previously obtained from allyl [10] or vinyl derivatives of nickel [11]. The complex CpNi($H_3CCH{=}CHCH_2Pr$) (Eq. (9)) undergoes hydrogen abstraction from methylene group of the alkene forming π-allyl complex **5** (Eq. (10)).



(10)

The complex **7** (Eq. (4)) can be formed by the addition of {CpNiH} to the one of the double bonds of 1,5-hexadiene and the intramolecular stabilisation of the resulting {CpNiCH(CH_3)$CH_2CH_2CH{=}CH_2$} species (Eq. (11))



(11)

4. Experimental

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. ^{1}H- and ^{13}C-NMR spectra were measured on a Varian Gemini-200 and Mercury-400 instruments. Mass spectra were recorded on an AMD-604 and AMD M-40 mass spectrometers.

4.1. Reaction of nickelocene with sodium and *trans*-3-hexene in THF

Nickelocene (2.17 g, 11.5 mmol), *trans*-3-hexene (3 cm^3, 2.04 g, 24.3 mmol), sodium (0.37 g, 16.2 mmol) and 70 cm^3 of THF were placed in a Schlenk flask and stirred at −30 °C for 2 h and then at room temperature (r.t.) overnight. After the reaction was completed, the solvent was evaporated and the residue was extracted with two portions of toluene (70 cm^3 each). Extracts were filtered through the alumina layer, collected together and the solvent was evaporated. The residue was dissolved (6 cm^3 of hexane + 5 cm^3 of toluene) and chromatographed on alumina (deactivated with 5% of water) with hexane and hexane–toluene mixture as eluents. Five coloured bands were separated, collected and then evaporated to dryness.

The first green fraction (hexane–toluene 20:1) gave traces of solid identified as unreacted nickelocene.

The second green fraction (hexane–toluene 10:1) gave solid identified as di-(cyclopentadienylnickel)-3-hexyne complex **1** (yield 0.057 g, 0.17 mmol, ca. 3%). EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 328 [M$^+$, 39%], 246 (97%), 188 (100%), 123 (58%). ^{1}H-NMR (C_6D_6) δ (ppm): 5.19 (s, 10H, Cp), 2.38 (q, 4H, $-CH_2-$), 1.23 (t, 6H, $-CH_3$). ^{13}C-NMR (C_6D_6) δ (ppm): 106.99 (*C*), 87.12 (Cp), 25.04 ($-CH_2-$), 16.69 ($-CH_3$).

The third blue fraction (hexane–toluene 5:1) gave solid identified as di-(cyclopentadienylnickel)cyclopentadiene complex **2** (yield 0.072 g, 0.23 mmol, ca. 4%). The compound was identified by means of ^{1}H-, ^{13}C-NMR and mass spectra, which were in a good agreement with the literature ones [4].

The fourth brown fraction (hexane–toluene 4:1) gave brown solid identified as **3a** (yield 0.139 g, 0.31 mmol, ca. 8%). EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 451 [M$^+$, 89%], 381 (12%), 369 (84%), 303 (22%), 246 (23%), 188 (34%), 123 (15%). The crystal and molecular structure of **3a** was determined by X-ray measurements.

The fifth black fraction (hexane–toluene 3:1) gave black solid, identified as a mixture of clusters **4** (yield 0.100 g, 0.20 mmol, ca. 7%, identified by NMR and mass spectra [2,5]).

4.2. Crystal structure determination of **3a**

Single crystal of **3a** suitable for X-ray diffraction studies was placed in a thin walled capillary tube (Lindemann glass) in a nitrogen atmosphere, plugged with grease and flame sealed. Crystal data were collected with subsequent φ and ω scans on a Nonius KappaCCD diffractometer with graphite monochromated Mo–K_α radiation, using diffractometer control program 'Collect' [12]. Unit cell parameters and data reductions were processed with Denzo and Scalepak [13]. The structures were solved by direct methods using SHELXS-97 [14]. Full-matrix least-squares refinement method against F^2 values was carried out by using the SHELXL-97 [15] program. Due to bad quality of the crystal (high mosaicity, small number of reflections collected) only Ni atoms were refined with anisotropic displacement parameters. Carbon atoms were refined isotropically. All the hydrogen atoms were placed in calculated

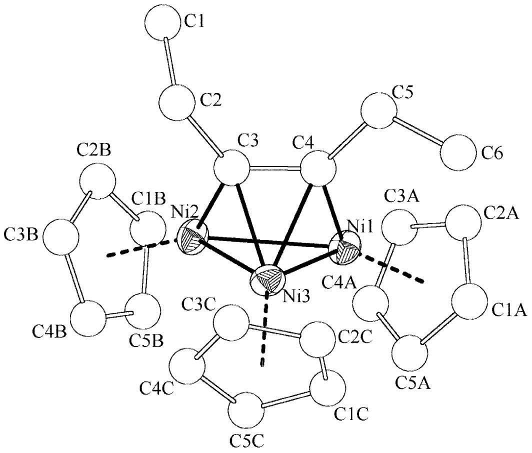


Fig. 1. Molecular structure of **3a** with atom numbering. Thermal ellipsoids shown at 50% probability level.

positions and refined using a riding model. The crystal structure is presented on Fig. 1. The crystal data, data collection and refinement parameters for the compound are given in Table 3. Tables 4 and 5 present the observed bond lengths and bond angles.

4.3. *Reaction of nickelocene with sodium and cis-2-heptene in THF*

Nickelocene (2.09 g, 11.1 mmol), *cis*-2-heptene (3 cm^3, 2.12 g, 21.7 mmol), sodium (0.36 g, 15.6 mmol) and 60 cm^3 of THF were placed in Schlenk flask and stirred at −30 °C for 3 h and then at r.t. overnight. After the reaction was completed, the solvent was removed and the residue was extracted with two portions of toluene (70 cm^3 each). Extracts were filtered through the alumina layer, collected together and the solvent was evaporated. The residue was dissolved (8 cm^3 of hexane+5 cm^3 of toluene) and chromatographed on alumina (deactivated with 5% of water) with hexane and hexane–toluene mixture as eluents. Five coloured bands were separated, collected and evaporated to dryness.

The first violet fraction (hexane) gave dark oil identified as π-allyl complex **5** (yield 0.244 g, 1.10 mmol, ca. 10%). EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 220 [M$^+$, 100%], 188 (11%), 154 (82%), 126 (76%), 123 (48%), 112 (23%), 98 (17%). ^{1}H-NMR (C_6D_6) δ (ppm), signals of three isomers were present in the spectrum and assigned: **a**: 5.22 (s, 5H, Cp), 4.78 (t, 1H, CH), 2.05 (m, 2H, CH), 1.04 (d, 3H, CH_3), 0.75–1.50 (alkyl), **b**: 5.24 (s, 5H, Cp), 4.95 (dd, 1H, CH), 3.40 (m, 1H, CH), 2.80 (m, 1H, CH), 0.64 (d, 3H, CH_3), 0.75–1.50 (alkyl), **c**: 5.29 (s, 5H, Cp), 5.06 (dd, 1H, CH), 3.40 (m, 1H, CH), 2.80 (m, 1H, CH), 1.14 (d, 3H, CH_3), 0.75–1.50 (alkyl); ^{13}C-NMR (C_6D_6) δ (ppm): (one isomer) 93.08, 89.08, 60.15, 54.29, 37.27, 24.39, 20.74, 14.22.

The second green fraction (hexane–toluene 20:1) gave traces of solid identified as unreacted nickelocene.

Table 3
Crystal data and structure refinement for **3a**

Empirical formula	$C_{21}H_{25}Ni_3$
Crystal size (mm)	0.30 × 0.26 × 0.18
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	
a (Å)	13.929(3)
b (Å)	47.353(9)
c (Å)	8.498(2)
Volume (Å^3)	5605(2)
Z	12
Formula weight	443.42
Density (calc.) (mg m^{-3})	1.612
Temperature (K)	293(2)
Absorption coefficient (mm^{-1})	2.990
$F(000)$	2820
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å, graphite monochromator)
θ Range for data collection (°)	2.43–27.50
Scan type	$\omega - 2\theta$
Index ranges	$0 \le h \le 15$, $-60 \le k \le 61$, $0 \le l \le 9$
Reflections collected/unique	3191/2496 [$R_{int} = 0.0775$]
Absorption correction	Empirical
Max and min transmission	1 and 0.504
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2496/0/180
Goodness-of-fit on F^2	1.100
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1021$; wR_2 (refined) $= 0.2543$
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (0.0733P)^2$- $+8.9074P$; where $P = (F_0^2 + 2F_c^3)/3$
R indices (all data)	$R_1 = 0.1298$; $wR_2 = 0.2702$
Largest difference peak and hole (e Å^{-3})	0.978 and −0.690

$R_1 = \Sigma(F_o - F_c)/\Sigma\ F_o$; $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

Table 4
Selected bond lengths (Å) in **3a***

C(1)–C(2)	1.495(33)
C(2)–C(3)	1.547(24)
C(3)–C(4)	1.371(20)
C(4)–C(5)	1.531(22)
C(5)–C(6)	1.521(26)
Ni(1)–Ni(2)	2.417(2)
Ni(2)–Ni(3)	2.411(3)
Ni(1)–Ni(3)	2.369(4)
C(4)–Ni(1)	1.896(18)
C(4)–Ni(3)	2.042(18)
C(3)–Ni(3)	1.964(18)
C(3)–Ni(2)	1.882(18)

*, Estimated S.D. in parentheses.

The third blue fraction (hexane–toluene 5:1) gave solid identified as **2** (yield 0.078 g, 0.25 mmol, ca. 4.5%).

The fourth brown fraction (hexane–toluene 4:1) gave 0.210 g of brown solid identified as a mixture of **3b** (EIMS (70 eV) *m/e* (^{58}Ni): 465 [M$^+$]) and **6a**, which could not be separated. As **3b** is paramagnetic, only

Table 5
Selected bond angles (°) in **3a***

Ni(1)–Ni(2)–Ni(3)	58.79(9)
Ni(2)–Ni(3)–Ni(1)	60.74(10)
Ni(3)–Ni(1)–Ni(2)	60.47(9)
Ni(2)–C(3)–Ni(3)	77.60(66)
C(3)–Ni(3)–Ni(2)	49.68(52)
Ni(3)–Ni(2)–C(3)	52.72(53)
Ni(1)–C(4)–Ni(3)	73.87(68)
C(4)–Ni(3)–Ni(1)	50.25(54)
Ni(3)–Ni(1)–C(4)	55.88(59)
Ni(3)–C(4)–C(3)	66.94(100)
C(4)–C(3)–Ni(3)	73.08(105)

*, Estimated S.D. in parentheses.

signals of **6a** could be observed in the NMR spectrum of the mixture of **3b** and **6a**. ^{1}H-NMR of **6a**: (C_6D_6) δ (ppm): 5.18 (s, 15H, Cp), 3.71 (t, 2H, $\equiv$C–C*H*$_2$–), 2.11 (m, 2H, –C*H*$_2$–), 1.64 (m, 2H, –C*H*$_2$–), 1.44 (m, 4H, 2 × –C*H*$_2$–), 0.98 (t, 3H, –C*H*$_3$); ^{13}C-NMR of **6a**. (C_6D_6) δ (ppm): 295.21 (*C* alkylidyne), 87.97 (Cp), 57.93 (–*C*H$_2$–), 36.02 (–*C*H$_2$–), 32.49 (–*C*H$_2$–), 30.21 (–*C*H$_2$–), 24.07 (–*C*H$_2$–), 13.88 (–*C*H$_3$). EIMS of **6a**. (70 eV) *m/e* (rel. int.) (^{58}Ni): 466 [M$^+$, 87%], 398 (82%), 371 (31%), 344 (44%), 330 (35%), 304 (78%), 246 (44%), 188 (36%), 123 (16%).

The fifth black fraction (hexane–toluene 3:1) gave black solid identified as a mixture of clusters **4** (yield 0.124 g, 0.25 mmol, ca. 9%).

4.4. Reaction of nickelocene with sodium and 2,3-dimethyl-2-butene in THF

Nickelocene (1.98 g, 10.5 mmol), 2,3-dimethyl-2-butene (2.5 cm^3, 1.77 g, 21.1 mmol), sodium (0.335 g, 14.6 mmol) and 50 cm^3 of THF were placed in Schlenk flask and stirred at −30 °C for 2 h and then at r.t. overnight. After the reaction was completed, the solvent was removed and the residue was extracted with two portions of toluene (60 cm^3 each). Extracts were filtered through the alumina layer, collected together and the solvent was evaporated. The residue was dissolved (6 cm^3 of hexane + 6 cm^3 of toluene) and chromatographed on alumina (deactivated with 5% of water) with hexane and hexane–toluene mixture as eluents. Four coloured bands were separated, collected and evaporated to dryness.

The first green fraction (hexane–toluene 20:1) gave traces of unreacted nickelocene.

The second blue fraction (hexane–toluene 5:1) gave solid identified as **2** (yield 0.084 g, 0.27 mmol, ca. 5%).

The third brown fraction (hexane–toluene 4:1) gave 0.110 g (0.24 mmol, 7%) of brown solid identified as **6b**. EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 452 [M$^+$, 48%], 382 (27%), 368 (25%), 304 (73%), 246 (100%), 188 (24%), 123 (12%). ^{1}H-NMR (C_6D_6) δ (ppm): 5.14 (s, 15H, Cp), 3.44 (m, 1H, –C*H*–), 2.62 (m, 1H, –C*H*–), 1.49 (d, 3H, –C*H*$_3$), 1.21 (d, 3H, –C*H*$_3$), 1.06 (d, 3H, –C*H*$_3$). ^{13}C-NMR (C_6D_6) δ (ppm): 302.19 (*C* alkylidyne), 88.09 (Cp), 63.01 (–*C*H–), 35.80 (–*C*H–), 23.17 (–*C*H$_3$), 19.33 (–*C*H$_3$), 17.38 (–*C*H$_3$).

The fourth black fraction (hexane–toluene 3:1) gave black solid identified as a mixture of clusters **4** (yield 0.112 g, 0.23 mmol, ca. 8.5%).

4.5. Reaction of nickelocene with lithium and 1,5-hexadiene in THF

Nickelocene (2.21 g, 11.8 mmol), 1,5-hexadiene (2 cm^3, 1.38 g, 16.8 mmol), lithium (0.115 g, 16.4 mmol) and 50 cm^3 of THF were placed in Schlenk flask and stirred at r.t. overnight. After the reaction was completed, the solvent was removed and the residue was extracted with two portions of toluene (70 cm^3 each). Extracts were filtered through the alumina layer, collected together and the solvent was evaporated. The residue was dissolved (8 cm^3 of hexane + 6 cm^3 of toluene) and chromatographed on alumina (deactivated with 5% of water) with hexane and hexane–toluene mixture as eluents. Five coloured bands were separated, collected and then evaporated to dryness.

The first red fraction (hexane) gave dark oil identified as **7** (yield 0.304 g, 1.50 mmol, ca. 12.5%). EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 206 [M$^+$, 47%], 140 (93%), 123 (48%), 98 (54%), 58 (100%). ^{1}H-, ^{13}C-NMR (C_6D_6) see Tables 1 and 2.

The second green fraction (hexane–toluene 20:1) gave traces of solid identified as unreacted nickelocene.

The third blue fraction (hexane–toluene 5:1) gave solid identified as **2** (yield 0.055 g, 0.18 mmol, ca. 3%).

The fourth brown fraction (hexane–toluene 4:1) gave 0.212 g (0.47 mmol, 12%) of brown solid identified as **6c**. EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 450 [M$^+$, 51%], 384 (90%), 344 (52%), 330 (63%), 304 (66%), 246 (25%), 188 (60%), 123 (77%), 58 (28%). ^{1}H-NMR of **6c**. (C_6D_6) δ (ppm): 5.99 (m, 2H, =C*H*$_2$), 5.15 (m, 1H, =C*H*–), 5.15 (s, 15H, Cp), 3.67 (t, 2H, –C*H*$_2$–), 2.37 (q, 2H, –C*H*$_2$–), 2.18 (m, 2H, –C*H*$_2$–). ^{13}C-NMR (C_6D_6) δ (ppm): 294.41 (*C* alkylidyne), 139.31 (=*C*H–), 114.93 (=*C*H$_2$), 87.91 (Cp), 57.15 (–*C*H$_2$–), 35.08 (–*C*H$_2$–), 34.53 (–*C*H$_2$–).

The fifth black fraction (hexane–toluene 3:1) gave black solid identified as a mixture of clusters **4** (yield 0.087 g, 0.18 mmol, ca. 6%).

5. Supplementary material

Crystallographic data for the compound **3a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 186779. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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