

Synthesis and structure of (η^5 -cyclopentadienyl)(η^5 -(1-(η^5 -cyclopentadienyl)-2-phenyl-3- methyl-1-nickelindenyl)nickel – the first analogue of nickelocene with a nickelacyclopentadienyl ring

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Abstract

A new metallacyclic compound (η^5 -cyclopentadienyl)(η^5 -(1-(η^5 -cyclopentadienyl)-2-phenyl-3-methyl-1-nickelindenyl)nickel was synthesised and characterised. Its molecular and crystal structure was determined by X-ray measurements. It crystallises from hexane:THF mixture in the monoclinic crystal system and the $P2_1/c$ space group. This is the first example of the homometallic metallocene of nickel. Like in nickelocene the central nickel atom has 20 valence electrons, so the compound can be regarded as the first nickelacyclic analogue of nickelocene.

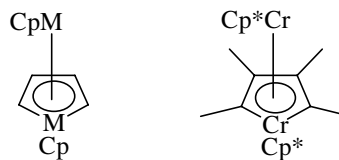
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1. Introduction

Metallametalloenes are compounds in which one cyclopentadienyl group in a symmetric metallocene is replaced with metallacyclopentadienyl ring.

All metallametalloenes of the type shown in the picture below, which were synthesised up to now, belong to group 8 (iron) and 9 (cobalt) and their central atom possesses 18 or 19 VE [1]. The only exception is the analogue of chromocene with 16 valence electrons [2].



So far nickelanickelocene (analogue of nickelocene) was not synthesised. Nickelocene is the only metallocene with metal atom possessing 20 VE.

Activation of C–H bonds in hydrocarbons by various transition metal compounds has been examined thoroughly for many years. In order to extend this knowledge we have dealt with activation of olefins

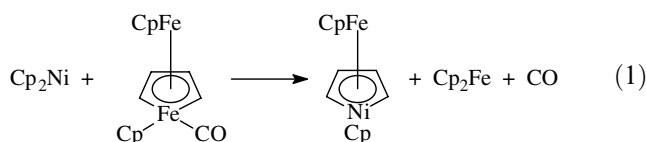
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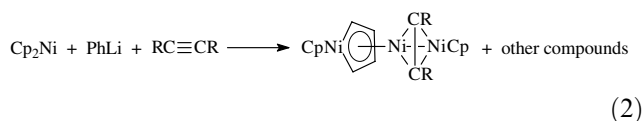
by cyclopentadienylnickel species formed during reduction of nickelocene. Earlier reductions of nickelocene were carried out using such reducing agents as organolithium or organomagnesium compounds [3,4], Na(Hg)/ROH [5], K/liquid NH₃ [6] or sodium naphthalenide in THF [7].

We have found that while reducing nickelocene in polar solvents with alkali metals, very reactive organonickel species {NiCp} are formed. Having employed them in activation of different olefins we obtained several interesting organonickel products [8,9]. Jonas [10] has found that other metallocenes may react with alkali metals with the formation of half-sandwich complexes.

Only few examples of complexes possessing nickela-cyclopentadienyl ring are known so far. The first one was prepared by Simpson and co-workers [11] by an insertion of a {NiCp} species into a labile ferracyclopentadiene (Eq. (1)).



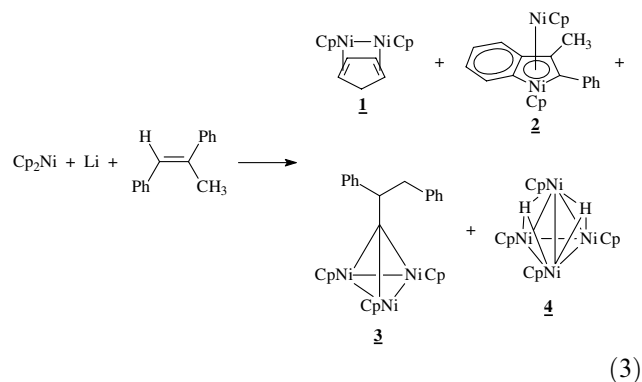
We have synthesised compound containing nickela-cyclopentadienyl ring in the reaction of nickelocene with phenyllithium and diphenylacetylene [12] (Eq. (2)).



In this paper, we describe the synthesis and structure of (η⁵-cyclopentadienyl)(η⁵-(1-(η⁵-cyclopentadienyl)-2-phenyl-3-methyl-1-nickelindenyl)nickel – an analogue of nickelocene.

2. Results

Nickelocene was reduced with lithium in the presence of *trans*-1,2-diphenylpropene (molar ratio 1:1.4:1) in THF. Products of the reaction were chromatographed on alumina. Four coloured, air-sensitive bands were obtained. The first one (green) contained unreacted nickelocene, the second one (blue) – dinickel compound (NiCp)₂CpH [13] **1**, the third one (brown) – new compound **2**. The last fourth fraction (deep-brown) contained compound **3** and previously described cluster **4** [3] (Eq. (3)).



EIMS spectrum of **2** showed the parent ion at *m/e* 438 (⁵⁸Ni calc.) with an isotopic pattern characteristic for two nickel atoms in a molecule. In the ¹H NMR spectrum of **2** there were no signals in the range between 0 and 10 ppm due to paramagnetic properties of this complex. Crystals of **2** appropriate for X-ray diffraction studies were obtained from hexane:THF solution. The molecular structure of **2** is presented in 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 compound crystallises in a monoclinic crystal system. Ni–Ni distance (2.42 Å) is within the range of nickel–nickel single bonds. Four carbon atoms and Ni(2) atom form a five-membered nickela-cyclopentadienyl ring (Fig. 1). Ni(1) atom is bonded to this ring and to cyclopentadienyl group. Ni(1)–C(11) and Ni(1)–C(12) distances (2.25 and 2.21 Å) are longer than Ni(1)–C(17) and Ni(1)–C(18) ones (2.19 and 2.12 Å, respectively). The latter are comparable with distances in other compounds where a nickel atom is bonded to nickela-cyclopentadienyl ring [12].

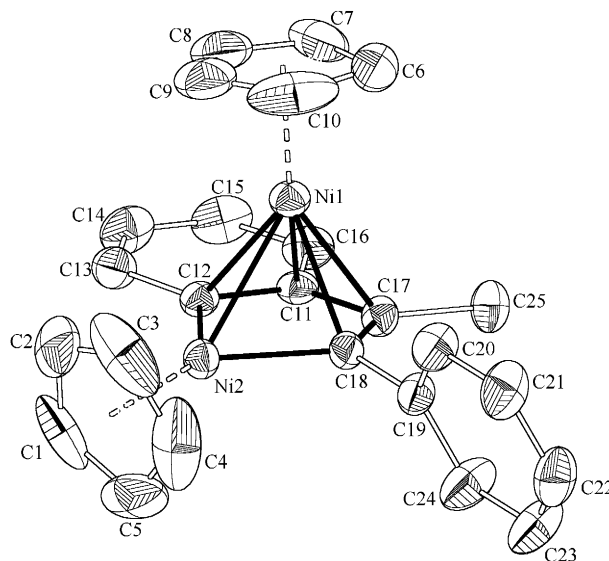


Fig. 1. ORTEP view of the molecular structure of **2** showing atom numbering scheme. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Crystal data and structure refinement parameters for **2**

Empirical formula	C ₂₅ H ₂₂ Ni ₂
Crystal size (mm)	0.7 × 0.5 × 0.4
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
<i>a</i> (Å)	15.999(3)
<i>b</i> (Å)	8.980(2)
<i>c</i> (Å)	13.954(3)
α (°)	90
β (°)	94.59(3)
γ (°)	90
Volume (Å ³)	1998.4(7)
Z	4
Formula weight	439.85
Density (calculated) (Mg m ⁻³)	1.462
Temperature (K)	297(2)
Absorption coefficient (mm ⁻¹)	1.890
F(000)	912
Radiation	Mo Kα (λ = 0.71073 Å, graphite monochromator)
θ Range for data collection (°)	2.55–25.08
Scan type	ω–2θ
Index ranges	–19 ≤ <i>h</i> ≤ 18, –10 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 16
Reflections collected/unique	3206/3100 [<i>R</i> _{int} = 0.0316]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3100/20/245
Goodness-of-Fit on <i>F</i> ²	1.080
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> ₁ = Σ(<i>F</i> _o – <i>F</i> _c)/Σ <i>F</i> _o	<i>R</i> ₁ = 0.0390
<i>wR</i> ₂ = {Σ[<i>w</i> (<i>F</i> _o ² – <i>F</i> _c ²)]/Σ[<i>w</i> (<i>F</i> _o ²)]} ^{1/2}	<i>wR</i> ₂ (refined) = 0.1124
Weighting scheme	<i>w</i> ⁻¹ = σ ² (<i>F</i> _o ²) + (0.0836 <i>P</i>) ² + 0.1850 <i>P</i> , where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0623; <i>wR</i> ₂ = 0.1219
Extinction coefficient	0.0013(6)
Largest difference peak and hole (e Å ⁻³)	0.624 and –0.329

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

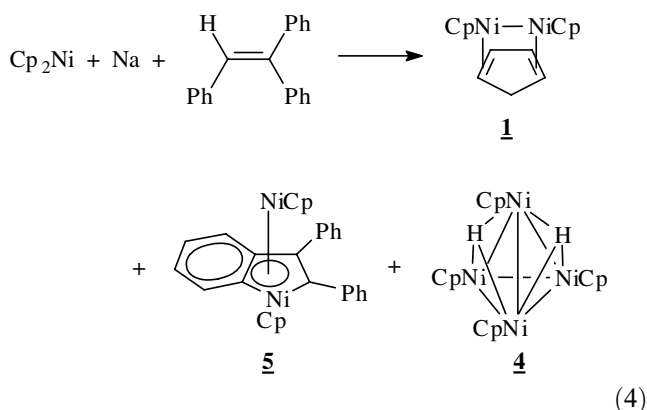
Ni(1)–Ni(2)	2.4162(9)	Ni(2)–C(18)	1.917(4)
Ni(1)–C(12)	2.213(4)	Ni(1)–Cp(1) (centre)	1.795(1)
Ni(1)–C(11)	2.251(4)	Ni(2)–Cp(2) (centre)	1.744(10)
Ni(1)–C(17)	2.190(4)	C(11)–C(12)	1.426(6)
Ni(1)–C(18)	2.118(4)	C(11)–C(17)	1.455(6)
Ni(2)–C(12)	1.891(4)	C(17)–C(18)	1.379(6)
C(12)–Ni(2)–C(18)	84.36(18)	C(11)–C(12)–Ni(2)	114.3(3)
Ni(2)–C(18)–C(17)	114.7(3)	Ni(1)–Ni(2)–Cp(2) (centre)	141.81(3)
C(18)–C(17)–C(11)	113.7(4)	Ni(2)–Ni(1)–Cp(1) (centre)	139.16(3)
C(17)–C(11)–C(12)	112.6(4)		

^a Estimated standard deviations in parentheses.

The next compound formed in the reaction was the trinickel cluster **3**. EIMS spectrum of **3** showed the parent ion at *m/e* 562 (⁵⁸Ni calc.) with an isotopic pattern

characteristic for three nickel atoms in a molecule. In the ¹H NMR spectrum of **3** signals for Cp (5.07 ppm), Ph (7–7.4 ppm) and alkyl (3.6–4.8 ppm) groups were present. In the ¹³C NMR spectrum there was a very characteristic signal of alkylidyne carbon atom (293.6 ppm) and signals of Ph (125–148 ppm), Cp (88.16 ppm), and alkyl (50.09, 72.49 ppm) groups.

After isolation and characterisation of **2** we tried to synthesise a similar compound from triphenylethene hoping to get a higher yield. In case of *trans*-1,2-diphenylpropene, hydrogen atoms from methyl group were activated by nickel species and this reaction was interfering with *ortho*-metallation. Triphenylethene, which did not contain alkyl hydrogen atoms, was chosen and reacted it with nickelocene and sodium (Eq. (4)).



Only three products were isolated. Among them there was an analogue of **2** – dinickel compound **5**. Unfortunately the yield of this product was also very low (2%).

EIMS spectrum of **5** showed the parent ion at *m/e* 500 (⁵⁸Ni calc.) with an isotopic pattern characteristic for two nickel atoms in a molecule. In the ¹H NMR spectrum of **5** there were no signals in the range between 0–10 ppm due to paramagnetic properties of this complex.

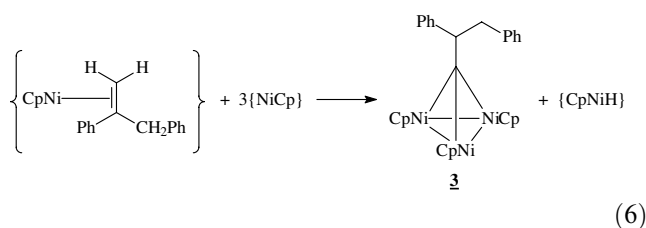
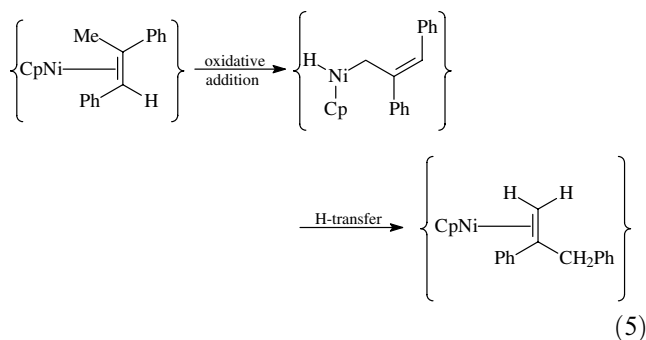
3. Discussion

An analogue of nickelocene possessing nickelacyclopentadienyl ring **2** was isolated from the reaction of nickelocene with sodium in presence of *trans*-methylstilbene. Wadepohl et al. reported related rhodium and cobalt complexes formed from CpM(C₂H₄)₂ and alkenylbenzene or alkenylnaphthalene derivatives [1(k,l)].

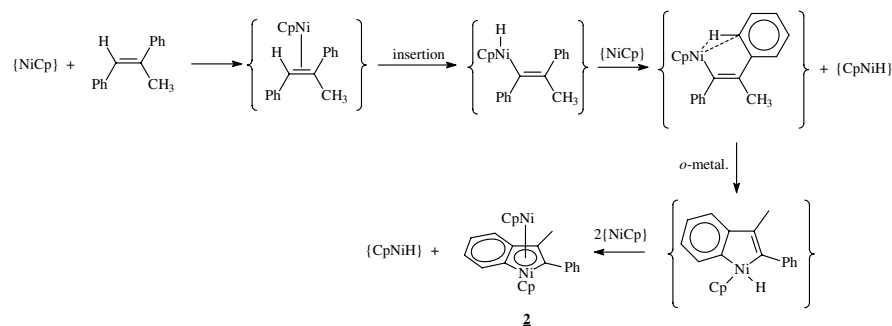
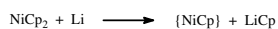
The products formed and results of our previous studies on the reactions of nickelocene with organolithium and magnesium compounds let us suggest the following scheme of the reaction, although no direct evidence of proposed intermediates was observed. Nickelocene reacts with lithium or sodium forming an unstable {NiCp} species. This species, in the presence of an

alkene, forms a π -complex. Elimination of vinyl hydrogen atom and further *ortho*-metallation leads to the formation of a substituted nickelacyclopentadienyl ring, which reacts with $\{\text{NiCp}\}$ species forming the final product **2**. Similar C–H activation and orthometallation by ruthenium species was reported by Johnson et al. [14]. The two hydrogen atoms eliminated from the alkene form, in the reaction with $\{\text{NiCp}\}$, an unstable cyclopentadienylnickelhydride $\{\text{CpNiH}\}$ (Scheme 1).

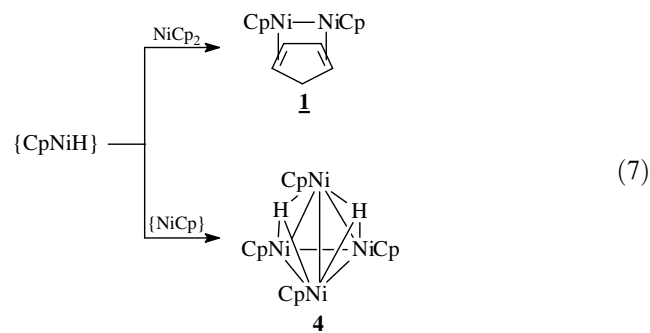
Beside compound **2**, also compound **3** is formed in this reaction. We suggest that in the first step an isomerisation of alkene occurs. The alkene forming a complex with $\{\text{NiCp}\}$ species undergoes oxidative addition and after hydrogen transfer to γ -carbon atom a new complex with α -alkene is formed (Eq. (5)). Further reaction with $\{\text{CpNi}\}$ species leads to the formation of trinickel cluster (Eq. (6)). We have previously reported the mediating role of nickel atom in hydrogen atom transfer [15].



The unstable species $\{\text{CpNiH}\}$ may react with nickelocene with the formation of complex **1**. Compound **4** is formed from the two unstable species $\{\text{CpNi}\}$ and $\{\text{CpNiH}\}$ (Eq. (7)).



Scheme 1.



4. Experimental details

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

4.1. Reaction of nickelocene with lithium and *trans*-1,2-diphenylpropene in THF

Nickelocene (2.42 g, 12.9 mmol), *trans*-1,2-diphenylpropene (3.75 g, 19.3 mmol), lithium (0.127 g, 18 mmol) and 80 cm³ of THF were placed in a Schlenk flask and stirred at room temperature overnight. After the reaction was completed, the solvent was removed and the residue was extracted with two portions of toluene (70 cm³ each). Extracts were filtered through an alumina bed and the solvent was evaporated. The residue was dissolved (8 cm³ of hexane + 8 cm³ 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 green fraction (hexane:toluene, 20:1), after evaporation to dryness, gave traces of green solid identified as unreacted nickelocene.

The second blue fraction (hexane:toluene, 5:1) gave a solid identified as **1** [3] (yield 0.070 g, 0.22 mmol, ca. 3.5%).

The third brown fraction (hexane:toluene, 4:1) gave 0.042 g (0.1 mmol, 1.5%) of brown solid identified as **2**. Crystals of **2** suitable for X-ray measurements were obtained from hexane:THF solution. Anal. Calc. for $C_{25}H_{22}Ni_2$: C, 68.27; H, 5.04. Found: C, 69.09; H, 5.41. EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 438 (M^+ , 100%), 372 ($CpNi_2C_{15}H_{11}^+$, 25%), 246 ($Cp_2Ni_2^+$, 6%), 220 ($Ni_2C_8H_8^+$, 6%), 188 (Cp_2Ni^+ , 9%), 123 ($CpNi^+$, 4%), 58 (Ni^+ , 3%).

The fourth brown fraction (hexane:toluene, 4:1) gave 0.405 g of brown solid identified as a mixture of **3** and **4**. Fractional crystallisation from hexane allowed to isolate small amounts of pure compounds **3** and **4** [4]. EIMS of **3** (70 eV) *m/e* (rel. int.) (^{58}Ni): 562 (M^+ , 20%), 496 ($Cp_2Ni_3Ph_2C_3H_2^+$, 86%), 471 ($Cp_3Ni_3PhC_2H^+$, 14%), 405 ($Cp_3Ni_3C_3^+$, 20%), 304 ($Cp_2Ni_3^+$, 7%), 246 ($Cp_2Ni_2^+$, 5%), 188 (Cp_2Ni^+ , 8%), 123 ($CpNi^+$, 6%), 58 (Ni^+ , 3%). 1H NMR of **3**. (C_6D_6) δ (ppm): 7.00–7.40 (m, 10H, Ph), 5.07 (s, 15H, Cp), 4.83 (dd, $^3J = 3.8$ Hz, $^3J = 10.4$ Hz, 1H, =CH–), 3.83 (dd, $^2J = -13.3$ Hz, $^3J = 3.8$ Hz, 1H, –CH₂–), 3.57 (dd, $^2J = -13.3$ Hz, $^3J = 10.4$ Hz, 1H, –CH₂–). ^{13}C NMR (C_6D_6) δ (ppm): 293.60 (C alkylidyne), 125–148 (Ph), 88.16 (Cp), 72.49 (=CH–), 50.09 (–CH₂–).

4.2. Reaction of nickelocene with sodium and triphenylethene in THF

Nickelocene (2.05 g, 10.9 mmol), triphenylethene (2.5 g, 9.8 mmol), sodium (0.35 g, 15.3 mmol) and 80 cm³ of THF were placed in Schlenk flask and stirred at room temperature overnight. After the reaction was completed, the solvent was removed and the residue was extracted with two portions of toluene (80 cm³ each). Extracts were filtered through the alumina bed and the solvent was evaporated. The residue was dissolved (8 cm³ of hexane + 8 cm³ 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 green fraction (hexane:toluene, 20:1) after evaporation to dryness gave traces of a solid identified as unreacted nickelocene.

The second blue fraction (hexane:toluene, 5:1) gave a solid identified as **1** (yield 0.077 g, 0.25 mmol, ca. 4.5%).

The third brown fraction (hexane:toluene, 3:1) gave 0.055 g (0.11 mmol, 2%) of brown solid identified as **5**. Anal. Calc. for $C_{30}H_{24}Ni_2$: C, 71.79; H, 4.82. Found: C, 72.19; H, 5.01. EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni): 500 (M^+ , 100%), 434 ($CpNi_2C_{20}H_{13}^+$, 25%), 376 ($CpNiC_{20}H_{13}^+$, 34%), 246 ($Cp_2Ni_2^+$, 6%), 220 ($Ni_2C_8H_8^+$, 14%), 188 (Cp_2Ni^+ , 29%), 123 ($CpNi^+$, 19%), 58 (Ni^+ , 13%).

The fourth brown fraction (hexane:toluene, 3:1) gave 0.108 g of brown solid identified as **4**.

4.3. Crystal structure determination

The crystal was sealed in a glass capillary under nitrogen stream. Preliminary examination and intensities data collection was carried out on a KUMA KM4 four-circle diffractometer [16] using graphite-monochromated Mo K α radiation (0.71073 Å). Intensities were collected with ω – 2θ scan technique up to $\theta = 25^\circ$. After each group of 100 reflection standard intensities were monitored and no evidence of crystal decay was observed. An absorption correction was applied using DIFABS [17] procedure, but no changes to the geometrical data resulted, so the recorded data were corrected for Lorentz and polarization factors, only. The structure was solved by direct methods (SHELXS86) [18] and refined by full-matrix least-squares program (SHELXL93) [19]. The carbon bonded H-atoms were included in calculated the positions and refined using a riding model with isotropic displacement parameters equal to 1.2 U_{eq} of the attached C atom. The high degree of displacement parameters of some C atoms indicated possible disorders, but these could not be resolved.

Crystallographic data for the structural analysis of **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 244195. 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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