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Alkylation of cyclopentadienyl rings in the reactions of nickelocene with organolithium compounds☆

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Abstract

The reaction of nickelocene with *tert*-butyllithium has been studied. It was found that unstable species $\{CpNiC(CH_3)_3\}$, formed in this reaction, reacted further in two directions: β-H elimination and homolytic cleavage of Ni–C bond. Hydrogen elimination product formed trinickel cluster $(NiCp)_3CCH(CH_3)_2$ **1**, while *t*-butyl radical alkylated cyclopentadienyl rings to form several compounds. One of these compounds, $\{Ni[C_5H_4C(CH_3)_3]\}_2[C_5H_5C(CH_3)_3]$ **3**, has been isolated and fully characterised. The compound crystallizes from hexane in a triclinic crystal system and $P\bar{1}$ space group. Corresponding unit cell parameters were determined as $a = 7.520(2)$ Å; $b = 13.150(5)$ Å; $c = 13.625(4)$ Å; $\alpha = 113.77(3)°$; $\beta = 97.42(3)°$; $\gamma = 90.02(3)°$; $V = 1220.7(7)$ Å^3; $Z = 2$. It is the first example of alkylation of cyclopentadienyl rings bonded to nickel by organolithium compounds. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Nickel; Lithium; Cyclopentadienyl; Alkylation; Crystal structure

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1. Introduction

Unstable species {CpNiR} are formed in the reactions of nickelocene with organolithium or -magnesium compounds:

$$NiCp_2 + MR \rightarrow \{CpNiR\} + MCp$$

where M = Li, MgX; R = alkyl, aryl, vinyl.

These species undergo further reactions with the formation of various organonickel and organic compounds. Our previous studies show that the course of the reaction and the products formed depend mainly on the hydrogen elimination from R group and its further transfer to ligand's carbon atom [1]. If R is an alkyl group possessing α-H [$R = CH_3$, $CH_2C(CH_3)_3$, $CH_2C_6H_5$, $CH_2Si(CH_3)_3$] hydrogen elimination leads mainly to the formation of trinickel clusters $(NiCp)_3CR'$ where $R' = CH_3$, $C(CH_3)_3$, C_6H_5, $Si(CH_3)_3$ [2–4]. If R possesses α- and β-hydrogen ($R = CH_2CH_3$, $(CH_2)_5CH_3$, $(CH_2)_7CH_3$, $CH_2CH(Ph)CH_3$) trinickel clusters are also formed [5]. If $R = C_6H_5$ the main reaction is coupling of phenyl groups. Various nickel clusters are also formed in this reaction [6].

For vinyl ligands possessing α-H ($R = CH{=}CH_2$, $CH{=}C(CH_3)_2$) α-H elimination leads to the formation of trinickel clusters $(NiCp)_3CCH_3$ or $(NiCp)_3$-$CCH(CH_3)_2$, and for vinyl ligands possessing β- or γ-H π-allylnickel complexes were formed [7].

The purpose of this paper was to study the reaction of nickelocene with *tert*-butyllithium (*tert*-butyl group possesses only β-H and does not possess α-H) to find out whether trinickel cluster $(NiCp)_3C{-}CH(CH_3)_2$ was formed in this reaction. There has been no evidence up to now whether trinickel clusters are formed via α- or β-H elimination as all the previously studied reactions were with R ligand possessing only α- or both α- and β-hydrogen atoms.

☆ Dedicated to Professor Dirk Walther on the occasion of his 60th birthday.

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2. Results and discussion

The reaction of nickelocene with *tert*-butyllithium was carried out in THF at the temperature range from $-40°C$ to room temperature. The products were hydrolysed with deoxygenated water and separated by column chromatography on neutral alumina. The second, red–brown band (eluent 9% toluene in hexane) gave crystalline trinickel cluster $(NiCp)_3CCH(CH_3)_2$ **1** at about 6% yield. The cluster **1** has been characterised by elemental analysis and spectroscopic methods.

^1H-NMR revealed three signals: a doublet of methyl protons at $\delta = 1.56$ ppm, a septet of –CH= proton at 3.48 ppm and a singlet of cyclopentadienyl protons at 5.12 ppm. Four signals in ^{13}C-NMR spectrum were observed at following chemical shifts: 28.10 ppm (methyl carbons), 52.31 ppm (–CH= carbon), 87.74 ppm (cyclopentadienyl carbons) and 303.76 ppm (alkylidyne carbon).

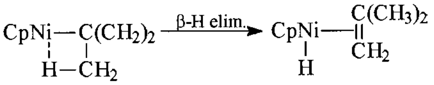
In the mass spectrum of **1** (EI, 70 eV) the parent ion $[Ni_3Cp_3CCH(CH_3)_2]^+$ was present at *m*/*e* 424 (calculated for ^{58}Ni). The fragmentation was very similar to that observed for the other obtained by us cyclopentadienyl trinickel clusters. The following ions were present at *m*/*e*: 369 $[Ni_3Cp_3)]^+$; 358 $[M{-}CpH]^+$; 344 $[Ni_3Cp_2CCH(CH_3)]^+$; 304 $[Ni_3Cp_2]^+$. For all the above ions the isotopic pattern was in a very good agreement with that calculated for three nickel atoms. The other ions present in the spectrum were at *m*/*e*: 246 $[Ni_2Cp_2]^+$ (isotopic pattern corresponded to two nickel atoms); 188 $[NiCp_2]^+$ and 123 $[NiCp]^+$.

We have previously established the crystal structure of two other tri(cyclopentadienylnickel) clusters, analogous to **1**: $(NiCp)_3C{-}CH_3$ [8] and $(NiCp)_3C{-}CH(Ph)CH_3$ [5].

The reaction proceeds according to the Eq. (1)

$$NiCp_2 + LiC(CH_3)_3 \rightarrow LiCp + \{CpNiC(CH_3)_3\} \rightarrow (NiCp)_3\underset{\mathbf{1}}{C}CH(CH_3)_2 + CH(CH_3)_3 \quad (1)$$

The initial step of the reaction is the ligand exchange between $NiCp_2$ and $LiC(CH_3)_3$ with the formation of unstable $\{CpNiC(CH_3)_3\}$ species. This species undergo β-H elimination forming a complex of {CpNiH} and *iso*-butene (Eq. (2)).



$$\begin{array}{cc} CpNi{-}C(CH_2)_2 \\ \vdots \quad | \\ H{-}CH_2 \end{array} \xrightarrow{\beta\text{-H elim.}} \begin{array}{cc} CpNi{-}\overset{C(CH_3)_2}{\underset{CH_2}{\|}} \\ | \\ H \end{array} \quad (2)$$

Further reactions of the olefinic C–H bond activation and aggregation of {NiCp} proceed as in previously described by us reactions of nickelocene with organolithium and -magnesium compounds [9].

The above and our previous studies [1,7] have shown that the formation of trinickel clusters can proceed via α-H elimination as well as via β-H one. Cyclopentadienyltrinickel clusters were formed from the {CpNiR} species possessed only α-H atoms ($R = CH_3$, $CH_2C(CH_3)_3$, $CH_2C_6H_5$, $CH_2Si(CH_3)_3$ [2–4]) or only β-H atoms ($R = C(CH_3)_3$; this work). Cyclopentadienyltrinickel clusters were formed also if R possessed both α- and β-hydrogen atoms [7]. It seems that in this case β-H elimination is the preferred course of the reaction.

The trinickel cluster above was not the only product isolated from the reaction mixture. The first chromatographic band (eluent 7% toluene in hexane) gave blue dinickel compound $[NiC_5H_4C(CH_3)_3]_2{\cdot}C_5H_5C(CH_3)_3$ **3**. It was characterised by ^1H- and ^{13}C-NMR, mass spectroscopy and by X-ray single crystal technique.

Assignments of NMR signals were based on standard ^1H- and ^{13}C-spectra, ^1H-, ^1H-COSY and $^1H{-}^{13}C$ correlation experiments. Atom numbering is shown on Fig. 1.

The ^1H-NMR spectrum showed: a singlet of methyl protons of *tert*-butyl substituent of cyclopentadiene ring (bonded to C4) at 0.79 ppm; a singlet of methyl protons of *tert*-butyl substituent of cyclopentadienyl groups (bonded to C10) at 1.31 ppm; a singlet of HC1 proton at 2.05 ppm. This signal was expected to be coupled with other protons of cyclopentadiene ring but the coupling was not observed, probably due to the puckering of C1 from the ring plane and therefore out of plane position of the proton. Two multiplets of protons bonded to C2 and C3 appeared at 2.97 and 5.17 ppm. Protons of cyclopentadienyl rings were not equivalent and appeared as four multiplets at 4.53, 4.98, 5.09 and 5.20 ppm.

In the ^{13}C-NMR spectrum the signals appeared at the following chemical shifts: methyl carbon atoms bonded to C4 at 27.04 and bonded to C10 at 32.26 ppm; C4 at 34.85 and C10 at 31.70 ppm. Signals of cyclopentadiene ring carbons were present at 66.89 (C1), 55.33 and 55.72 ppm (C2 and C3). Cyclopentadienyl rings carbon atoms showed five resonances at 123.15 (C5), 85.48; 86.10; 86.77 and 88.93 ppm (C6–C9).

In the mass spectrum of **3** (EI, 70 eV) the parent ion $\{Ni[C_5H_4C(CH_3)_3]\}_2[C_5H_5C(CH_3)_3]^+$ was present at m/e 480 (calculated for ^{58}Ni; the isotopic pattern was characteristic for two nickel atoms). The other ions were present at *m*/*e*: 358 $\{Ni_2[(C_5H_4C(CH_3)_3]_2\}^+$; 342

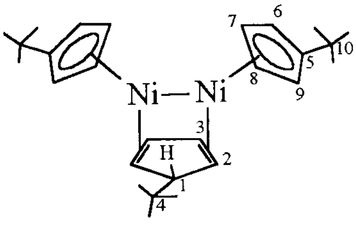


Fig. 1. A schematic view of **3** with atom numbering.

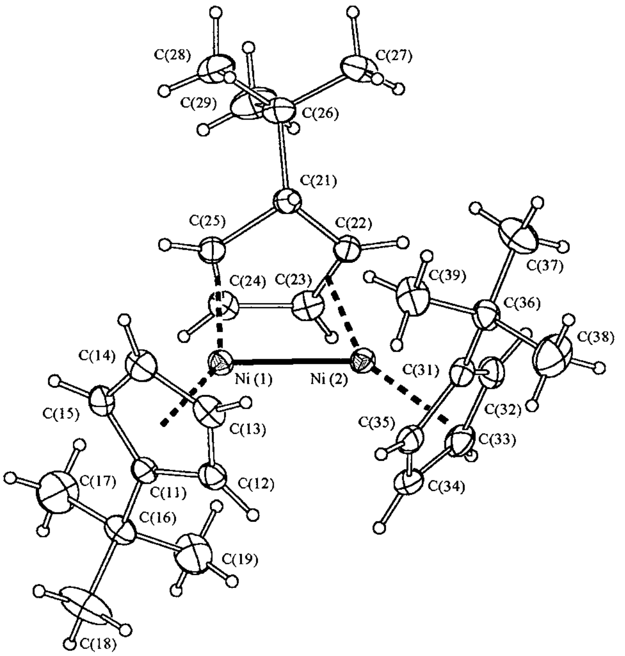


Fig. 2. The ORTEP drawing of **3** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

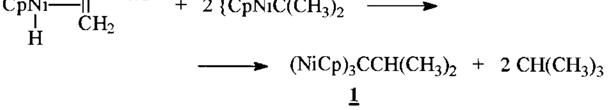
$\{Ni_2[C_5H_4C(CH_3)_3][(C_5H_4C(CH_3)CH_2]\}^+$; 300 $\{Ni[(C_5H_4C(CH_3)_3]_2\}^+$ and ions derived from fragmentation of organic ligands.

The X-ray measurements show that the complex is composed of two Ni atoms, two *tert*-butylcyclopentadienyl ligands and one 1-*tert*-butylcyclopentadiene molecule (Fig. 2). Both cyclopentadienyl rings form typical C_5 bonds with Ni atoms, whereas the *tert*-butylcyclopentadiene ligand form bonds to two metal atoms. In spite to the flatted cyclopentadienyl rings, the cyclopentadiene system is puckered (C (21) $-0.476(3)$ Å) and some of its C–C bonds are longer than the other ones (average 1.515(5) Å), because of the sp^3 hybridisation of the C(212) carbon atom. Crystal data, fractional atomic coordinates, selected bond lengths and angles are presented in Tables 1–4.

The structure of the compound **3** is analogous to the previously characterised compound **6** $(NiCp)_2(\mu\text{-}C_5H_6)$ [7], but possessed both cyclopentadienyl and cyclopentadiene rings substituted by *tert*-butyl groups. According to our knowledge it is the first example of alkylation of cyclopentadienyl rings bonded to nickel by alkyllithium compound. The length of the Ni–Ni bond in **3** is equal to 2.432 Å and is similar to that in **6** (2.411 Å [7]), but is substantially longer than in other di(cyclopentadienylnickel) compounds with bridging ligands. For example: 2.345 Å in $(NiCp)_2{\cdot}HC{\equiv}CH$ [10], 2.329 Å in $(NiCp)_2{\cdot}PhC{\equiv}CPh$ [11], 2.329 Å in $(NiCp)_2{\cdot}C_6F_5C{\equiv}CC_6F_5$ [12], 2.361 and 2.348 Å (molecules A and B) in $(NiCp)_2{\cdot}(CO)_2$ [13] (2.363 and 2.351 Å also in $(NiCp)_2{\cdot}(CO)_2$ [14]). In fact the Ni–Ni bond in **3** is even longer than in di(cyclopentadienylnickel) compound with non-bridging ligands e.g. 2.407 Å in $(CpNi{\cdot}PEt_3)_2$ [15]. The elongation of Ni–Ni bond in **3** and **6** is probably forced by the distance of the centres of C=C bonds in cyclopentadiene ring to achieve proper π-interaction.

The reaction of nickelocene with $LiC(CH_3)_3$ can proceed as follow: an unstable species $\{CpNiC(CH_3)_3\}$ is initially formed (Eq. (1)). This species can eliminate β-hydrogen and undergo homolytic scission of Ni–C bond to form radicals (Scheme 1).

The complex resulted from β-H elimination reacts with $\{CpNiC(CH_3)_3\}$ to form a stable trinickel cluster **1** (Eq. (3)).



$$\underset{\displaystyle H}{CpNi}\!-\!\overset{C(CH_3)_2}{\underset{CH_2}{\|}} + 2\,\{CpNiC(CH_3)_2 \longrightarrow\; \longrightarrow (NiCp)_3CCH(CH_3)_2 + 2\,CH(CH_3)_3$$

1

(3)

Table 1
Crystal data and structure refinement for **3**

Empirical formula	$C_{27}H_{40}Ni_2$
Crystal size (mm)	0.4 × 0.4 × 0.4
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.520(2)
b (Å)	13.150(5)
c (Å)	13.625(4)
α (°)	113.77(3)
β (°)	97.42(3)
γ (°)	90.02(3)
Volume (Å^3)	1220.7(7)
Z	2
Formula weight	481.99
Density$_{(calc.)}$ (g cm^{-3})	1.309
Temperature (K)	299(2)
Absorption coefficient (mm^{-1})	1.552
$F(000)$	514
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å, graphite monochromator)
θ range for data collection	2.74 to 25.05 °
Scan type	ω–2θ
Index ranges	$0 \le h \le 8$, $0 \le k \le 14$, $-15 \le l \le 15$
Reflections collected /unique	3872/3654 [$R_{int} = 0.0090$]
Absorption correction	Gaussian
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3654/0/271
Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	
$R_1 = \Sigma\,(F_o - F_c)/\Sigma\,F_o$	$R_1 = 0.0259$
$wR_2 = \{\Sigma\,[w(F_0^2 - F_c^2)^2] / \Sigma\,[w(F_0^2)^2]\}^{1/2}$ [a]	wR_2 (refined) = 0.0711
R indices (all data)	$R_1 = 0.0363$
Largest difference peak and hole (e·Å^{-3})	0.343 and −0.325

[a] Weighting scheme $w^{-1} = \sigma^2(F_0^2) + (0.0403P)^2 + 0.5831P$ where $P = (F_0^2 + 2F_c^2)/3$

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **3**

Atom	x	y	z	U_{eq} [a]
Ni(1)	0.18478(4)	0.25918(3)	0.23200(2)	0.03358(10)
Ni(2)	0.41111(4)	0.15237(3)	0.28566(2)	0.03404(11)
C(11)	0.1655(3)	0.2945(2)	0.0872(2)	0.0364(6)
C(12)	0.1651(4)	0.1797(2)	0.0623(2)	0.0400(6)
C(13)	0.0112(4)	0.1483(2)	0.0982(2)	0.0449(7)
C(14)	−0.0782(4)	0.2436(3)	0.1477(2)	0.0481(7)
C(15)	0.0169(4)	0.3340(2)	0.1424(2)	0.0435(6)
C(16)	0.2950(4)	0.3608(2)	0.0559(2)	0.0457(7)
C(17)	0.2866(6)	0.4848(3)	0.1225(4)	0.0843(12)
C(18)	0.2467(6)	0.3357(4)	−0.0636(3)	0.0911(14)
C(19)	0.4883(4)	0.3298(3)	0.0762(3)	0.0742(11)
C(21)	0.1821(3)	0.2663(2)	0.4492(2)	0.0376(6)
C(22)	0.3759(4)	0.2388(2)	0.4380(2)	0.0397(6)
C(23)	0.4582(4)	0.3071(2)	0.3971(2)	0.0435(6)
C(24)	0.3213(4)	0.3699(2)	0.3664(2)	0.0420(6)
C(25)	0.1543(4)	0.3385(2)	0.3861(2)	0.0387(6)
C(26)	0.1459(4)	0.3253(2)	0.5691(2)	0.0473(7)
C(27)	0.1847(5)	0.2463(3)	0.6251(3)	0.0734(11)
C(28)	−0.0541(4)	0.3499(3)	0.5702(3)	0.0608(8)
C(29)	0.2595(5)	0.4334(3)	0.6293(3)	0.0719(10)
C(31)	0.3988(3)	−0.0239(2)	0.2399(2)	0.0392(6)
C(32)	0.5708(4)	0.0227(2)	0.2977(2)	0.0454(7)
C(33)	0.6577(4)	0.0713(3)	0.2399(3)	0.0501(7)
C(34)	0.5397(4)	0.0598(2)	0.1483(2)	0.0477(7)
C(35)	0.3790(4)	0.0010(2)	0.1481(2)	0.0422(6)
C(36)	0.2665(4)	−0.0931(2)	0.2666(2)	0.0434(6)
C(37)	0.2999(5)	−0.0693(3)	0.3866(3)	0.0668(9)
C(38)	0.2903(6)	−0.2159(3)	0.2005(4)	0.0812(12)
C(39)	0.0748(4)	−0.0658(3)	0.2391(3)	0.0605(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Reasonably stable *tert*-butyl radical reacts with an excess of nickelocene to form the alkylated compound **2** (Scheme 2).

Unstable species **2** can split into {NiCp} and $C_5H_5C(CH_3)_3$. It can also hydrogenate cyclopentadienyl ring (with mediated role of nickel) to form $\{NiC_5H_4C(CH_3)_3\}$ and C_5H_6. These species form a mixture of products **3**–**6**. The compound **3** was isolated and characterised by ^{1}H-, ^{13}C-NMR, mass spectrometry and X-ray analysis. The presence of remaining compounds **4**, **5** and **6** was confirmed by the presence of their molecular ions in mass spectra of the post-reaction mixture. We have previously established the molecular structure of **6** [7].

Because of stability of *tert*-butyl radicals, a homolytic dissociation of $\{CpNiC(CH_3)_3\}$ is a concurrent reaction to β-H elimination and products formed as result of hydrogen elimination as well as cyclopentadienyl ring alkylation are present in the reaction mixture.

The results of above and previous studies are in favour of a radical mechanism of the reaction. Up to now there were no cyclopentadienyl ring alkylation products found in the reactions of nickelocene with organolithium compounds. This was probably due to the fact that none of the studied R groups formed stable radicals. An ionic cleavage of $LiC(CH_3)_3$ and an attack of $C(CH_3)_3^{(-)}$ anion on cyclopentadienyl ring of nickelocene should be also excluded from mechanistic considerations. Werner et all proved, that triphenylmethyl chloride dissociated heterolytically and the cation $CPh_3^{(+)}$ attacked nickelocene to alkylate cyclopentadienyl ring [16]. Unfortunately alkylated nickelocene was not formed in this reaction but it decomposed with the formation of $C_5H_5CPh_3$ and $NiCl_2$. In case of ferrocene, an organolithium compound metallates a cyclopentadienyl ring [17] (Eq. (4)).

$$FeCp_2 + BuLi \rightarrow CpFeC_5H_4Li + BuH \qquad (4)$$

Table 3
Selected interatomic distances (Å) in **3** [a]

Ni(1)–C(24)	1.973(3)
Ni(1)–C(25)	1.977(3)
Ni(1)–C(13)	2.096(3)
Ni(1)–C(12)	2.103(3)
Ni(1)–C(14)	2.121(3)
Ni(1)–C(15)	2.151(3)
Ni(1)–C(11)	2.190(3)
Ni(1)–Ni(2)	2.432(1)
Ni(2)–C(22)	1.977(3)
Ni(2)–C(23)	1.985(3)
Ni(2)–C(35)	2.100(3)
Ni(2)–C(34)	2.134(3)
Ni(2)–C(32)	2.134(3)
Ni(2)–C(31)	2.143(3)
Ni(2)–C(33)	2.174(3)
C(11)–C(12)	1.407(4)
C(11)–C(15)	1.409(4)
C(11)–C(16)	1.516(4)
C(12)–C(13)	1.434(4)
C(13)–C(14)	1.383(4)
C(14)–C(15)	1.419(4)
C(16)–C(18)	1.518(4)
C(16)–C(17)	1.519(5)
C(16)–C(19)	1.531(4)
C(21)–C(22)	1.514(4)
C(21)–C(25)	1.516(4)
C(21)–C(26)	1.561(4)
C(22)–C(23)	1.411(4)
C(23)–C(24)	1.444(4)
C(24)–C(25)	1.412(4)
C(26)–C(29)	1.518(4)
C(26)–C(27)	1.526(4)
C(26)–C(28)	1.539(4)
C(31)–C(35)	1.406(4)
C(31)–C(32)	1.420(4)
C(31)–C(36)	1.520(4)
C(32)–C(33)	1.413(4)
C(33)–C(34)	1.389(4)
C(34)–C(35)	1.433(4)
C(36)–C(37)	1.522(4)
C(36)–C(39)	1.522(4)
C(36)–C(38)	1.524(4)

[a] Estimated standard deviations in parentheses.

Table 4
Selected bond angles (°) in **3** [a]

C(13)–Ni(1)–C(12)	39.95(11)
C(13)–Ni(1)–C(14)	38.28(11)
C(14)–Ni(1)–C(15)	38.81(11)
C(12)–Ni(1)–C(11)	38.20(10)
C(15)–Ni(1)–C(11)	37.88(10)
C(24)–Ni(1)–Ni(2)	76.14(9)
C(25)–Ni(1)–Ni(2)	88.57(9)
C(24)–Ni(1)–C(25)	41.91(11)
C(22)–Ni(2)–C(23)	41.71(11)
C(22)–Ni(2)–Ni(1)	88.55(8)
C(23)–Ni(2)–Ni(1)	74.96(9)
C(35)–Ni(2)–C(34)	39.57(11)
C(35)–Ni(2)–C(31)	38.70(10)
C(32)–Ni(2)–C(31)	38.78(10)
C(34)–Ni(2)–C(33)	37.61(11)
C(32)–Ni(2)–C(33)	38.26(11)
C(12)–C(11)–C(16)	126.6(2)
C(15)–C(11)–C(16)	127.0(2)
C(12)–C(11)–C(15)	106.3(2)
C(11)–C(12)–C(13)	108.8(2)
C(14)–C(13)–C(12)	107.6(2)
C(13)–C(14)–C(15)	108.0(2)
C(11)–C(15)–C(14)	109.3(3)
C(22)–C(21)–C(26)	113.9(2)
C(25)–C(21)–C(26)	113.8(2)
C(22)–C(21)–C(25)	100.7(2)
C(23)–C(22)–C(21)	110.7(2)
C(22)–C(23)–C(24)	108.1(2)
C(25)–C(24)–C(23)	108.5(2)
C(24)–C(25)–C(21)	110.2(2)
C(35)–C(31)–C(36)	126.3(2)
C(32)–C(31)–C(36)	127.6(3)
C(35)–C(31)–C(32)	105.9(2)
C(33)–C(32)–C(31)	109.6(3)
C(34)–C(33)–C(32)	107.6(3)
C(33)–C(34)–C(35)	107.8(3)
C(31)–C(35)–C(34)	109.0(3)

[a] Estimated standard deviations in parentheses.

Metallation of cyclopentadienyl rings has not been observed in reactions of nickelocene with organolithium compounds.

Ring exchange reactions between alkylated and non-alkylated cyclopentadienyl rings bonded to nickel cannot be excluded from mechanistic considerations [18].

We hope that described here reaction of cyclopentadienyl ring alkylation could be applied for the preparation of alkylated nickelocenes (difficult to prepare by other methods) or other organonickel compounds.

3. Experimental

All reactions were carried out under an atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. ^{1}H- and ^{13}C-NMR spectra were measured on a Varian VXR-300 instrument. Mass spectra were recorded on an AMD-604 mass spectrometer.

3.1. Reactions of nickelocene with *tert*-butyl lithium

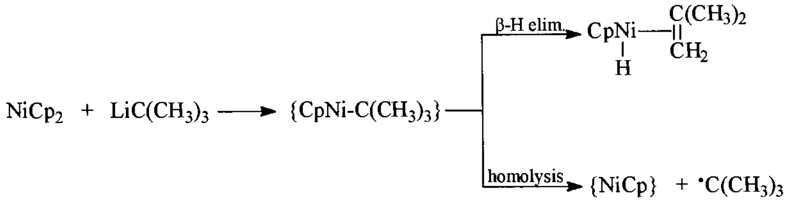
A solution of *tert*-butyllithium in pentane (4 cm^3, 7 mmol) was added within 1 h at -40 to -50°C to a solution of NiCp$_2$ (1.2 g, 6.35 mmol) in 95 cm^3 THF and kept at this temperature within 1 h. The reaction mixture was then allowed to warm up to room temperature and stirred overnight. The volatile substances were removed under reduced pressure; 5 cm^3 of THF and 50 cm^3 of hexane were added and products were hydrolysed with 50 cm^3 of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was redissolved in a mixture of toluene and hexane and chromatographed on alumina (37 × 2 cm^2 deactivated with 5% of water) using hexane and hexane-toluene as eluents. The following compounds were isolated and characterised.

3.1.1. *CpNi(η^3-C$_5$H$_7$)*

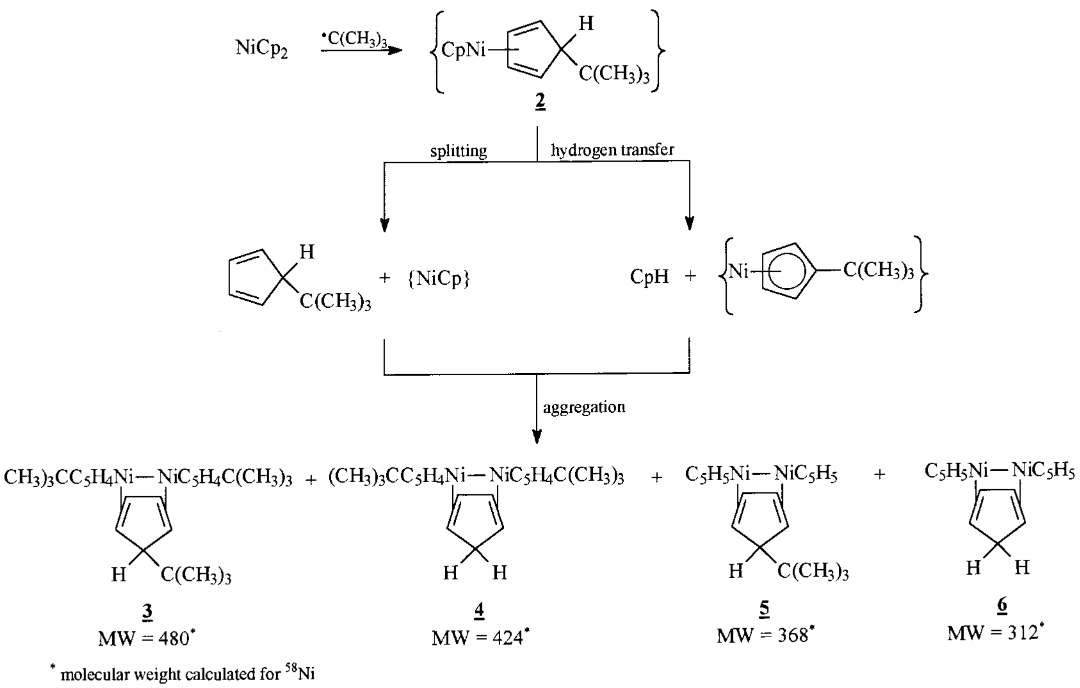
The first pink band eluted with hexane, small amount. The compound has been characterised previously [19].

3.1.2. *[Ni-η^5-C$_5$H$_4$C(CH$_3$)$_3$]$_2$[μ-C$_5$H$_5$C(CH$_3$)$_3$]*, **3**

Blue-band eluted with a mixture of 7% toluene in hexane. The compound was recrystallised from hexane forming deep blue crystals. Yield 0.60 g; 19.6%. It was characterised by ^{1}H-, ^{13}C-NMR, mass spectroscopy and single crystal X-ray analysis. ^{1}H-NMR [C$_6$D$_6$] δ ppm (carbon numbering as on Fig. 1) 0.79 (s, 9 H, C(4)H$_3$), 1.31 (s, 18 H, C(10)H$_3$), 2.05 (s, 1 H, C(1)H); 2.97 (m, 2H, C(2)H or C(3)H), 5.17 (m, 2H, C(2)H or C(3)H), 4.53, 4.98, 5.09, 5.20 (four multiplets, 1 H each, C(6)H–C(9)H). ^{13}C-NMR [C$_6$D$_6$] δ ppm 27.04 (CH$_3$ bonded to C(4)), 31.70 (C(10)), 32.26 (CH$_3$ bonded to C(10)), 34.85 (C(4)), 55.33 (C(2) or C(3)), 55.72 (C(2) or C(3)), 66.89 (C(1)), 85.48, 86.10, 86.77 and 88.93 (C(6)–



Scheme 1.



Scheme 2.

C(9)), 123.15 (C(5)). EIMS (70 eV, masses calculated for ^{58}Ni) *m*/*e*: 480, the parent ion $\{Ni[C_5H_4C(CH_3)_3]\}_2[C_5H_5C(CH_3)_3]^+$ (isotopic pattern characteristic for two nickel atoms); 358 $\{Ni_2[(C_5H_4C(CH_3)_3]_2\}^+$; 342 $\{Ni_2[C_5H_4C(CH_3)_3][(C_5H_4C(CH_3)CH_2]\}^+$; 300 $\{Ni[(C_5H_4C(CH_3)_3]_2\}^+$.

3.1.3. (NiCp)$_3$CCH(CH$_3$)$_2$, 1

Orange–brown band eluted with a mixture of 9% toluene in hexane. Yield 0.16 g, 5.9%. Elemental analysis: found: C 54.00; H 5.25; Ni 40.89%, calculated for $C_{19}H_{22}Ni_3$ (MW 426.45): C 53.51; H 5.20; Ni 41.29%. ^{1}H-NMR [C_6D_6] δ ppm 1.56 (d, 6 H, CH_3), 3.48 (septet, 1 H, –CH=), 5.12 (s, 15 H, C_5H_5). ^{13}C-NMR [C_6D_6] δ ppm 28.10 (CH_3), 52.31 (–CH=), 87.74 (C_5H_5) and 303.76 (≡C–). EIMS (70 eV, masses calculated for ^{58}Ni) *m*/*e*: 424, the parent ion $[Ni_3Cp_3CCH(CH_3)_2]^+$, 369 $[Ni_3Cp_3)]^+$; 358 $[M-CpH]^+$; 344 $[Ni_3Cp_2CCH(CH_3)]^+$; 304 $[Ni_3Cp_2]^+$ (for all the above ions the isotopic pattern was in a very good agreement with that calculated for three nickel atoms), 246 $[Ni_2Cp_2]^+$ (isotopic pattern corresponded to two nickel atoms), 188 $[NiCp_2]^+$, 123 $[NiCp]^+$.

3.2. Crystal structure determination

The crystal was sealed in a glass capillary under nitrogen stream. Intensities were collected with a Kuma KM4 four circle diffractometer [20] in the ω–2θ mode with crystal of dimensions $0.4 \times 0.4 \times 0.4$ mm^2 and Mo–K$_\alpha$ radiation (0.71073 Å) up to $2\theta = 50°$. After each group of 100 reflections, standard intensities were monitored and no evidence of crystal decay was observed. A total of 3872 recorded data were corrected for Lorentz and polarisation factors. An absorption correction as for sphere was also applied. The structure was solved by direct methods (SHELXS97 [21]) and refined on F^2 by full-matrix least-squares program (SHELXL97 [22]). The carbon bonded H-atoms were included in calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 U_{eq} of the attached C atom. Least-squares converged with $R = 0.0259$ and $R_w = 0.0711$ for 3158 reflections with $I > 2\sigma(I)$ and 271 refined parameters. The crystal structure with the atom numbering system is presented on Fig. 2. Data collection and structure analysis parameters are given in Table 1, fractional atomic coordinates in Table 2. Selected bond lengths and bond angles are listed in Tables 3 and 4.

4. Supplementary material

Crystallographic data for the structure (listings of bond lengths and angles, anisotropic thermal parameters, tables of calculated and observed structure factors) have been deposited with the Cambridge Crystallographic data centre. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK. Tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@chemcrys.ca..ac.uk.

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