

# New insights into the reaction of nickelocene with methyllithium: the isolation and crystal structure of $(\text{NiCp})_3(\mu_3\text{-CH})$

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## Abstract

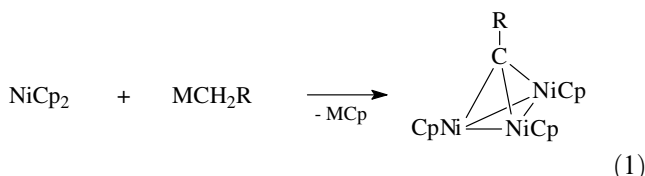
Thermolysis of the cyclopentadienylnickelmethyl complex  $[\text{NiCp}(\text{CH}_3)(\eta^2\text{CH}_2=\text{CHC}_4\text{H}_9)]$  in various solvents was studied. Separation of products by means of column chromatography allowed to isolate and crystallographically characterise  $(\mu_3\text{-methylidyne})\text{tris}(\text{cyclopentadienylnickel})$  cluster  $(\text{NiCp})_3(\mu_3\text{-CH})$  (**1**). Cluster **1** crystallised from a hexane/THF mixture in hexagonal crystal system and  $P6_3$  space group. Ni–Ni and Ni–C(methylidyne) distances were 2.3558(10) and 1.823(4) Å, respectively. Detailed studies showed that cluster  $(\text{NiCp})_3(\mu_3\text{-CH})$  (**1**) was produced during the chromatography on alumina. The plausible precursor to **1** is described as  $(\text{NiCp})_6\text{C}$ .

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**Keywords:** Nickel; Clusters; Alkylidyne clusters; Cyclopentadienyl; Crystal structure

## 1. Introduction

Bis(cyclopentadienyl)nickel (nickelocene) reacts with benzylmagnesium compounds at room temperature in ether yielding diamagnetic  $\mu_3\text{-benzylidyne}$  cyclopentadienyltrinickel clusters (Eq. (1),  $\text{R} = \text{C}_6\text{H}_5$  or  $\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$ ,  $\text{M} = \text{MgCl}$ ) [1].



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Since this initial report, clusters of the general formula  $(\text{NiCp})_3(\mu_3\text{-CR})$  have attracted considerable attention for both mechanistic and structural investigations [2]. The synthetic routes to these clusters established up to now include reactions of nickelocene with suitably substituted alkylolithium or Grignard reagents (Eq. (1),  $\text{R} = -\text{C}(\text{CH}_3)_3$ ,  $-\text{Si}(\text{CH}_3)_3$ ,  $\text{M} = \text{Li}$  [3];  $\text{R} = \text{CH}(\text{CH}_3)\text{Ph}$ ,  $\text{CH}_3$ ,  $(\text{CH}_2)_6\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{M} = \text{MgBr}$  [4]), reactions of nickelocene with vinylolithium compounds possessing an  $\alpha\text{-H}$  atom [5], and reaction of  $\sigma\text{-alkyl}$  complexes  $[\text{NiCp}(\text{CH}_2\text{R})(\text{PPh}_3)]$  with  $n\text{-butyllithium}$  in the presence of an excess of nickelocene [3]. Stepwise substitution of isolobal groups in  $[\text{Co}(\text{CO})_3]_3(\mu_3\text{-CCO}_2\text{CH}_3)$  using  $[\text{CpNi}(\text{CO})]_2$  as a metal exchange reagent also yields a trinickel cluster  $(\text{NiCp})_3(\mu_3\text{-CCO}_2\text{CH}_3)$  [6]. More recently, we have reported that these clusters were also formed as a result of C–H bond activation when nickelocene reacted with phenyllithium (Eq. (2),  $\text{R} =$



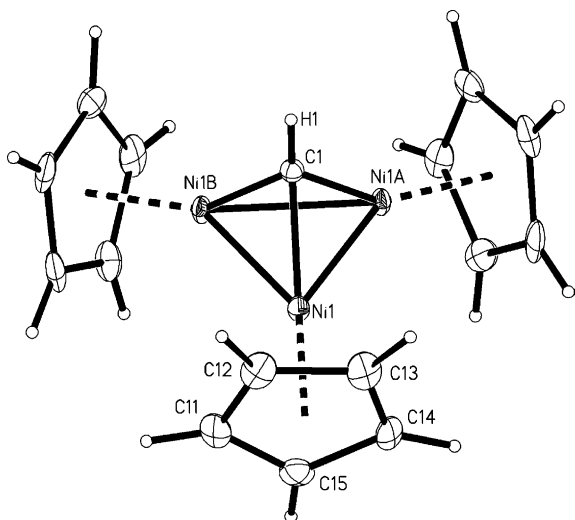


Fig. 1. The ORTEP drawing of **1** with atom numbering scheme. The thermal displacement ellipsoids are drawn at the 50% probability level.

for  $R = \text{CH}(\text{CH}_3)\text{Ph}$  [4]). Also the Ni–C(1) distance in **1** (1.823(4) Å) does not differ from the others (from 1.808(5) Å for  $R = \text{C}_4\text{H}_9$  [9] to 1.888(4) Å for  $R = \text{CH}(\text{CH}_3)\text{Ph}$  [4]). The average nickel to the centre

of the cyclopentadienyl ring distances are similar in all published compounds (1.742 Å in **1**, 1.738 Å [9], 1.747 Å [4] and 1.755 Å for  $R = -\text{CH}_3$  [5]). The Ni–Ni and Ni–C(1) bonds in  $(\text{NiCp}^*)_3(\mu_3\text{-CH})(\mu\text{-H})$  [12] are longer than the corresponding bonds in **1** (Ni–Ni: 2.415 and 2.3558 Å; Ni–C(1): 1.913 and 1.823 Å, respectively). This is probably caused by the differences in the size of the methylated and non-methylated cyclopentadienyl rings in both compounds.

Our attempts were initially dedicated to searching for a solvent that would favour formation of cluster **1** versus **2**. To test this idea, we have examined the crude reaction mixtures by  $^1\text{H}$  NMR and mass spectroscopy in order to estimate the ratio of the two clusters. However, only the ethylidyne cluster **2** was unambiguously detected in the crude reaction mixtures from the thermolysis of **3** in THF,  $\text{Et}_2\text{O}$  or cyclohexane. Surprisingly, **1** was not present in these residues. Therefore, we propose that **1** was actually formed upon treatment of the crude reaction mixture with  $\text{Al}_2\text{O}_3$  during the column chromatography. In line with this proposal, adding  $\text{Al}_2\text{O}_3$  to the crude reaction mixture and stirring for a few days allows for the detection of **1** in the mixture by  $^1\text{H}$  NMR.

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

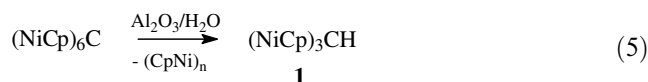
Empirical formula	$\text{C}_{16}\text{H}_{16}\text{Ni}_3$
Crystal size (mm)	$0.1 \times 0.1 \times 0.05$
Crystal system	Hexagonal
Space group	$P6_3$ (No. 173)
Unit cell dimensions	
$a$ (Å)	9.012(3)
$b$ (Å)	9.012(3)
$c$ (Å)	9.701(2)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	120
$V$ (Å <sup>3</sup> )	682.3(4)
$Z$	2
Formula weight	384.36
$D_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.871
$T$ (K)	100(1)
Absorption coefficient ( $\text{mm}^{-1}$ )	4.075
$F(000)$	392
Radiation	Mo $K\alpha$ ( $\lambda = 0.71073$ Å, graphite monochromator)
$\theta$ Range for data collection (°)	4.20–28.44
Scan type	$\omega$
Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 9, -12 \leq l \leq 12$
Reflections collected/unique ( $R_{\text{int}}$ )	4683/1076 (0.0885)
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1076/0/61
Goodness-of-fit on $F^2$	1.056
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0357$
$R = \sum(F_o - F_c) / \sum F_o$	$wR_2$ (refined) = 0.0886
$wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$	$w^{-1} = \sigma^2(F_o^2) + (0.0591P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
Weighting scheme	$R_1 = 0.0380; wR_2 = 0.0900$
$R$ indices (all data)	0.009(2)
Extinction coefficient	0.986 and $-0.721$
Largest difference peak and hole ( $e \text{ \AA}^{-3}$ )	

Table 2  
Selected bond lengths (Å) and bond angles (°) in **1**<sup>a</sup>

Ni1–Ni1A	2.3558(10)	Ni1–Cp(centre)	1.742(1)
Ni1–C1	1.823(4)	C1–H1	0.89(8)
Ni1–C11	2.109(4)	C11–C15	1.425(6)
Ni1–C14	2.112(4)	C11–C12	1.421(7)
Ni1–C13	2.115(4)	C12–C13	1.393(6)
Ni1–C12	2.117(4)	C13–C14	1.428(7)
Ni1–C15	2.144(4)	C14–C15	1.429(6)
C1–Ni1–Ni1A	49.7 (2)	C13–C12–C11	108.7(4)
Ni1–C1–H1	131.7(2)	C12–C13–C14	107.8(4)
Ni1A–Ni1–Ni1B	60.0	C13–C14–C15	108.5(4)
Ni1–C1–Ni1A	80.5(2)	C11–C15–C14	106.5(4)
C12–C11–C15	108.4(3)		

<sup>a</sup> Estimated standard deviations in parentheses.

Mass spectra of the crude reaction mixtures featured peaks at  $m/z = 750$  (<sup>58</sup>Ni) with an isotopic pattern consistent with the presence of six nickel atoms and at  $m/z = 642$  (<sup>58</sup>Ni) with an isotopic pattern consistent with the presence of five nickel atoms. They can be assigned to molecular peaks of (NiCp)<sub>6</sub>C and (NiCp)<sub>5</sub>(μ-CCH<sub>3</sub>), respectively. All attempts to isolate these clusters by column chromatography on Al<sub>2</sub>O<sub>3</sub> failed so far. However, extraction of sparingly soluble thermolysis residues produced deep-brown solutions which yielded a brown powder after crystallisation. This material was characterised by mass spectra that were consistent with the molecular formula of (NiCp)<sub>6</sub>C. <sup>1</sup> Cluster (NiCp)<sub>6</sub>C was previously detected by mass spectroscopy in mixtures obtained from reaction of nickelocene with methyllithium [2,13,21]. Pathways leading to the formation of this cluster from transient {CpNiCH<sub>3</sub>} species were discussed by Pasynkiewicz [13,21]. Because cluster **2** is stable to purification on alumina and has been isolated in a number of cases without any traces of **1** [5,10], we assume that cluster (NiCp)<sub>6</sub>C is the most likely precursor to **1** (Eq. (5)).



In conclusion, we have isolated and structurally characterised cluster (NiCp)<sub>3</sub>(μ<sub>3</sub>-CH) (**1**). The title compound was apparently formed during the column chromatography of residues obtained from the thermolysis of the complex **3**. We also identified by mass spectroscopy cluster (NiCp)<sub>6</sub>C which we consider the most probable source of cluster **1**.

<sup>1</sup> To the best of our knowledge, only one hexameric cyclopentadienylnickel cluster, i.e. (NiCp)<sub>6</sub>, has been characterised by X-ray diffraction so far [20].

### 3. Experimental

#### 3.1. Techniques and materials

All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were distilled from potassium benzophenone ketyl. Solutions of metyllithium were prepared from CH<sub>3</sub>Br and Li in Et<sub>2</sub>O. Nickelocene was prepared according to the literature procedure [22]. Al<sub>2</sub>O<sub>3</sub> (Merck, neutral) was deactivated with 5% wt of degassed water; 1-hexene (Fluka) was distilled under argon and stored over MS 4A. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Mercury-400BB spectrometer in C<sub>6</sub>D<sub>6</sub> at ambient temperature. Mass spectra (EI, 70 eV) were measured on an AMD-604 mass spectrometer. Elemental analyses (C, H) were performed on Perkin–Elmer 2400 analyser.

Complex **3** was prepared from nickelocene and LiCH<sub>3</sub> in the presence of 1-hexene in Et<sub>2</sub>O/THF (1:1) as described previously [15]. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 5.04 (s, Cp, 5H), 3.53 (bs, =CH, 1H), 2.93 (bs, =CH, 1H), 2.78 (bs, =CH, 1H), 1.31 (m, CH<sub>2</sub>, 6H), 0.88 (bs, CH<sub>3</sub>, 3H), –0.71 (s, Ni–CH<sub>3</sub>, 3H).

#### 3.2. Synthesis of (NiCp)<sub>3</sub>(μ<sub>3</sub>-CH) (**1**)

Complex **3**, freshly prepared from 1.09 g (5.78 mmol) of NiCp<sub>2</sub>, was dissolved in 40 cm<sup>3</sup> of THF at 0 °C. This solution was warmed to room temp. and stirred for 7 days. The resulting mixture was evaporated to dryness, then re-dissolved in toluene (40 cm<sup>3</sup>) and filtered to remove a black solid (see below). The filtrate was chromatographed on Al<sub>2</sub>O<sub>3</sub> using hexane/toluene (1:1). The first eluted fraction was identified as (NiCp)<sub>3</sub>(μ<sub>3</sub>-CCH<sub>3</sub>) (**2**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 5.15 (s, Cp, 15H), 3.71 (s, CH<sub>3</sub>, 3H). EI-MS (70 eV)  $m/z$  (relative intensity) (<sup>58</sup>Ni): 396 (M<sup>+</sup>, 40%), 330 ([M – CpH]<sup>+</sup>, 33%), 304 ([Ni<sub>3</sub>Cp<sub>2</sub>]<sup>+</sup>, 51%), 246 ([Ni<sub>2</sub>Cp<sub>2</sub>]<sup>+</sup>, 32%), 188 ([NiCp<sub>2</sub>]<sup>+</sup>, 28%), 123 ([NiCp]<sup>+</sup>, 17%) [5,10,15]. The second fraction consisted of a mixture of (NiCp)<sub>3</sub>(μ<sub>3</sub>-CCH<sub>3</sub>) (**2**) and (NiCp)<sub>3</sub>(μ<sub>3</sub>-CH) (**1**). This fraction was reduced in volume to ca. 5 ml and subjected to the second chromatography using hexane/toluene (1:1). Cluster **1** was eluted after cluster **2** as a pink band. It was further purified by crystallisation from hexane/THF and obtained as a brown-red solid. (NiCp)<sub>3</sub>(μ<sub>3</sub>-CH) (**1**): no melting observed up to 290 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 12.85 (s, CH, 1H), 5.17 (s, Cp, 15H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ, ppm): 262.2 (CH), 87.59 (Cp). EI-MS (70 eV)  $m/z$  (relative intensity) (<sup>58</sup>Ni): 382 (M<sup>+</sup>, 89%), 314 ([M – C<sub>5</sub>H<sub>8</sub>]<sup>+</sup>, 14%), 304 ([Ni<sub>3</sub>Cp<sub>2</sub>]<sup>+</sup>, 63%), 246 ([Ni<sub>2</sub>Cp<sub>2</sub>]<sup>+</sup>, 47%), 188 ([NiCp<sub>2</sub>]<sup>+</sup>, 26%), 123 ([NiCp]<sup>+</sup>, 15%), 66 (CpH<sup>+</sup>, 13%), 65 (Cp<sup>+</sup>, 12%), 58 (Ni<sup>+</sup>, 8%). HRMS Calc. for C<sub>16</sub>H<sub>16</sub><sup>58</sup>Ni<sub>3</sub>: 381.93124; found: 381.92951. Anal. Calc.

for  $C_{16}H_{16}Ni_3$ : C, 50.0; H, 4.20. Found: C, 49.6; H, 4.25%.

Reactions in cyclohexane,  $Et_2O$  and  $Bu_2O$  were carried out similarly. For cyclohexane, cluster **2** was isolated in 8% yield (calculated for nickelocene used) together with traces of **1**. For  $Et_2O$  cluster **2** was isolated in 13% yield. For  $Bu_2O$  mixtures of **2** and **1** were eluted from the column.

### 3.3. Isolation of $(NiCp)_6C$

The black solid separated by filtration of the thermolysis products of complex **3** was extracted with THF ( $3 \times 40 \text{ cm}^3$ ). The combined extracts were filtered and evaporated to dryness. A black residue was obtained, which was washed several times with hexane and toluene, then re-dissolved in THF ( $20 \text{ cm}^3$ ) and layered with hexane ( $50 \text{ cm}^3$ ). A brown powder precipitated after several days.  $(NiCp)_6C$  (0.058 g): EI-MS (70 eV)  $m/z$  (relative intensity) ( $^{58}Ni$ ): 750 ( $M^+$ , 3%), 562 ( $[M - NiCp_2]^+$ , 12%), 496 ( $[M - NiCp_2 - CpH]^+$ , 2%), 188 ( $[NiCp_2]^+$ , 26%), 123 ( $[NiCp]^+$ , 32%), 66 ( $CpH^+$ , 100%), 65 ( $Cp^+$ , 69%).

### 3.4. Treatment of the crude reaction mixture with $Al_2O_3$

The crude reaction mixture from thermolysis of **3** in THF was examined by  $^1H$  NMR and MS. Peaks corresponding to **1** (i.e. the singlet at 12.8 ppm and  $M^+$  at  $m/z = 382$  ( $^{58}Ni$ )) were not observed. Then the mixture was re-dissolved in toluene and filtered as described above.  $Al_2O_3$  (deactivated with 5% wt of  $H_2O$ ) was added to the filtrate and the resulting slurry was stirred at room temp. for 7d after which time the supernatant was transferred to another Schlenk tube. The remaining  $Al_2O_3$  was washed with toluene. The combined solutions were evaporated to dryness to afford a black solid. The following peaks were identified in the  $^1H$  NMR spectrum ( $C_6D_6$ ,  $\delta$ , ppm): 12.84 (s, CH, **1**), 5.17 (s, Cp, **1**), 5.15 (s, Cp, **2**, ca. 1:0.8 vs. Cp of **1**), 3.71 (s,  $CH_3$ , **2**).

### 3.5. Crystal structure determination

Crystals suitable for X-ray determination were grown from a hexane/THF (ca. 20:1) solution at 20 °C. The crystal was mounted on glass fibre and then flash-frozen to 100 K (Oxford Cryosystem-Cryostream Cooler). Preliminary examination and intensity data collections were carried out on a Kuma KM4 CCD  $\kappa$ -axis diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Crystals were positioned at 65 mm from the KM4CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 35 sec. The data were corrected for Lorentz and polarization effects. The absorption correction was also applied. Data reduction and analysis were carried out with the Kuma Diffraction programs [23].

The structure was solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXTL programs [24]. All hydrogen atoms were found by Fourier synthesis. The positions of the H atoms were determined from difference electron-density maps, but for Cp bonded H atoms positions were finally calculated after each cycle of refinement using a riding model. Hydrogen atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the carbon atom to which they are bonded. Application of the twin matrix (0 1 0,  $-1 -1 0$ , 0 0  $-1$ ) led to an immediate benefit upon least-squares analysis and the refinement proceeded smoothly to the final reported model. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

## 4. Supplementary data

Crystallographic data for the structural analysis of **1** have been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 234672. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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