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Journal of Organometallic Chemistry 597 (2000) 133–138

Journal of Organo metallic Chemistry

Reactions of nickelocene with sodium in the presence of terminal alkenes

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Received 4 August 1999; received in revised form 28 September 1999

Dedicated to our master Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday in recognition of his outstanding contributions to organometallic chemistry.

Abstract

A novel reduction of nickelocene with metallic sodium in the presence of 1-pentene and 1-hexene was studied. It was found that two products of alkene activation were formed. The first one was a (μ_3-hydrido)-(μ_3-alkylidyne)-trinickel cluster (**1**) and the second one a (μ_3-alkylidyne)-trinickel cluster (**3**). Both types of clusters were characterised by spectroscopic methods and by single-crystal X-ray diffraction measurements. The first cluster crystallised from hexane in a monoclinic system in the $C2/c$ space group and the second one from methanol, also as a monoclinic system in the $P2_1/c$ space group. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel; Sodium; Clusters; Cyclopentadienyl; Crystal structure

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1. Introduction

We have previously found that nickelocene reacts with phenyllithium in the presence of terminal alkenes to form tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters $(NiCp)_3C–R$ [1,2]. The unstable species {CpNiPh} formed in the above reactions easily couples forming coordinately and electronically unsaturated species $\{(NiCp)_2\}$ (Eq. (1)):

$$NiCP_2 + LiPh \rightarrow \{CpNiPh\} \rightarrow \{(NiCp)_2\} + Ph–Ph \qquad (1)$$

$\{(NiCp)_2\}$ activates the sp^2 C–H bond in alkenes giving, after hydrogen elimination and aggregation of another {(NiCp)}, alkylidynetrinickel clusters $(CpNi)_3C–R$ [3].

The aim of this work was to examine reactions of nickelocene with metallic sodium in the presence of terminal alkenes and to find out whether alkylidynetrinickel clusters are formed in these reactions.

Sodium amalgam Na(Hg) in methanol has been previously used for reduction of nickelocene. Only metallic nickel and CpNi(η^3-C_5H_7) were obtained in this reaction [4]. Paquette and Dahl reduced nickelocene by treatment of its THF solution with an equimolar amount of sodium naphthalenide. This reaction produced several cyclopentadienylnickel clusters. Only one of them, $(NiCp)_6$, was obtained in a pure form and fully characterised [5]. Jonas et al. reported the reduction of several metalocenes with alkali metals in the presence of alkenes [6]. In case of nickelocene they obtained nickel(0)–alkene complexes. A formation of nickel clusters was not reported.

2. Results and discussion

Reaction of nickelocene with metallic sodium and alkene (1-pentene, 1-hexene) (molar ratio 1:1.4:2.5) in THF was carried out at −30°C for 3 h and then overnight at room temperature. Solvent and unreacted alkene 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 using hexane and hexane–toluene as eluents. Three main fractions were collected.

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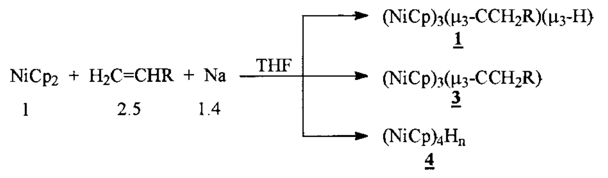
PII: S0022-328X(99)00656-7



where R = **a**–$(CH_2)_2CH_3$; **b**–$(CH_2)_3CH_3$

The first fraction from the reaction with 1-pentene consisted of red, paramagnetic solid $(NiCp)_3(\mu_3\text{-}CCH_2CH_2CH_2CH_3)(\mu_3\text{-}H)$ (**1a**) and traces of $(CpNi)_2CpH$ (**2**) [7]. After crystallisation from hexane, long needles of **1a** were obtained (yield ~ 10%). The mass spectrum revealed the parent ion at m/e 439 (^{58}Ni calc.) with an isotopic pattern characteristic of three nickel atoms in a molecule. The presence of a hydride in the cluster changes dramatically the fragmentation pattern of the molecule in comparison with the fragmentation of alkylidynetrinickel clusters [2,8], in which CpH is first detached giving $\{Ni_3Cp_2R\}^+$ (where R stands for a fragment of an alkyl chain). In the case of cluster **1a**, the weaker-bonded alkyl chain and hydride are first detached giving a three-nuclear fragment $\{Ni_3Cp_3\}^+$. This fragment is not formed during the fragmentation of alkylidynetrinickel clusters. The room temperature EPR spectrum consists of a single line at $g = 2.023$. The low-temperature spectrum (91 K, liquid nitrogen) is axial with $g_\perp = 2.119$ and $g_\| = 1.999$. These values are similar to those observed in $(Cp^*Ni)_3(\mu_3\text{-}CH)(\mu_3\text{-}H)$ [9] and confirm the 49-electron structure of **1a**. In the IR spectrum $\nu(Ni_3(\mu_3\text{-}CR))$ is not observed because it is hidden within C–H modes at ca. 3000 cm^{-1}; $\nu(Ni_3(\mu_3\text{-}H))$ is observed at 1004 cm^{-1}, which is in agreement with data for the cluster $(Cp^*Ni)_3(\mu_3\text{-}CH)(\mu_3\text{-}H)$ [9].

The second fraction consisted of a brown solid $(NiCp)_3(\mu_3\text{-}CCH_2CH_2CH_2CH_3)$ (**3a**), which after crystallisation from acetonitrile gave thin plates (yield ~ 25%). In the mass spectrum the parent ion at m/e 438 (^{58}Ni calc.) is characteristic of three nickel atoms in a molecule. Fragmentation of this cluster is similar to fragmentation of other alkylidynetrinickel clusters described previously [2,8]. The ^{1}H-NMR spectrum reveals a singlet of protons of cyclopentadienyl groups at δ 5.16 ppm, a triplet of protons of the CH_2 group bonded to the alkylidyne carbon atom at 3.69 ppm and two multiplets and a triplet of the remaining protons of the alkyl chain in the range between 1.1 and 2.1 ppm. The ^{13}C-NMR spectrum shows a signal at δ 295.42 ppm characteristic of an alkylidyne carbon atom, a signal at 87.93 ppm of the carbon atoms of a cyclopentadienyl ring and four signals from 14.59 to 57.63 ppm of the carbon atoms of the alkyl chain.

The last fraction obtained in this reaction formed a black crystalline solid and was identified by MS as a mixture of tetranickel clusters of general formula $(NiCp)_4H_x$ (**4**) (where $x = 1, 2, 3$).

Products of the reaction with 1-hexene were similar to those from reaction with 1-pentene. The product obtained from the first fraction formed a red paramagnetic solid identified as $(NiCp)_3(\mu_3\text{-}CCH_2CH_2CH_2CH_2CH_3)(\mu_3\text{-}H)$ (**1b**) (yield ~ 10%). Traces of $(CpNi)_2CpH$ (**2**) were also present in this fraction. In the mass spectrum of **1b**, the parent ion at m/e 453 (^{58}Ni calc.) is in agreement with the isotopic pattern of three nickel atoms. Other fragments present in this spectrum are as follows: 383 $((NiCp)_3(\mu_3\text{-}CH)(\mu_3\text{-}H))^+$, 369 $((NiCp)_3)^+$, 343 $(Ni_3Cp_2C_3H_3)^+$, 329 $(Ni_3Cp_2C_2H)^+$, 303 $(Ni_3CpC_5H_4)^+$, 246 $(Ni_2Cp_2)^+$, 188 $(NiCp_2)^+$, 123 $(NiCp)^+$. The fragmentation pattern of **1b** is similar to that observed for **1a**. In the IR spectrum, as in **1a**, $\nu(Ni_3(\mu_3\text{-}CR))$ is not observed because it is hidden within C–H modes at ca. 3000 cm^{-1}; $\nu(Ni_3(\mu_3\text{-}H))$ is observed at 1004 cm^{-1}.

The second fraction consisted of a brown solid $(NiCp)_3(\mu_3\text{-}CCH_2CH_2CH_2CH_2CH_3)$ (**3b**), which after crystallisation from methanol gave thin plates (yield ~30%). This cluster was previously obtained in the reaction of nickelocene with phenyllithium in the presence of 1-hexene [2]. In the mass spectrum the parent ion at m/e 452 (^{58}Ni calc.) is characteristic for three nickel atoms in the molecule. Fragmentation of this cluster is similar to the fragmentation of **3a** and to other alkylidynetrinickel clusters described in the literature [2,8]. The ^{1}H-NMR spectrum of **3b** shows a singlet of protons of cyclopentadienyl groups at δ 5.17 ppm, a triplet of protons of the CH_2 group bonded to an alkylidyne carbon atom at 3.69 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 [2].

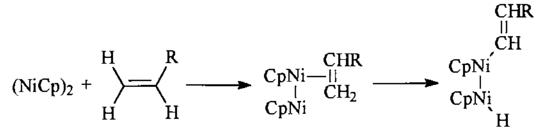
The last chromatographic band obtained in this reaction contained, as in the reaction with 1-pentene, a mixture of clusters $(NiCp)_4H_x$ (**4**).

The structures of **1a** and **3b** were determined by single-crystal X-ray diffraction studies. Both compounds crystallise in a monoclinic crystal system. A comparison of Ni–Ni and Ni–C(1) bond distances in both compounds indicates that the presence of a hydride in a molecule causes a prolongation of the lengths of these bonds, but the influence is not very big. The average Ni–Ni bond length in **1a** is 2.363 Å while in **3b** it is 2.310 Å. The average Ni–C(1) bond lengths are 1.839 Å in **1a** and 1.817 Å in **3b**. A comparison of Ni–Ni and Ni–C(1) bond distances in **3b** with known structures of similar tri(cyclopentadienylnickel) clusters [8,10,11] leads to the conclusion that a kind of R group bonded to C(1) has no big influence on the lengths of these bonds. Ni–Ni, and Ni–C(1) bonds in $(Cp^*Ni)_3(\mu_3\text{-}CH)(\mu_3\text{-}H)$ [9] are longer than the corresponding bonds in **1a** (Ni–Ni: 2.415 and 2.363 Å, respectively, Ni–C(1): 1.913 and 1.839 Å). This is probably caused by the differences in size of methylated and non-methylated cyclopentadienyl rings in both compounds.

The reaction between nickelocene and metallic sodium most probably begins from an abstraction of the cyclopentadienyl group from nickelocene by sodium (Eq. (2)):

$$NiCp_2 + Na \rightarrow \{NiCp\} + NaCp \qquad (2)$$

An unstable, 15-electron species {NiCp} dimerises forming {(NiCp)$_2$}. This dimer forms an active complex with an alkene in which hydrogen transfer occurs towards coordinately and electronically unsaturated nickel atom. At the same time the σ-bond C–Ni is formed (Eq. (3)).



(3)

Possible further steps of the reaction are shown in Scheme 1. In reaction (4) nickel hydride hydrogenates the cyclopentadienyl ring forming cyclopentadiene and the cluster **3**. The dimer {(NiCp)$_2$} reacts with cyclopentadiene forming complex **2**, which was described earlier [7]. In reaction (5) the starting complex reacts with the dimer {(NiCp)$_2$} forming cluster **3** and an unstable {CpNiH}, which forms the stable clusters **4**. In reaction (6) the starting dimer reacts with {NiCp} forming a new cluster **1**.

3. Experimental

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. Elemental analyses were performed on a Perkin–Elmer 2400 analyser. ^{1}H- and ^{13}C-NMR spectra were measured on Varian Gemini-200 and VXR-300 instruments. Mass spectra were recorded on AMD-604 and AMD M-40 mass spectrometers.

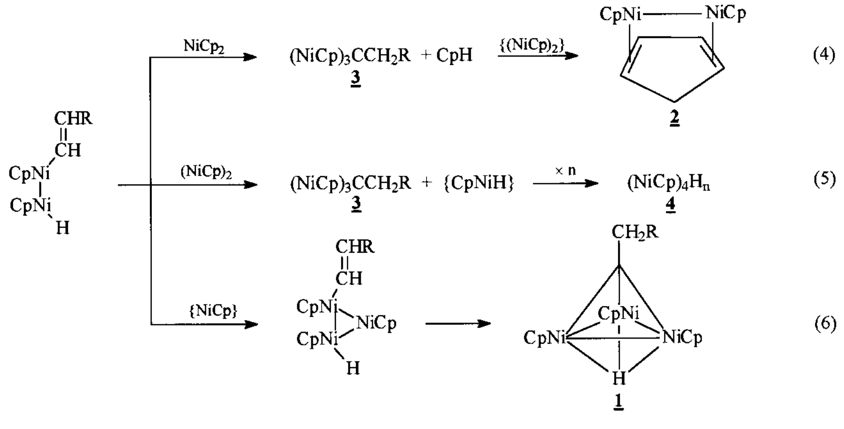
3.1. Reaction of nickelocene with sodium and 1-pentene in THF

Nickelocene (2.12 g, 11.3 mmol), 1-pentene (2.5 cm^3, 1.6 g, 22.9 mmol), sodium (0.35 g, 15.2 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 removed and the residue was extracted with two portions of toluene (70 cm^3 each). Extracts were filtered through an alumina bed, mixed with each other and the solvent was evaporated to dryness. The residue was dissolved (7 cm^3 of hexane + 5 cm^3 of toluene) and chromatographed on neutral alumina (deactivated with 5% of water) with hexane and hexane–toluene mixture as eluents. Four coloured bands were collected.

The first deep-red band (4:1 hexane–toluene) after evaporation of solvents gave a red solid identified as **1a** (yield 0.132 g, 0.3 mmol, ca. 8%). Elemental analysis: Anal. Calc. for $C_{20}H_{25}Ni_3$: C, 54.41; H, 5.71; Ni, 39.88. Found C, 54.11; H, 5.80; Ni, 39.42%. EIMS (70 eV) *m*/*e* (rel. int.) (^{58}Ni): 439 [M$^+$, 50%], 369 (92%), 343 (9%), 329 (28%), 303 (42%), 246 (17%), 188 (25%), 123 (24%). The crystal and molecular structure of **1a** was determined by X-ray measurements. Traces of cluster **2** were also present in this fraction.

The second brown fraction (4:1 hexane–toluene) gave a brown solid identified as **3a** (yield 0.412 g, 0.94 mmol, ca. 25%). Elemental analysis: Anal. Calc. for $C_{20}H_{24}Ni_3$: C, 54.54; H, 5.49; Ni, 39.97. Found: C, 54.26; H, 5.39; Ni, 39.58%. ^{1}H-NMR (C_6D_6) δ (ppm): 5.16 (s, 15H, Cp), 3.69 (t, 2H, ≡C–CH_2–), 2.10 (m, 2H, –CH_2–), 1.66 (m, 2H, –CH_2–CH$_3$), 1.09 (t, 3H, CH_3); ^{13}C-NMR (C_6D_6) δ (ppm): 295.42 (C alkylidyne), 87.93 (Cp), 57.63 (CH$_2$), 38.24 (CH$_2$), 23.50 (CH$_2$), 14.59 (CH$_3$). EIMS (70 eV) *m*/*e* (rel. int.) (^{58}Ni): 438 [M$^+$, 73%], 370 (38%), 344 (59%), 330 (31%), 304 (89%), 246 (41%), 188 (41%), 123 (33%).

The third black fraction (3:1 hexane–toluene) gave a black solid identified as a mixture of the clusters **4** (yield 0.125 g, ca. 9%).



Scheme 1.

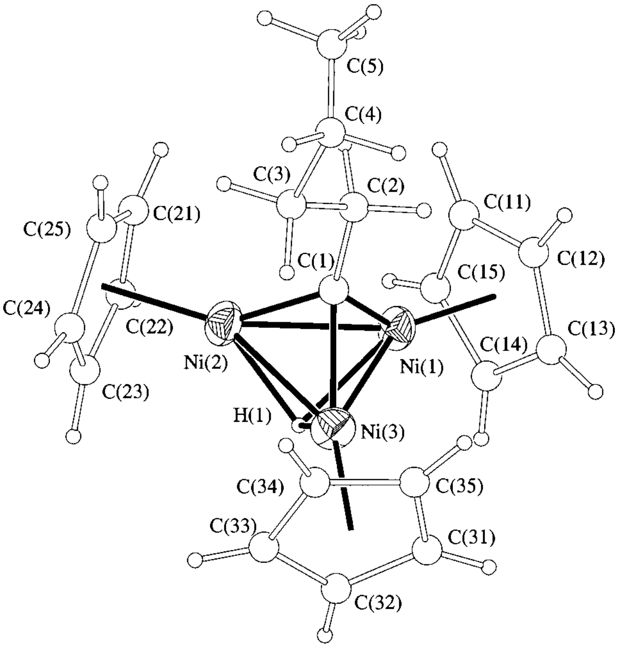


Fig. 1. Molecular structure of **1a** with atom numbering scheme.

3.2. Crystal structure determination of *1a*

The crystal was sealed in a glass capillary under dinitrogen stream. Preliminary examination and intensities data collections were carried out on a Kuma KM-4 four-circle diffractometer [12] using graphite-monochromated Mo–K_α radiation. Cell parameters were obtained from a least-squares fit of the setting angles of 30 reflections in the range $7° < \theta < 14°$. Intensities were collected with a $\omega - 2\theta$ scan mode up to $2\theta = 50°$. After each group of 100 reflections, three standard intensities were monitored and no evidence of crystal decay was observed. For all data, Lorentz and polarisation corrections were applied. The absorption corrections following the ABSORB [13] procedure was also used: minimum and maximum absorption corrections were 0.759–1.358. The structure was solved by direct method (SHELXS97) [14] and refined on F^2 by full-matrix least-squares program (SHELXL97) [15]. The carbon-bonded hydrogen atoms were placed in calculated positions and refined using a riding model. The H(1) atom was located from a difference Fourier map and refined without any restraints. The crystal structure with the atom numbering system is presented in Fig. 1. Data collection and structure analysis parameters are given in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

3.3. Reaction of nickelocene with sodium and 1-hexene in THF

Nickelocene (1.98 g, 10.5 mmol), 1-hexene (3 cm^3, 2.02 g, 24 mmol), sodium (0.33 g, 14.3 mmol) and 70 cm^3 of THF were placed in a 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

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

Empirical formula	$C_{20}H_{25}Ni_3$
Crystal size (mm)	0.7 × 0.5 × 0.2
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.621(2)
b (Å)	9.070(2)
c (Å)	22.012(4)
β (°)	95.73(3)
V (Å^3)	1911.2(7)
Z	4
Formula weight	441.49
$D_{\text{calc.}}$ (Mg m^{-3})	1.534
Temperature (K)	299(2)
Absorption coefficient (mm^{-1})	2.921
F(000)	916
Radiation	Mo–K_α ($\lambda = 0.71073$ Å, graphite monochromator)
Theta range for data collection (°)	2.13–25.04
Scan type	$\omega - 2\theta$
Index ranges	$0 \le h \le 11$, $0 \le k \le 10$, $-26 \le l \le 26$
Reflections collected/unique	2907/2779 [$R_{\text{int}} = 0.0286$]
Absorption correction	ABSORB procedure
Max./min. transmission	1.358/0.759
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2779/0/213
Goodness-of-fit on F^2	1.087
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0338$; wR_2 (refined) = 0.0931
Weighting scheme	$W^{-1} = \sigma^2(F_o^2) + (0.0563P)^2 + 1.5149P$ where $P = (F_o^2 + 2F_c^2)/3$
R indices (all data)	R_1 [a] = 0.0635; wR_2 [b] = 0.1051
Largest difference peak and hole (e Å^{-3})	0.398 and −0.448

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

Table 2
Selected bond lengths (Å) for **1a** *

Ni(1)–C(1)	1.843(5)
Ni(1)–H(1)	1.77(4)
Ni(1)–Ni(3)	2.3613(9)
Ni(1)–Ni(2)	2.3619(10)
Ni(2)–C(1)	1.839(5)
Ni(2)–H(1)	1.73(4)
Ni(2)–Ni(3)	2.3658(10)
Ni(3)–C(1)	1.836(5)
Ni(3)–H(1)	1.67(4)
C(1)–C(2)	1.490(7)
C(2)–C(3)	1.494(9)
C(3)–C(4)	1.534(14)
C(4)–C(5)	1.187(13)

* Estimated standard deviations in parentheses.

Table 3
Selected bond angles (°) for **1a** *

C(1)–Ni(1)–Ni(3)	49.93(16)
C(1)–Ni(1)–Ni(2)	50.01(16)
Ni(3)–Ni(1)–Ni(2)	60.12(3)
C(1)–Ni(2)–Ni(1)	50.19(15)
C(1)–Ni(2)–Ni(3)	49.86(16)
Ni(1)–Ni(2)–Ni(3)	59.93(3)
C(1)–Ni(3)–Ni(1)	50.21(15)
C(1)–Ni(3)–Ni(2)	49.98(16)
Ni(1)–Ni(3)–Ni(2)	59.95(3)
Ni(3)–C(1)–Ni(2)	80.2(2)
Ni(3)–C(1)–Ni(1)	79.9(2)
Ni(2)–C(1)–Ni(1)	79.8(2)
Ni(1)–Ni(3)–H(1)	48.6(14)
Ni(2)–Ni(3)–H(1)	46.9(13)
Ni(1)–Ni(2)–H(1)	48.4(14)
Ni(3)–Ni(2)–H(1)	44.9(13)
Ni(3)–Ni(1)–H(1)	44.9(14)
Ni(2)–Ni(1)–H(1)	46.8(13)
Ni(1)–H(1)–Ni(2)	84.8(14)
Ni(1)–H(1)–Ni(3)	86.5(13)
Ni(2)–H(1)–Ni(3)	88.2(13)

* Estimated standard deviations in parentheses.

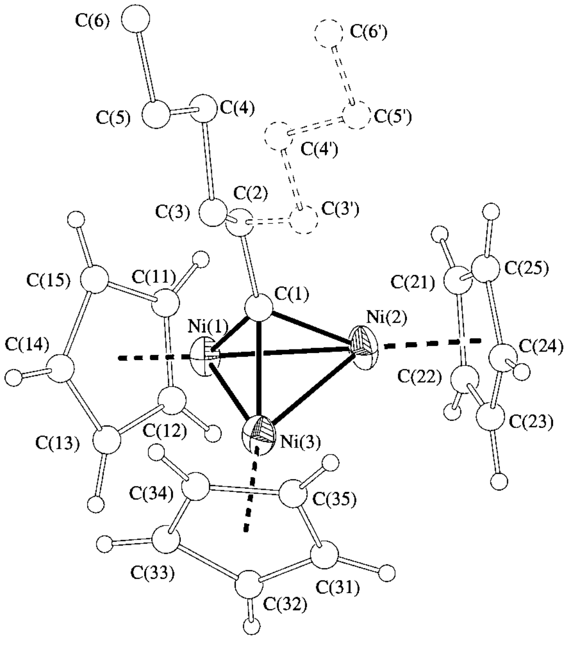


Fig. 2. Molecular structure of **3b** with atom numbering scheme.

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 + 4 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 and collected.

The first deep-red fraction (4:1 hexane–toluene) gave a red solid identified as **1b** (yield 0.143 g, 0.32 mmol, ca. 9%). Elemental analysis: Anal. Calc. for $C_{21}H_{27}Ni_3$: C, 55.37; H, 5.97; Ni, 38.65. Found: C, 55.03; H, 5.90; Ni, 38.38%. EIMS (70 eV) m/e (rel. int.) (^{58}Ni): 453 [M$^+$, 54%], 383 (20%), 369 (97%), 343 (15%), 329 (30%), 303 (43%), 246 (33%), 188 (37%), 123 (27%). Traces of cluster **2** were also present in this fraction.

The second brown fraction (4:1 hexane–toluene) after evaporation to dryness gave a brown solid identified as **3b** (yield 0.444 g, 0.98 mmol, ca. 28%). Elemental analysis: Anal. Calc. for $C_{21}H_{26}Ni_3$: C, 55.50; H, 5.77; Ni, 38.74. Found: C, 55.26; H, 5.80; Ni, 38.54%. ^{1}H-NMR (C_6D_6) δ (ppm): 5.17 (s, 15H, Cp), 3.69 (t, 2H, $\equiv C{-}CH_2{-}$), 2.13 (m, 2H, $-CH_2-$), 1.55 (m, 4H, 2 × $-CH_2-$), 1.02 (t, 3H, $-CH_3$); ^{13}C-NMR (C_6D_6) δ (ppm): 295.34 (C alkylidyne), 87.93 (Cp), 57.83 (CH_2), 35.73 (CH_2), 32.63 (CH_2), 23.22 (CH_2), 14.55 (CH_3). EIMS (70 eV) m/e (rel. int.) (^{58}Ni): 452 [M$^+$, 74%], 384 (58%), 344 (54%), 330 (44%), 304 (93%), 246 (39%), 188 (32%), 123 (26%). The crystal and molecular structure of **3b** was determined by X-ray measurements.

The third black fraction (3:1 hexane–toluene), after evaporation to dryness gave a black solid identified as a mixture of the clusters **4** (yield 0.104 g, ca. 8%).

3.4. Crystal structure determination of 3b

Crystals of **3b** were mounted on glass fibre and then frozen to 200 K. Preliminary examination and intensity data collections were carried out on a Kuma KM-4 four-circle diffractometer [12] with an Oxford Cryosystem-Cryostream Cooler. The data were corrected for Lorentz and polarisation effects. An empirical absorption correction was performed [16]. The structures were solved by direct methods (SHELXS97) [14] and refined on F^2 by full-matrix least-squares program (SHELXL97) [15]. Refinement of **3b** indicated possible disorder, which could not be resolved. Only for the C_6H_{11} substituent was it found that four carbon atoms are equivalently distributed over two positions. The carbon-bonded hydrogen atoms (except those of the C_6H_{11} ligand) were placed in calculated positions and refined using a riding model. The crystal structure with the atom numbering system is presented in Fig. 2. Data collection and structure analysis parameters are given in Table 4. Selected bond lengths and bond angles are listed in Tables 5 and 6, respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134324 for compound **1a** and CCDC no. 134325 for compound **3b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2

Table 4
Crystal data and structure refinement for **3b**

Empirical formula	$C_{21}H_{15}Ni_3$
Crystal size (mm)	$0.7\times0.5\times0.2$
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	32.564(7)
b (Å)	9.086(2)
c (Å)	14.727(3)
β (°)	115.37(3)
V (Å^3)	3937.1(15)
Z	8
Formula weight	443.42
$D_{calc.}$ (Mg m^{-3})	1.496
Temperature (K)	200(1)
Absorption coefficient (mm^{-1})	2.837
$F(000)$	1800
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å, graphite monochromator)
Theta range for data collection (°)	2.35–25.05
Scan type	$\omega-2\theta$
Index ranges	$0\leq h\leq35$, $0\leq k\leq10$, $-16\leq l\leq15$
Reflections collected/unique	3078/3048 [$R_{int}=0.0311$]
Absorption correction	Empirical
Max./min. transmission	1/0.504
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3048/0/253
Goodness-of-fit on F^2	1.070
Final R indices [$I>2\sigma(I)$]	$R_1=0.0395$; wR_2 (refined) = 0.1146
Weighting scheme	$w^{-1}=\sigma^2(F_o^2)+(0.0733P)^2+8.9074P$ where $P=(F_o^2+2F_c^2)/3$
R indices (all data)	R_1 [a] = 0.0592; wR_2 [b] = 0.1222
Largest difference peak and hole (e Å^{-3})	0.438 and -0.384

[a] $R_1=\Sigma(F_o-F_c)/\Sigma F_o$.

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

Table 5
Selected bond lengths (Å) for **3b** *

Ni(1)–C(1)	1.808(5)
Ni(1)–Ni(3)	2.304(1)
Ni(1)–Ni(2)	2.318(1)
Ni(2)–C(1)	1.812(5)
Ni(2)–Ni(3)	2.308(1)
Ni(3)–C(1)	1.830(6)
C(1)–C(2)	1.484(8)
C(2)–C(3)	1.120(16)
C(3)–C(4)	1.621(18)
C(4)–C(5)	1.49(2)
C(5)–C(6)	1.51(2)
C(2)–C(3′)	1.653(18)
C(3′)–C(4′)	1.544(16)
C(4′)–C(5′)	1.547(18)
C(5′)–C(6′)	1.50(2)

* Estimated standard deviations in parentheses.

Table 6
Selected bond angles (°) for **3b** *

Ni(3)–Ni(1)–Ni(2)	59.92(3)
Ni(3)–Ni(2)–Ni(1)	59.75(3)
Ni(1)–Ni(3)–Ni(2)	60.33(3)
C(1)–Ni(1)–Ni(3)	51.13(18)
C(1)–Ni(1)–Ni(2)	50.28(16)
C(1)–Ni(2)–Ni(3)	51.02(18)
C(1)–Ni(2)–Ni(1)	50.11(16)
C(1)–Ni(3)–Ni(1)	50.27(16)
C(1)–Ni(3)–Ni(2)	50.34(16)
Ni(1)–C(1)–Ni(2)	79.6(2)
Ni(1)–C(1)–Ni(3)	78.6(2)
Ni(2)–C(1)–Ni(3)	78.6(2)

* Estimated standard deviations in parentheses.

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Acknowledgements

The authors thank the State Committee for Scientific Research for financial support of this work (Grant no. 3 T09A 046 16).

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