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# New insights into the reaction of nickelocene with methyllithium: the isolation and crystal structure of (NiCp)<sub>3</sub>(µ<sub>3</sub>-CH)

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### Abstract

Thermolysis of the cyclopentadienylnickelmethyl complex [NiCp(CH<sub>3</sub>)( $\eta^2$ CH<sub>2</sub>=CHC<sub>4</sub>H<sub>9</sub>)] in various solvents was studied. Separation of products by means of column chromatography allowed to isolate and crystallographically characterise ( $\mu_3$ -methylidyne)tris(cyclopentadienylnickel) cluster (NiCp)<sub>3</sub>( $\mu_3$ -CH) (1). Cluster 1 crystallised from a hexane/THF mixture in hexagonal crystal system and *P*6<sub>3</sub> space group. Ni–Ni and Ni–C(methylidyne) distances were 2.3558(10) and 1.823(4) Å, respectively. Detailed studies showed that cluster (NiCp)<sub>3</sub>( $\mu_3$ -CH) (1) was produced during the chromatography on alumina. The plausible precursor to 1 is described as (NiCp)<sub>6</sub>C.

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## 1. Introduction

Bis(cyclopentadienyl)nickel (nickelocene) reacts with benzylmagnesium compounds at room temperature in ether yielding diamagnetic  $\mu_3$ -benzylidyne cyclopentadienyltrinickel clusters (Eq. (1), R = C<sub>6</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>, M = MgCl) [1].



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Since this initial report, clusters of the general formula (NiCp)<sub>3</sub>( $\mu_3$ -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 alkyllithium or Grignard reagents (Eq. (1),  $R = -C(CH_3)_3$ ,  $-Si(CH_3)_3$ , M = Li [3];  $R = CH(CH_3)Ph$ ,  $CH_3$ ,  $(CH_2)_6CH_3$ ,  $C_2H_5$ , M = MgBr [4]), reactions of nickelocene with vinyllithium compounds possessing an  $\alpha$ -H atom [5], and reaction of  $\sigma$ -alkyl complexes  $[NiCp(CH_2R)(PPh_3)]$  with *n*-butyllithium in the presence of an excess of nickelocene [3]. Stepwise substitution of isolobal groups in  $[Co(CO)_3]_3(\mu_3-CCO_2CH_3)$ using [CpNi(CO)]<sub>2</sub> as a metal exchange reagent also yields a trinickel cluster  $(NiCp)_3(\mu_3-CCO_2CH_3)$  [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), R = OTT

*n*-butyl, *n*-octyl) or sodium in the presence of a terminal alkene [7–9], as well as through the cleavage of THF by cyclopentadienylnickel species [10].

NiCp<sub>2</sub> + LiPh + CH<sub>2</sub>=CHR 
$$\xrightarrow{-\text{LiCp}}_{-\text{PhPh}}$$
 CpNi  $\xrightarrow{\text{CHR}}$  (2)

Despite this extensive experimental work, the first in the family of alkylidyne tri(cyclopentadienylnickel) clusters, i.e., methylidyne tri(cyclopentadienylnickel) (NiCp)<sub>3</sub>( $\mu_3$ -CH) (1), the expected product of the reaction of nickelocene with methyllithium (Eq. (1), R = H), has not been isolated and its crystal structure has not been determined up to now. The reaction of methyllithium with nickelocene yields the ethylidyne cluster (NiCp)<sub>3</sub>( $\mu_3$ -CCH<sub>3</sub>) (2) as the main product [5,11] (Eq. (3)).

$$3 \operatorname{NiCp}_2 + 4 \operatorname{LiCH}_3 \xrightarrow[-CH_4]{} CpNi \xrightarrow{-CH_4} CpNiCp (3)$$

Moreover, [NiCp\*(acac)] upon treatment with methyllithium in diethyl ether yields a paramagnetic trinickel cluster (NiCp\*)<sub>3</sub>( $\mu_3$ -CH)( $\mu$ -H) bearing both a  $\mu_3$ -methylidyne ligand and a bridging hydride [12]. Thus, **1** has been described as species unstable to the reaction conditions [13], or obtained in mixtures resulting from thermolyses of cyclopentadienylnickel alkene complexes [NiCp(CH<sub>3</sub>)( $\eta^2$ CH<sub>2</sub>=CHR)] [14,15]. In order to completely characterise this elusive cluster we have undertaken a more detailed study on the thermal decomposition of the 1-hexene complex **3** in various solvents.

#### 2. Results and discussion

Complex 3 was prepared as described earlier (Eq. (4), R = n-butyl) [15].



Nickelocene was reacted with methyllithium in a 1:1 mixture of  $Et_2O$  and THF at -40 °C followed by hydrolysis with water at 0 °C. Complex **3** was isolated by extraction with hexane at -78 °C as dark-red oil and identified by means of <sup>1</sup>H NMR [15].

A sample of complex **3** was dissolved in a solvent (THF, cyclohexane, Et<sub>2</sub>O or dibutyl ether) and stirred at ambient temperature for 7 days. The resulting brown-green mixture was subjected to column chromatography on Al<sub>2</sub>O<sub>3</sub> producing 3–4 coloured bands. The first one was identified as (NiCp)<sub>3</sub>( $\mu_3$ -CCH<sub>3</sub>) (**2**) [5,15] while the second one consisted of a mixture of clusters **2** and **1**. Repeated chromatography and crystallisation of the second fraction provided cluster **1** (Scheme 1).

We have previously traced back the origin of the ethylidyne ligand in 2 to the cleavage of THF when nickelocene was treated with phenyllithium in THF [10]. In the present case, the thermolysis of 3 afforded cluster 2regardless of the solvent used. While the origin of the two-carbon unit in cluster 2 remains to be elucidated, we assume that it does not involve a solvent molecule.

<sup>1</sup>H NMR spectrum of  $(NiCp)_3(\mu_3-CH)$  (1) features two singlets at 12.85 and 5.17 ppm corresponding to the methylidyne and cyclopentadienyl protons, respectively [15]. The chemical shift of the methylidyne proton is in the same range as reported for  $[Co(CO)_3]_3(\mu_3-CH)$ [16] and the analogous methylidyne mixed-metal clusters [17]. It is consistent with a negative charge on the carbyne carbon atom in 1. This conclusion is further supported by molecular calculations performed for  $[Co(CO)_3]_3(\mu_3$ -CH) [18,19]. The mass spectrum (EI) of 1 contains the parent ion at m/z = 382 (<sup>58</sup>Ni) and ions typical for the fragmentation of cyclopentadienyltrinickel clusters:  $[Ni_3Cp_2]^+$ ,  $[Ni_2Cp_2]^+$ ,  $[NiCp_2]^+$ ,  $[NiCp_1]^+$ . However, fragmentation by a loss of a CpH ligand, which is characteristic for cluster 2, is not evident here. The highest fragment is observed at m/z = 314 (<sup>58</sup>Ni) and corresponds to  $[M-C_5H_8]^+$ .

Crystallisation of 1 from a hexane/THF mixture afforded crystals suitable for single-crystal X-ray analysis. The molecular structure of  $(NiCp)_3(\mu_3-CH)$  (1) is presented on Fig. 1. Crystal data, data collection and refinement parameters are given in Table 1. Selected bond lengths and angles are shown in Table 2.

The H(1) atom was located from difference Fourier map and refined without any restrains. A comparison of bond lengths in **1** with those in other clusters (NiCp)<sub>3</sub>( $\mu_3$ -CR) [4–6,9] leads to the conclusion that size of the R group bonded to the C(1) has no significant influence on those distances. The Ni–Ni bond length in **1** (2.3558(10) Å) is close to those published for other clusters (from 2.304(1) Å for R = C<sub>4</sub>H<sub>9</sub> [9] to 2.355(1) Å





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

for R = CH(CH<sub>3</sub>)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 = C<sub>4</sub>H<sub>9</sub> [9] to 1.888(4) Å for R = CH(CH<sub>3</sub>)Ph [4]). The average nickel to the centre

Table 1

Crystal data and structure refinement for 1

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  $R = -CH_3$  [5]). The Ni–Ni and Ni–C(1) bonds in (NiCp\*)<sub>3</sub>( $\mu_3$ -CH)( $\mu$ -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 <sup>1</sup>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, Et<sub>2</sub>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  $Al_2O_3$  during the column chromatography. In line with this proposal, adding  $Al_2O_3$  to the crude reaction mixture and stirring for a few days allows for the detection of **1** in the mixture by <sup>1</sup>H NMR.

crystal data and structure remement for 1		
Empirical formula	C <sub>16</sub> H <sub>16</sub> Ni <sub>3</sub>	
Crystal size (mm)	$0.1 \times 0.1 \times 0.05$	
Crystal system	Hexagonal	
Space group	<i>P</i> 6 <sub>3</sub> (No. 173)	
Unit cell dimensions		
<i>a</i> (Å)	9.012(3)	
b (Å)	9.012(3)	
c (Å)	9.701(2)	
α (°)	90	
β (°)	90	
γ (°)	120	
$V(\text{\AA}^3)$	682.3(4)	
Ζ	2	
Formula weight	384.36	
$D_{\rm calc} ({\rm Mg}\;{\rm m}^{-3})$	1.871	
<i>T</i> (K)	100(1)	
Absorption coefficient (mm <sup>-1</sup> )	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	ω	
Index ranges	$-11 \leqslant h \leqslant 11, \ -11 \leqslant k \leqslant 9, \ -12 \leqslant l \leqslant 12$	
Reflections collected/unique $(R_{int})$	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 <i>R</i> indices $[I > 2\sigma(I)]$		
$R = \sum (F_{\rm o} - F_{\rm c}) / \sum F_{\rm o}$	$R_1 = 0.0357$	
$wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$	$wR_2$ (refined) = 0.0886	
Weighting scheme	$w^{-1} = \sigma^2 (F_o^2) + (0.0591P)^2$ where $P = (F_o^2 + 2F_c^2)/3$	
R indices (all data)	$R_1 = 0.0380; wR_2 = 0.0900$	
Extinction coefficient	0.009(2)	
Largest difference peak and hole (e $\dot{A}^{-3}$ )	0.986 and -0.721	

Table 2 Selected bond lengths (Å) and bond angles (°) in  $1^a$ 

U		0 ()	
Nil–NilA	2.3558(10)	Nil-Cp(centre)	1.742(1)
Ni1-C1	1.823(4)	C1-H1	0.89(8)
Nil-Cl1	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)
Nil-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- $CCH_3$ ), 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 vielded 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)).

$$(NiCp)_{6}C \xrightarrow[-(CpNi)_{n}]{Al_{2}O_{3}/H_{2}O} (NiCp)_{3}CH$$
(5)

In conclusion, we have isolated and structurally characterised cluster  $(NiCp)_3(\mu_3$ -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  $(NiCp)_6C$  which we consider the most probable source of cluster **1**.

## 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>,  $\delta$ , 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 $(NiCp)_3(\mu_3-CH)$ (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  $Al_2O_3$  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>,  $\delta$ , 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  $(NiCp)_3(\mu_3-CH)$  (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>,  $\delta$ , ppm): 12.85 (s, CH, 1H), 5.17 (s, Cp, 15H).<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , 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 ( $[Ni_3Cp_2]^+$ , 63%), 246 ( $[Ni_2Cp_2]^+$ , 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.

<sup>&</sup>lt;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].

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 cm<sup>3</sup>) and layered with hexane (50 cm<sup>3</sup>). A brown powder precipitated after several days. (NiCp)<sub>6</sub>C (0.058 g): EI-MS (70 eV) *m/z* (relative intensity) (<sup>58</sup>Ni): 750 (M<sup>+</sup>, 3%), 562 ([M – NiCp<sub>2</sub>]<sup>+</sup>, 12%), 496 ([M – NiCp<sub>2</sub> – CpH]<sup>+</sup>, 2%), 188 ([NiCp<sub>2</sub>]<sup>+</sup>, 26%), 123 ([NiCp]<sup>+</sup>, 32%), 66 (CpH<sup>+</sup>, 100%), 65 (Cp<sup>+</sup>, 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 <sup>1</sup>H NMR and MS. Peaks corresponding to **1** (i.e. the singlet at 12.8 ppm and M<sup>+</sup> at m/z = 382 (<sup>58</sup>Ni)) were not observed. Then the mixture was re-dissolved in toluene and filtered as described above. Al<sub>2</sub>O<sub>3</sub> (deactivated with 5% wt of H<sub>2</sub>O) 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<sub>2</sub>O<sub>3</sub> was washed with toluene. The combined solutions were evaporated to dryness to afford a black solid. The following peaks were identified in the <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , 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<sub>3</sub>, 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 (010, -1-10, 00-1) 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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