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Reaction of nickelocene with methyllithium in the presence of 2-butyne

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

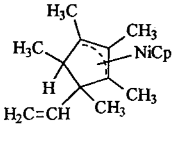
Abstract

Reaction of nickelocene with methyllithium in the presence of 2-butyne at the molar ratio of reactants 1:1:1 leads to the formation of several organinickel compounds. Five of these products were isolated and identified. A novel, 49-electron tri(cyclopentadienylnickel) nickel cluster $(CpNi)_3 \cdot (CH_3C{\equiv}CCH_3)$ (**5**) was fully characterized by spectroscopic and X-ray measurements. Alkyne ligand is bonded to three nickel atoms via two σ and one π bonds ($2\sigma + \pi$ bond system). Compound **5** crystallizes from hexane in a monoclinic crystal system and $P2_1/n$ space group. Corresponding unit cell parameters were determined as $a = 9.015(2)$ Å; $b = 14.608(3)$ Å; $c = 13.983(3)$ Å; $\beta = 108.47(3)°$; $V = 1746.6(6)$ Å^3; $Z = 4$. © 2000 Elsevier Science S.A. All rights reserved.

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

1. Introduction

We have previously found, that nickelocene reacts with methyllithium in the presence of an excess of 2-butyne (1:1:20) to form compounds **1** and **2** [1].



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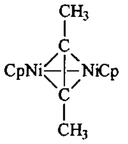
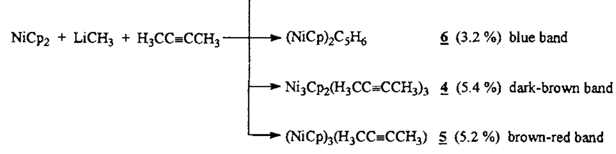


2

The purpose of the present work was to study the reaction of nickelocene with methyllithium and 2-butyne at the molar ratio of reactants 1:1:1. Compound **1** is formed as the result of triple complexation and insertion reactions what requires an excess of 2-butyne, therefore for the equimolar ratio of reactants a formation of other products could be expected.

2. Results and discussion

The reaction was carried out as follows: an etheral solution of methyllithium was added drop by drops at − 55°C to a cooled solution of nickelocene and 2-butyne in THF. The reaction mixture was then allowed to warm up to room temperature and was stirred for further 12 h. The solvents were evaporated and products were dissolved in 60 cm^3 of hexane with a small amount of THF. A total of 40 cm^3 of deoxygenated water was added. The organic layer was concentrated and chromatographed on neutral alumna deactivated with 5% of water (eluent hexane with variable amount



Scheme 1.

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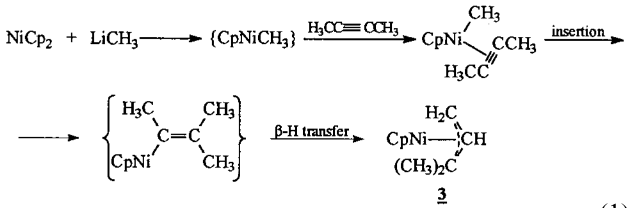
of toluene). Five colored bands were separated. The composition of the products formed is presented on Scheme 1.

The compound isolated from the first pink band was identified as (η^3-1,1-dimethylallyl)(η^5-cyclopentadienyl)nickel (**3**). This compound was characterized by us earlier [2]. The course of the reaction is presented below (Eq. (1)).

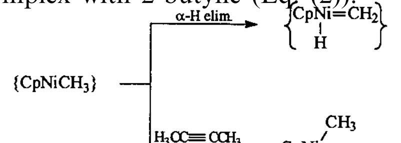


(1)

An unstable species {$CpNiCH_3$} formed in the reaction of nickelocene with methyllithium is complexed with 2-butyne. The insertion of 2-butyne into the nickel–methyl bond is followed by nickel mediated hydrogen shift to form compound **3**. This compound was fully characterized by spectroscopic methods.

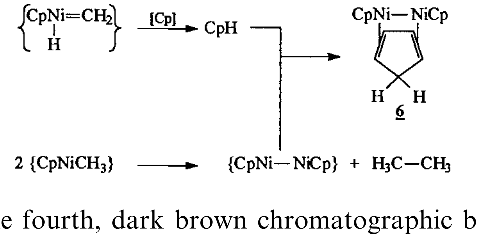
The second chromatographic band contained green dinickel complex with 2-butyne $(NiCp)_2\cdot(H_3CC{\equiv}CCH_3)$ (**2**). Crystal data of its structure was published previously [3]. In this work it was identified spectroscopically.

The third blue band contained the dinickel compound **6** $(NiCp)_2(\mu\text{-}C_5H_6)$. It was obtained by us previously in the reaction of nickelocene with methyllithium and fully characterized spectroscopically and crystallographically [4]. Its presence among the reaction products proves that the unstable species {$CpNiCH_3$}, formed initially in the reaction, can react into two directions: (i) it can eliminate α-hydrogen or (ii) it can form a complex with 2-butyne (Eq. (2)).



(2)

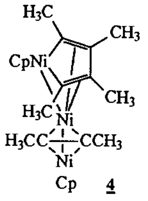
The nickel hydride can hydrogenate a cyclopentadienyl ring to form cyclopentadiene, which in the reactions with the coupling product {$(NiCp)_2$} forms compound **6** (Eq. (3)) [4].



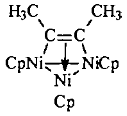
(3)

The fourth, dark brown chromatographic band contained the compound **4** of the formula $Ni_3Cp_2(CH_3C{\equiv}CCH_3)_3$. The compound was characterized by spectroscopic methods. ^{1}H-NMR reveals two singlets of five cyclopentadienyl protons each at δ 5.22 and 5.23 ppm and three singlets of methyl protons (integration ratio 1:1:1 corresponding to six protons in each signal) at δ 1.43, 2.01 and 2.14 ppm. ^{13}C-NMR spectrum contains two signals of cyclopentadienyl carbons at 87.91 and 91.58 ppm, three signals of methyl carbons at 13.75, 17.07 and 31.16 ppm and three signals of other carbons at 90.22, 102.93 and 169.13. MS spectrum contains molecular peak at *m*/*e* 466 and the fragments at *m*/*e* 412 $[Ni_3Cp_2(CH_3C{\equiv}CCH_3)_3]^+$ and 304 $(Ni_3Cp_2)^+$). All that three fragments have the isotopic pattern characteristic for three nickel atoms. The other peaks present in the spectrum appearing *m*/*e* 246 $[(NiCp)_2]^+$; 188 $(NiCp_2)^+$ and 123 $(NiCp)^+$ are characteristic for fragmentation of many cyclopentadienylnickel complexes.

Based on the above results we presume that the compound **4** has a structure analogous to the previously characterized by us compound $Ni_3Cp_2(PhC{\equiv}CPh)_3$ [5]. We have previously thought the compound **4** could have another structure [6]. The final solution will be possible if the crystals suitable for X-ray measurements will be grown.



The fifth chromatographic band was eluted with hexane/toluene (4:1) mixture. Recrystallization from hexane with an addition of small amount of methylene chloride afforded compound **5** of the formula $(CpNi)_3\cdot(CH_3C{\equiv}CCH_3)$ as red–brown crystals suitable for X-ray measurements. The crystal structure of **5** is shown on Fig. 1. It crystallizes in monoclinic crystal system with four molecules in a unit cell. Analysis of structural parameters leads to the conclusion that alkyne ligand is bonded to three nickel atoms via two σ and one π bonds ($2\sigma + \pi$ or μ_3-η^2). This type of bonding is found in homo- and heterometallic alkyne clusters [7] but is novel for trinickel clusters. The schematic bond system of **5** is presented below:



The conclusion concerning the bonding system was drawn based on the following features (atom numbering as on Fig. 1): C(2)–C(3) bond distance (1.366(5) Å) is well within the range of carbon–carbon double bond lengths. Also angles C(4)–C(3)–Ni(3); C(2)–C(3)–C(4);

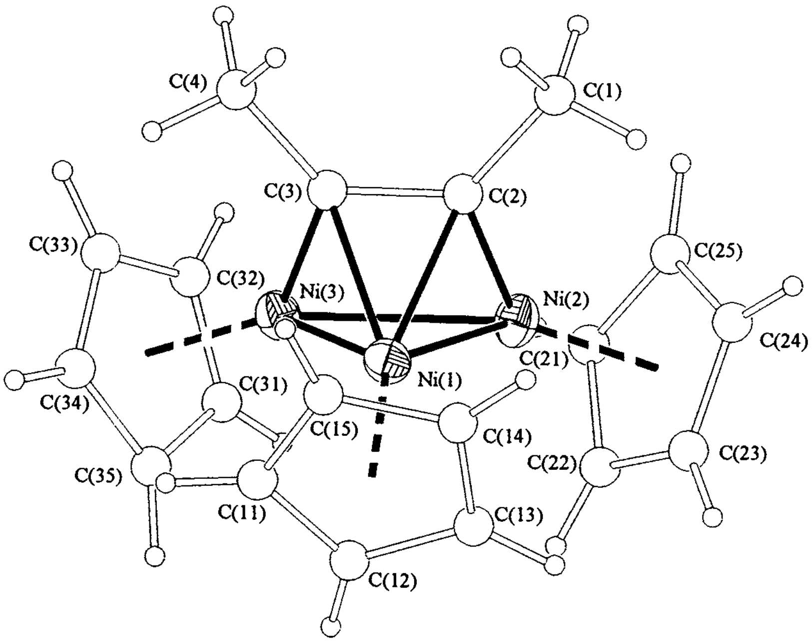
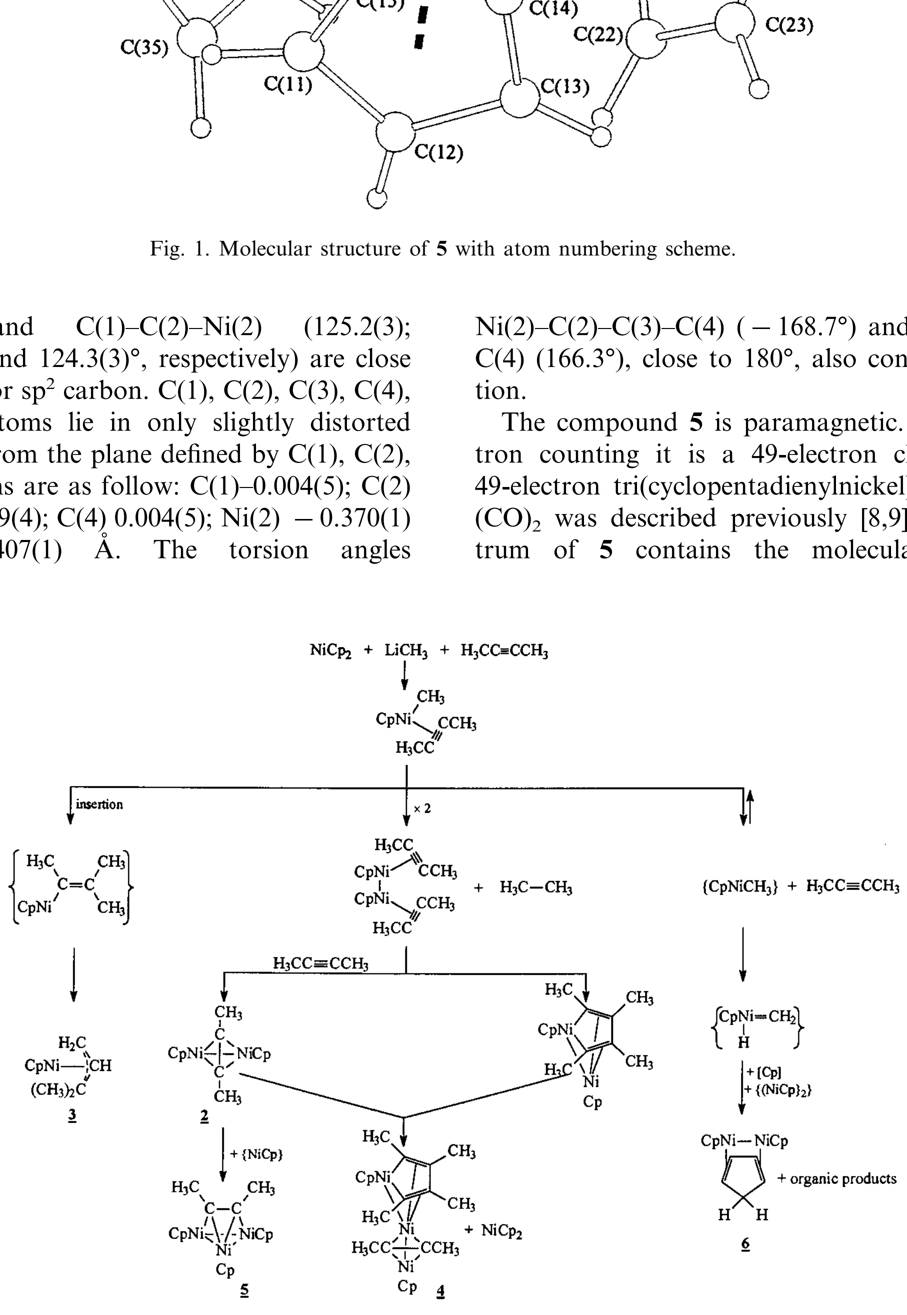


Fig. 1. Molecular structure of **5** with atom numbering scheme.

C(3)–C(2)–C(1) and C(1)–C(2)–Ni(2) (125.2(3); 127.9(3); 127.5(3) and 124.3(3)°, respectively) are close to those expected for sp^2 carbon. C(1), C(2), C(3), C(4), Ni(2) and Ni(3) atoms lie in only slightly distorted plane. Deviations from the plane defined by C(1), C(2), C(3) and C(4) atoms are as follow: C(1)–0.004(5); C(2) 0.009(4); C(3) –0.009(4); C(4) 0.004(5); Ni(2) $-0.370(1)$ and Ni(3) $-0.407(1)$ Å. The torsion angles Ni(2)–C(2)–C(3)–C(4) ($-168.7°$) and C(1)–C(2)–C(3)–C(4) (166.3°), close to 180°, also confirm this assumption.

The compound **5** is paramagnetic. In terms of electron counting it is a 49-electron cluster. The other 49-electron tri(cyclopentadienylnickel) cluster $(NiCp)_3(CO)_2$ was described previously [8,9]. The mass spectrum of **5** contains the molecular ion $[(NiCp)_3$-



Scheme 2.

$CH_3C{\equiv}CCH_2]^+$ at *m*/*e* 423 with the isotopic pattern characteristic for three nickel atoms. The other trinickel ions $(NiCp)_3^+$ ($m/e = 369$), $(Ni_3Cp_2)^+$ (304), dinickel ion $[(NiCp)_2]^+$ at *m*/*e* 246, and mononickel ions $(NiCp_2)^+$ (188), $(NiCp)^+$ (123) and Ni^+ (58) are also present in the spectrum. The course of the reaction and formation of the products **2**–**6** are shown on Scheme 2.

Besides the isolated compounds **2**–**6**, other products were eluted from the chromatographic column, but they were not fully separated and characterized. However, π-allyl complex **1** was not present among the reaction products. This complex is formed in the reaction of nickelocene with methyllithium in the presence of an excess of 2-butyne [1], what is understandable, as threefold insertion of 2-butyne is required for ring closure and the formation of **1**.

3. Experimental details

Reaction was 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 VXR-300 instruments. Mass spectra were recorded on an AMD-604 and AMD M-40 mass spectrometers.

3.1. Reaction of nickelocene with methyllithium in the presence of 2-butyne

A solution of 1.9 g of $NiCp_2$ (10.1 mmol) and 0.8 cm^3 of 2-butyne (10.1 mmol) in 70 cm^3 THF was cooled to −55°C. A solution of methyllithium in Et_2O (7.1 cm^3, 11.1 mmol) was then added over 1 h (temperature was maintained at −55 to −50°C). The mixture was stirred at this temperature for the next hour, then it was allowed to warm up slowly to room temperature. Stirring was continued overnight. The volatile substances were removed under reduced pressure, 20 cm^3 of THF and 60 cm^3 of hexane were added and the products were hydrolyzed with 40 cm^3 of the deoxygenated water. The organic layer was separated and dried, then solvents were evaporated, the residue was re-dissolved in hexane and chromatographed on Al_2O_3 (deactivated with 5.5% of water) using hexane/toluene mixture as an eluent.

A small amount of red $CpNi(\eta^3\text{-}C_5H_9)$ (**3**) [2] (yield 3.8%; eluent: hexane) was eluted. It was identified by means of mass spectroscopy. EI MS (70 eV) *m*/*e* (calc. for ^{58}Ni) 192 (M^+, 100%), 123 (18%), 58 (15%).

The next green band containing $(NiCp)_2(CH_3C{\equiv}CCH_3)$ (**2**) [3] was collected (yield 54%; eluent: hexane). The compound was characterized by ^{1}H-NMR (C_6D_6) δ [ppm] 5.18 (s, 10H), 2.24 (s, 6H); ^{13}C-NMR (C_6D_6) δ [ppm] 99.74, 87.44, 18.13; EI MS (70 eV) *m*/*e* (calc. for ^{58}Ni) 300 (M^+, 45%), 246 (75%), 188 (100%), 123 (40%), 58 (20%).

The next blue band was eluted with 5% toluene in hexane. It contained a compound identified as $(NiCp)_2C_5H_6$ (**6**) [4] (yield 3.2%) by means of mass spectroscopy. EI MS (70 eV) *m*/*e* (calc. for ^{58}Ni) 312 (M^+, 32%), 246 (100%), 188 (100%), 123 (35%), 58 (10%).

The next dark brown band was also collected (eluent: 10% toluene in hexane). It was evaporated to dryness, re-dissolved in hexane and purified by an additional column chromatography (eluent: 1% THF in hexane). The compound isolated was identified as $Cp_2Ni_3(CH_3C{\equiv}CCH_3)_3$ (**4**) (yield 5.4%). ^{1}H-NMR (C_6D_6) δ [ppm] 5.23 (s, 5H), 5.22 (s, 5H), 2.14 (s, 6H), 2.01 (s, 6H), 1.42 (s, 6H); ^{13}C-NMR (C_6D_6) δ [ppm] 13.71 ($H_3\mathit{C}$–C(C)=), 17.02 ($H_3\mathit{C}$–C≡), 31.12 ($H_3\mathit{C}$–C(Ni)=), 87.91 (C_5H_5), 90.22 (H_3C–*C*(C)=), 91.58 (C_5H_5), 102.99 (H_3C–*C*≡), 169.18 (H_3C–*C*(Ni)=); EI MS (70 eV) *m*/*e* 466 (M^+, 74%), 410 (100%), 368 (8%), 304 (47%), 246 (22%), 188 (16%), 123 (17%), 58 (7%).

Table 1
Crystal data and structure refinement for **5**

Empirical formula	$C_{19}H_{21}Ni_3$
Formula weight	425.45
Crystal size (mm)	0.5 × 0.4 × 0.1
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	
a (Å)	9.015(2)
b (Å)	14.608(3)
c (Å)	13.983(3)
β (°)	108.47(3)
V (Å^3)	1746.6(6)
Z	4
$D_{calc.}$ (g cm^{-3})	1.618
Temperature (K)	299(2)
Absorption coefficient (mm^{-1})	3.193
F(000)	876
Radiation	Mo–K_α ($\lambda = 0.71073$ Å, graphite monochromator)
θ range for data collection (°)	2.07–25.05
Scan type	$\omega - 2\theta$
Index ranges	$0 \le h \le 10$, $0 \le k \le 17$, $-16 \le l \le 15$
Reflections collected/unique	3011/2830 [$R_{int} = 0.0141$]
Absorption correction	Absorption procedure [0.85–1.13]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2830/0/201
Goodness-of-fit on F^2	1.069
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0262$; wR_2 (refined) = 0.0708
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.0403P)^2 + 0.5831P$ where $P = (F_o^2 + 2F_c^2)/3$
R indices (all data) [a,b]	$R_1 = 0.0388$; $wR_2 = 0.0757$
Largest difference peak and hole (e Å^{-3})	0.359 and −0.383

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

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

The next brown band was eluted with 25% toluene in hexane. It was evaporated to dryness, re-dissolved in hexane and purified by an additional column chromatography (eluent: 1% THF in hexane). The brown solid was obtained. It was identified as $(NiCp)_3(CH_3C{\equiv}CCH_3)$ (**5**) (yield 5.2%). EI MS (70 eV) m/e (calc. for ^{58}Ni) 423 (M^+, 99%), 369 (100%), 246 (36%), 188 (56%), 123 (32%), 58 (10%). The crystal structure was determined by X-ray analysis.

3.2. Crystal structure determination.

The crystal was sealed in a glass capillary under nitrogen stream. Intensities were collected with Kuma KM4 four circle diffractometer [10] in the $\omega - 2\theta$ mode with crystal of dimensions $0.5 \times 0.4 \times 0.1$ mm and Mo–K_α 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 3011 recorded data were corrected for Lorentz and polarization factors. An absorption correction following the Absorb procedure was also applied. The structure was solved by direct methods (SHELXS-97 [11]) and refined on F^2 by full-matrix least-squares program (SHELXL-97 [12]). 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 $R = 0.0262$ and $R_w = 0.0708$ for 2830 reflections with $I > 2\sigma(I)$ and 201 refined parameters. The crystal structure with the atom numbering system is presented on Fig. 1. 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.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**

Atom	x	y	z	U_{eq} [a]
Ni(1)	1478(1)	1683(1)	4189(1)	37(1)
Ni(2)	−1073(1)	2360(1)	3657(1)	41(1)
Ni(3)	1107(1)	3152(1)	3390(1)	39(1)
C(1)	−1036(5)	720(3)	2390(3)	61(1)
C(2)	−233(4)	1568(2)	2914(2)	39(1)
C(3)	1010(4)	2011(2)	2765(2)	39(1)
C(4)	1901(5)	1749(3)	2064(3)	59(1)
C(11)	3808(5)	1634(4)	5141(3)	71(1)
C(12)	2831(5)	1855(4)	5694(3)	69(1)
C(13)	1819(6)	1142(5)	5636(4)	86(2)
C(14)	2144(8)	475(4)	5034(5)	102(2)
C(15)	3386(7)	791(4)	4725(4)	93(2)
C(21)	−2842(8)	3329(4)	3540(7)	115(3)
C(22)	−2129(7)	3137(4)	4559(6)	102(2)
C(23)	−2382(6)	2214(4)	4704(4)	80(2)
C(24)	−3227(6)	1837(4)	3807(5)	78(1)
C(25)	−3516(5)	2515(5)	3077(5)	101(2)
C(31)	834(8)	4554(3)	3669(7)	102(2)
C(32)	694(8)	4435(4)	2718(6)	102(2)
C(33)	1985(14)	4121(4)	2616(6)	121(3)
C(34)	3042(6)	4034(4)	3545(9)	118(3)
C(35)	2335(12)	4295(4)	4232(4)	115(3)

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

Table 3
Selected bond lengths (Å) in **5** [a]

Ni(1)–C(3)	1.96(3)	Ni(3)–C(34)	2.124(5)
Ni(1)–C(2)	1.961(3)	Ni(3)–C(35)	2.139(5)
Ni(1)–C(12)	2.086(4)	C(1)–C(2)	1.503(5)
Ni(1)–C(15)	2.098(4)	C(2)–C(3)	1.366(5)
Ni(1)–C(11)	2.102(4)	C(3)–C(4)	1.500(5)
Ni(1)–C(13)	2.103(4)	C(11)–C(15)	1.364(7)
Ni(1)–C(14)	2.104(4)	C(11)–C(12)	1.382(6)
Ni(1)–Ni(3)	2.3928(7)	C(12)–C(13)	1.371(7)
Ni(1)–Ni(2)	2.3945(8)	C(13)–C(14)	1.378(8)
Ni(2)–C(2)	1.868(3)	C(14)–C(15)	1.400(8)
Ni(2)–C(21)	2.100(5)	C(21)–C(22)	1.393(10)
Ni(2)–C(25)	2.105(4)	C(21)–C(25)	1.397(9)
Ni(2)–C(22)	2.133(5)	C(22)–C(23)	1.393(8)
Ni(2)–C(24)	2.158(4)	C(23)–C(24)	1.360(7)
Ni(2)–C(23)	2.163(4)	C(24)–C(25)	1.387(7)
Ni(2)–Ni(3)	2.4089(7)	C(31)–C(32)	1.306(9)
Ni(3)–C(3)	1.871(3)	C(31)–C(35)	1.385(9)
Ni(3)–C(32)	2.077(5)	C(32)–C(33)	1.300(10)
Ni(3)–C(33)	2.085(5)	C(33)–C(34)	1.352(10)
Ni(3)–C(31)	2.113(5)	C(34)–C(35)	1.364(10)

[a] Estimated standard deviations in parentheses.

Table 4
Selected bond angles (°) in **5** [a]

C(3)–Ni(1)–C(2)	40.79(14)	C(3)–C(2)–C(1)	127.5(3)
C(3)–Ni(1)–Ni(3)	49.70(10)	C(3)–C(2)–Ni(2)	106.7(2)
C(2)–Ni(1)–Ni(3)	72.49(10)	C(1)–C(2)–Ni(2)	124.3(3)
C(3)–Ni(1)–Ni(2)	72.96(10)	C(3)–C(2)–Ni(1)	69.57(19)
C(2)–Ni(1)–Ni(2)	49.57(10)	C(1)–C(2)–Ni(1)	129.2(3)
Ni(3)–Ni(1)–Ni(2)	60.42(2)	Ni(2)–C(2)–Ni(1)	77.39(13)
C(2)–Ni(2)–Ni(1)	53.04(10)	C(2)–C(3)–C(4)	127.9(3)
C(2)–Ni(2)–Ni(3)	73.57(10)	C(2)–C(3)–Ni(3)	105.7(2)
Ni(1)–Ni(2)–Ni(3)	59.76(2)	C(4)–C(3)–Ni(3)	125.2(3)
C(3)–Ni(3)–Ni(1)	53.02(10)	C(2)–C(3)–Ni(1)	69.64(19)
C(3)–Ni(3)–Ni(2)	74.04(10)	C(4)–C(3)–Ni(1)	127.9(3)
Ni(1)–Ni(3)–Ni(2)	59.82(2)	Ni(3)–C(3)–Ni(1)	77.28(12)

[a] Estimated standard deviations in parentheses.

4. Supplementary material available

Crystallographic data for the structure (listings of bond lengths and angles, anisotropic thermal parameters, hydrogen atom 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.cam.ac.uk).

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