

# Synthesis and structural characterisation of novel nickelaindenyl and nickelafluorenyl compounds: Differences in the bonding modes of nickelacyclic rings

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## Abstract

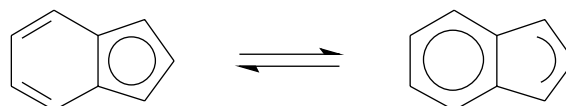
New binuclear nickelacyclic compounds **1** ( $\eta^5$ -pentamethylcyclopentadienyl)( $\eta^3$ -(1-( $\eta^5$ -pentamethylcyclopentadienyl))-1-nickelafluorenyl)nickel and **2** ( $\eta^5$ -pentamethylcyclopentadienyl)( $\eta^3$ -(1-( $\eta^5$ -pentamethylcyclopentadienyl))-2-phenyl-3-ethyl-1-nickelaindenyl)nickel were synthesised in reactions of dilithioorganic compounds with  $\text{Cp}^*\text{Ni}(\text{acac})$  and characterised by high resolution mass spectrometry, magnetic moment determination and X-ray single crystal analysis. The bonding mode of the central nickel atom to the nickelaindenyl and nickelafluorenyl ligands was not  $\eta^5$  like in the previously described analogues of nickelocene but half way between  $\eta^3$  and  $\eta^5$ . © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Nickel; Organolithium compounds; Clusters; Cyclopentadienyl; Metallacyclic compounds

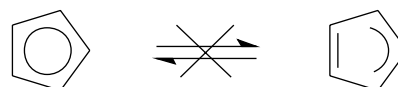
## 1. Introduction

The well known structure of nickelocene reveals that both cyclopentadienyl rings are flat and parallel to each other [1], and they are bonded to the nickel atom in  $\eta^5$  manner. It is still the same in derivatives of nickelocene in which one or both rings are substituted by various ligands [2] no matter if the nickelocene molecule is neutral or cationic [3]. The exceptions are indenyl [4] and indacenyl [5] complexes, in which the slippage of the ring occurs and the coordination mode of the nickel atom changes from  $\eta^5$  to  $\eta^3$ . The consequence of it is also that the five-membered rings in these compounds are not flat. Taylor and Marder suggested that the relative ease of the ring slippage for indenyl complexes should had been attributed to the rehy-

bridization of the indenyl  $\pi$ -system which increased the aromatic character of the benzene ring but also disrupted the aromatic character of the five-membered ring [4a]



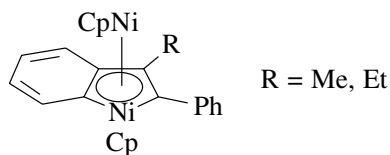
Such disruption would be a higher energy process for cyclopentadienyl ligands therefore in the cyclopentadienyl complexes the rings are flat and bonded to nickel atom in  $\eta^5$  manner



We have recently described the synthesis of analogues of nickelocene possessing nickelaindenyl ring [6]. In these

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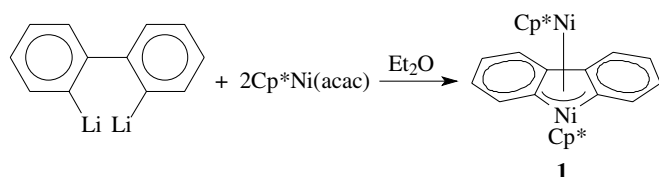
compounds the X-ray studies proved that the central nickel atom was bonded to the cyclopentadienyl ring and to the flat, metalated indenyl ring. The bonding mode of the nickel atom to the nickelaindenyl ring was  $\eta^5$ . Such structure is quite different from the structures of the known indenyl nickel complexes where the ring is bent and  $\eta^3$  bonded to the central nickel atom [4]



In this work we present synthesis and structure of two new compounds, derivatives of decamethylnickelocene, with nickelaindenyl and nickelafluorenyl rings. The influence of pentamethylcyclopentadienyl ligands on the bonding mode of the central nickel atom to the nickelacyclic rings is shown.

## 2. Results

Pentamethylcyclopentadienylnickelacetylacetonate was reacted with 2,2'-dilithiobiphenyl in diethyl ether at  $-30^\circ\text{C}$  for 1 h and then at room temperature overnight. The reaction mixture was chromatographed on neutral alumina deactivated with 5% of water. Only one red-brown fraction was collected which after evaporation of solvents gave brown solid characterised as **1** (yield 96%)



EIMS spectrum of **1** showed the parent ion at  $m/e$  538 ( $^{58}\text{Ni}$  calc.) with an isotopic pattern characteristic for two nickel atoms in the molecule.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) spectrum of **1** revealed four broad signals at 19 ppm, 11 ppm,  $-82$  ppm and  $-108$  ppm. Magnetic moment of **1** in toluene solution at 295 K is  $2.786 \mu_B$ , what indicates that the compound is paramagnetic with two unpaired electrons per molecule. There were no signals in EPR spectrum of **1** neither at room temperature nor at 77 K, neither in solid state nor in benzene solution.

Crystals of **1** appropriate for X-ray diffraction studies were grown from hexane solution. The molecular structure of **1** is presented in Fig. 1. Selected bond lengths and angles are shown in Table 2. Crystal data, data collection and refinement parameters are given in Table 1. The compound crystallises in orthorhombic crystal system. There are two independent molecules (A and B) in an asymmetric unit cell. The Ni–Ni bond (2.4 Å) is within the range of nickel–nickel single bonds. Carbon atoms (C1, C1, C6, C6) and nickel atom (Ni1) form a five-membered heterocyclic ring. This ring is not planar. Four carbon atoms are sit-

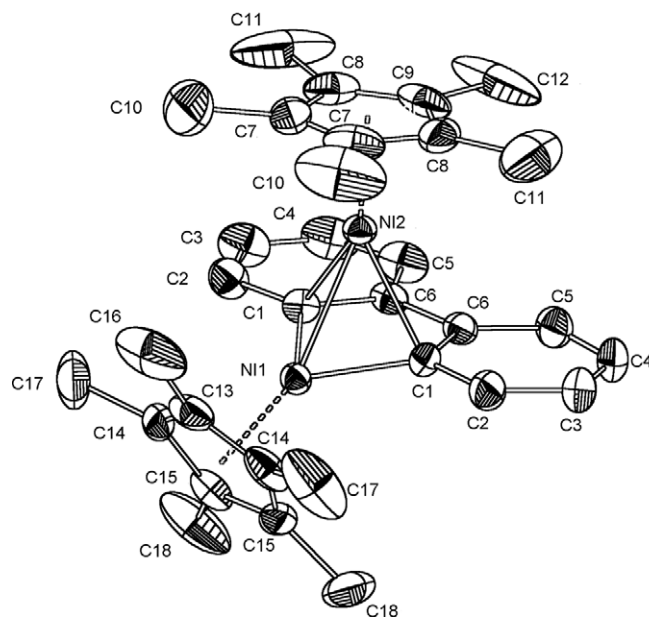
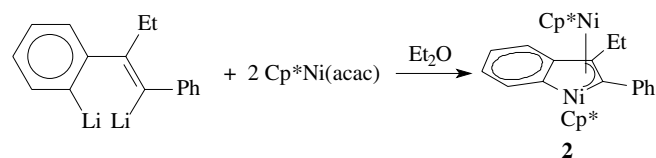


Fig. 1. ORTEP view of the molecular structure of **1** showing the atom numbering scheme. Thermal ellipsoids drawn at 30% probability level. Hydrogen atoms were omitted for the clarity.

uated in one plane while nickel atom is deviated by  $0.378 \text{ \AA}$  (molecule A) and  $0.492 \text{ \AA}$  (molecule B) from this plane. The hinge angle, defined as the dihedral angle between the planes C1–C6–C6–C1 and C1–Ni1–C1 is  $15.4^\circ$  in molecule A and  $20.0^\circ$  in molecule B. The central nickel atom (Ni2) is bonded to the pentamethylcyclopentadienyl ring and the nickelacyclic ring. To define a bonding mode of the central nickel atom (Ni2) to the nickelafluorenyl ring, we have determined the degree of slip-fold distortion, using parameters as described in [4a]. The slip parameter defined as  $\Delta_{M-C} = \text{avg } d(\text{Ni2}-\text{C1}) - \text{avg } d(\text{Ni2}-\text{C6})$  is  $0.253 \text{ \AA}$  in molecule A and  $0.324 \text{ \AA}$  in molecule B. These values show that the coordination mode of the nickelacyclic ring to the nickel atom (Ni2) is in between  $\eta^3$  and  $\eta^5$ .

The compound **2** was synthesised in the reaction of pentamethylcyclopentadienylnickelacetylacetonate with (*E*)-1-lithio-1-phenyl-2-(2-lithiophenyl)ethane in diethyl ether at  $-30^\circ\text{C}$  for 1 h and then at room temperature overnight. The reaction mixture was chromatographed on neutral alumina deactivated with 5% of water. One brown fraction was collected which after evaporation of solvents gave brown solid characterised as **2** (isolated yield 16%)



EIMS spectrum of **2** showed the parent ion at  $m/e$  592 ( $^{58}\text{Ni}$  calc.) with an isotopic pattern characteristic for two nickel atoms in a molecule.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) spectrum of **2** revealed seven broad signals at 14 ppm, 13 ppm, 8 ppm,

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

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>32</sub> H <sub>38</sub> Ni <sub>2</sub>	C <sub>36</sub> H <sub>44</sub> Ni <sub>2</sub>
Crystal size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.3
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>
Unit cell dimensions		
<i>a</i> (Å)	21.3622(2)	17.2540(5)
<i>b</i> (Å)	16.3400(2)	17.0855(5)
<i>c</i> (Å)	15.6996(3)	20.1488(6)
α (°)	90	90
β (°)	90	97.983(2)
γ (°)	90	90
Volume (Å <sup>3</sup> )	5480(1)	5882(4)
<i>Z</i>	8	8
Formula weight	540.03	594.13
Density (calculated) (Mg m <sup>-3</sup> )	1.291	1.342
Temperature (K)	294(2)	150(2)
Absorption coefficient (mm <sup>-1</sup> )	1.391	1.303
<i>F</i> (000)	2228	2528
Radiation	Mo Kα (λ = 0.71073 Å, graphite monochromator)	
θ Range for data collection (°)	2.97–27.49	2.91–27.51
Scan type	ω–2θ	ω–2θ
Index ranges	–27 ≤ <i>h</i> ≤ 27, –21 ≤ <i>k</i> ≤ 21, –20 ≤ <i>l</i> ≤ 20	–22 ≤ <i>h</i> ≤ 22, –22 ≤ <i>k</i> ≤ 20, –26 ≤ <i>l</i> ≤ 26
Reflections collected/unique ( <i>R</i> <sub>int</sub> )	43,084/6493 (0.0280)	36,054/13,442 (0.0671)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data/restraints/parameters	6493/0/357	13,442/0/708
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.030	0.950
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> <sub>1</sub> = Σ( <i>F</i> <sub>o</sub> – <i>F</i> <sub>c</sub> )/Σ <i>F</i> <sub>o</sub>	<i>R</i> <sub>1</sub> = 0.0461	<i>R</i> <sub>1</sub> = 0.0530
<i>wR</i> <sub>2</sub> = {Σ[ <i>w</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> – <i>F</i> <sub>c</sub> <sup>2</sup> )]/Σ[ <i>w</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> )]} <sup>1/2</sup>	<i>wR</i> <sub>2</sub> (refined) = 0.1171	<i>wR</i> <sub>2</sub> (refined) = 0.0944
Weighting scheme	<i>w</i> <sup>-1</sup> = σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0668 <i>P</i> ) <sup>2</sup> + 2.7186 <i>P</i> where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	<i>w</i> <sup>-1</sup> = σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0463 <i>P</i> ) <sup>2</sup> + 0.0000 <i>P</i>
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0710; <i>wR</i> <sub>2</sub> = 0.1259	<i>R</i> <sub>1</sub> = 0.1323; <i>wR</i> <sub>2</sub> = 0.1163
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.486 and –0.342	0.639 and –0.656

Table 2  
Selected interatomic distances (Å) and angles (°) for **1**

	Molecule A	Molecule B
Ni1–Ni2	2.4003(7)	2.391(1)
Ni1–C1	1.922(3)	1.932(3)
C1–C6	1.421(4)	1.416(4)
C6–C6	1.464(6)	1.460(6)
Ni2–C1	2.162(3)	2.162(3)
Ni2–C6	2.415(3)	2.486(3)
Ni1–C1–C6	113.4(2)	111.9(2)
C1–C6–C6	113.01(17)	113.50(16)
C1–Ni1–C1	84.14(17)	84.10(17)
Ni1–Ni2–Cg	151.35(3)	152.39(3)
Ni2–Ni1–Cg	152.47(3)	152.39(3)

–28 ppm, –38 ppm, –42 ppm and –53 ppm. The compound **2** is paramagnetic. Magnetic moment of **2** in toluene solution at 293 K is 3.85 μ<sub>B</sub>. The total number of valence electrons and the value of the magnetic moment suggested that there are 2 or 4 unpaired electrons per molecule. There were no signals observed in EPR spectrum of **2** neither at room temperature nor at 77 K, neither in solid state nor in benzene solution.

Crystals of **2** appropriate for X-ray diffraction studies were grown from hexane solution. The molecular structure of **2** is presented in Fig. 2. Selected bond lengths and angles are shown in Table 3. Crystal data, data collection and refinement parameters are given in Table 1. The compound crystallises in monoclinic crystal system. There are two independent molecules (A and B) in the unit cell. The Ni–Ni bond is long (2.48 Å) but still in the range of nickel–nickel single bonds [7]. Four carbon atoms (C1, C6, C7, C8) and nickel atom (Ni1) form the five-membered non-planar nickelacyclic ring which is fused to the six-membered carbocyclic ring. The hinge angle, defined as the dihedral angle between planes Ni1–C7–C8 and Ni1–C1–C6–C7 is 5.11° in molecule A and 3.78° in molecule B. The central nickel atom (Ni2) is bonded to the pentamethylcyclopentadienyl ring and the nickelacyclic ring. The slip parameter defined as Δ<sub>M–C</sub> = avg*d*(Ni2–C1, Ni2–C6) – avg*d*(Ni2–C7, Ni2–C8) is 0.299 Å in molecule A and 0.305 Å in molecule B. These values show that the coordination mode of the nickelacyclic ring to the central nickel atom (Ni2) is in between η<sup>3</sup> and η<sup>5</sup>, the same as in compound **1**.

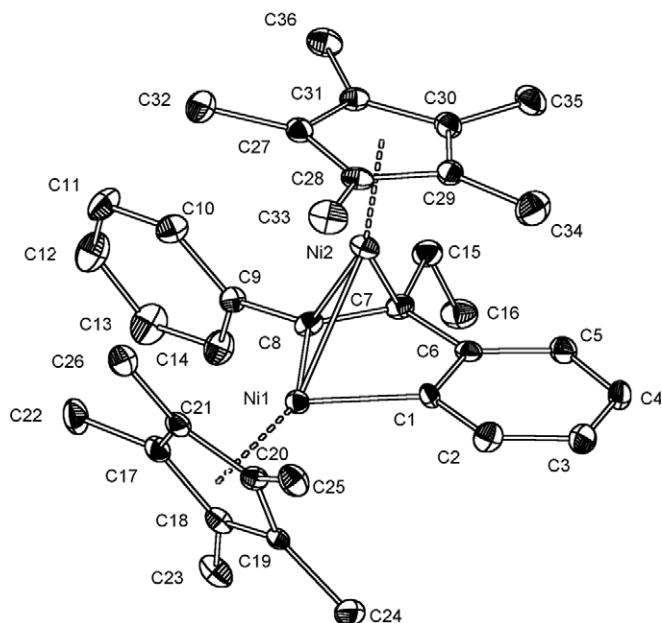


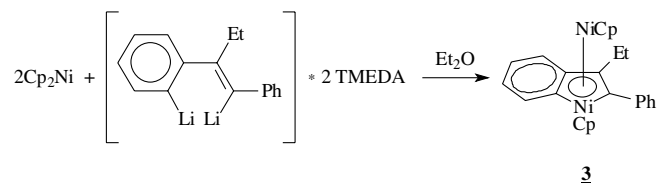
Fig. 2. ORTEP view of the molecular structure of **2** showing atom numbering scheme. Thermal ellipsoids drawn at 30% probability level. Hydrogen atoms were omitted for the clarity.

Table 3  
Selected interatomic distances (Å) and angles (°) for **2**

	Molecule A	Molecule B
Ni1–Ni2	2.4778(6)	2.4761(6)
Ni1–C8	1.910(3)	1.898(4)
Ni1–C1	1.924(4)	1.915(4)
C1–C6	1.429(5)	1.429(5)
C8–C7	1.412(5)	1.415(5)
C7–C6	1.462(5)	1.463(5)
Ni2–C8	2.027(4)	2.028(4)
Ni2–C7	2.131(4)	2.112(4)
Ni2–C1	2.367(4)	2.374(4)
Ni2–C6	2.388(4)	2.376(4)
Ni1–C1–C6	113.77(25)	113.69(25)
C1–C6–C7	112.28(31)	112.36(30)
C7–C8–Ni1	114.15(25)	114.36(26)
C8–Ni1–C1	84.75(15)	85.13(15)
Ni1–Ni2–Cg	147.08(3)	146.82(3)
Ni2–Ni1–Cg	150.58(3)	151.32(2)

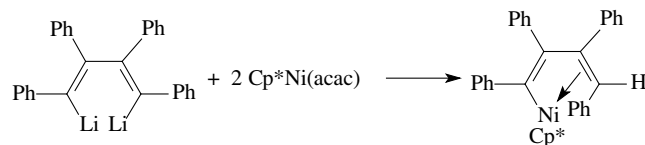
### 3. Discussion

We have recently reported the synthesis of analogues of nickelocene in which one of the cyclopentadienyl rings was replaced with nickelaindenyl ring [6]. We have found that the reactions of dilithioorganic compounds with nickelocene are the excellent method of the synthesis of complexes with five-membered nickelacyclic ring [6b]



In these complexes the central nickel atom had 20 VE, the same as the nickel atom in nickelocene. Contrary to bis-indenylnickel, where ring slippage occurred and nickel atom was bonded to indenyl ring in the  $\eta^3$  manner, the donor properties of nickelaindenyl ring in the complex **3** were decreased due to the replacement of one carbon atom by nickel atom, what allowed the central nickel atom to be bonded to all five atoms of the flat nickelacyclic ring. At the same time aromatic character of the benzene ring was reduced. Similar structures were previously reported for analogues of metallocenes of other than nickel metals with metalindenyl [8] or metalafluorenyl [9] rings. The bonding mode of the central metal atom to the metalacycle in these compounds was  $\eta^5$ .

We decided to synthesise complexes similar to the compound **3** in the reactions of 2,2'-dilithiobiphenyl and (*E*)-1-lithio-1-phenyl-2-(2'-lithiophenyl)ethane with pentamethylcyclopentadienylnickelacetylacetonate ( $\text{Cp}^*\text{Ni}(\text{acac})$ ). Wilke reported the reaction of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene with  $\text{Cp}^*\text{Ni}(\text{acac})$  in which he obtained complex of the type  $\text{Cp}^*\text{Ni}(\text{alkene})\text{alkyl}$ , but not the compound with nickelacyclopentadienyl ring [4c]



We believed that compounds with nickelacyclic ring could be formed in similar reactions, but they could be stable if the nickelacycle was fused to one or two aromatic rings. In fact in both investigated by us reactions nickelacyclic complexes were synthesised: the first one with nickelafuorenyl ring **1** and the second one with nickelaindenyl ring **2**. Such reactions proved to be the new and easy method of the synthesis of nickelacycles. Contrary to compound **3**, the bonding mode of the central nickel atom to the nickelacycle in complexes **1** and **2** was in between  $\eta^3$  and  $\eta^5$ . Also the nickelacyclic ring was not flat but bent and the nickel atom was moved towards three atoms of the five-membered ring (Fig. 3).

The inductive effect of methyl groups in pentamethylcyclopentadienyl ring increased the electron density of both nickel atoms. This caused the slippage and folding of nickelaindenyl ring in the complex **2** and the bonding mode of central nickel atom (Ni2) changed from  $\eta^5$  to half way between  $\eta^3$  and  $\eta^5$ . Additionally the aromatic character of the benzene ring was increased.

Similar situation arose in compound **1**. The nickel atom (Ni2) was bonded to only three atoms of nickelafuorenyl ring. The higher electron density on the central nickel atom pushed it away from the two carbon atoms (C6). Steric hindrances between two pentamethylcyclopentadienyl ligands caused that the second nickel atom moved out of the plane defined by four carbon atoms (C1, C1, C6, C6).

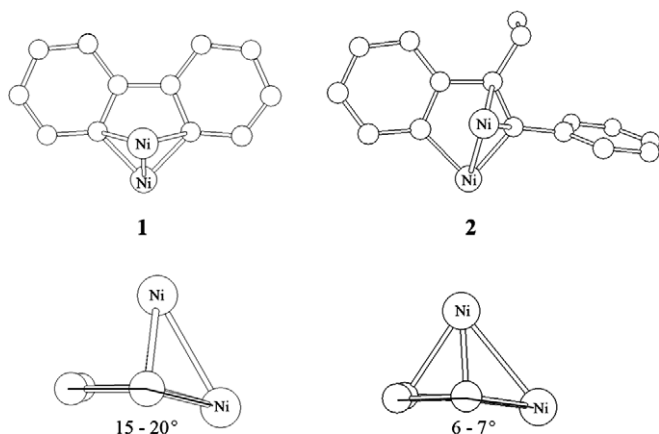


Fig. 3. View of the bonding mode between the central nickel atom and nickelacyclic ring.

#### 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.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Varian Mercury 400 MHz instrument. Mass spectra were recorded on an AMD-604 spectrometer. EPR spectra were measured on Bruker ESP 300 spectrometer in X-band. Magnetic susceptibility was determined by NMR measurements at 298 K according to Evans method [10], from differences in chemical shifts of methyl group protons of toluene used as the solvent and as the external standard. The magnetic moment was calculated from the measurements of magnetic susceptibility. (*E*)-1-lithio-1-phenyl-2-(2'-lithiophenyl)ethene was synthesised from diphenylacetylene and ethyllithium as it was described for *n*-butyl derivative [11]; 2,2'-dibromobiphenyl was synthesised according to [12] and pentamethylcyclopentadienylnickelacetylacetonate according to [13]. 2,2'-Dilithiobiphenyl was synthesised from lithium and 2, 2'-dibromobiphenyl in diethyl ether.

##### 4.1. Reaction of pentamethylcyclopentadienylnickelacetylacetonate with 2,2'-dilithiobiphenyl

Pentamethylcyclopentadienylnickelacetylacetonate (0.97 g, 3.32 mmol) and 20 cm<sup>3</sup> of diethyl ether were placed in a Schlenk flask and cooled to  $-30\text{ }^\circ\text{C}$ . The solution of 2,2'-dilithiobiphenyl in diethyl ether (17 cm<sup>3</sup>, 0.105 mol/dm<sup>3</sup>, 1.79 mmol) was added. The reaction was stirred for 1 h at  $-30\text{ }^\circ\text{C}$ , and then at room temperature overnight. After the reaction was completed, the solvent was removed and the residue was extracted with 40 cm<sup>3</sup> of toluene. Extract was filtered through the alumina layer and then the solvent was evaporated. The residue was dissolved in 10 cm<sup>3</sup> of hexane and chromatographed on neutral alumina (deactivated with 5% of water). One red-brown band was collected (hexane/toluene 4:1). The solvents were removed and brown solid compound **1** was obtained (0.86 g, 1.6 mmol, 96%).

Crystals appropriate for X-ray measurements were grown from hexane solution. EIMS (70 eV) *m/e* (rel. int.) ( $^{58}\text{Ni}$ ): 538 ( $\text{M}^+$ , 100%), 404 ( $\text{C}_{22}\text{H}_{24}\text{Ni}_2^+$ , 38%), 382 ( $\text{C}_{20}\text{H}_{26}\text{Ni}_2^+$ , 60%), 248 ( $\text{C}_{10}\text{H}_{12}\text{Ni}_2^+$ , 15%), 212 ( $\text{C}_{12}\text{H}_{10}\text{Ni}^+$ , 11%), 192 ( $\text{C}_{10}\text{H}_{14}\text{Ni}^+$ , 9%), 152 ( $\text{C}_{12}\text{H}_8^+$ , 11%), 133 ( $\text{C}_{10}\text{H}_{13}^+$ , 10%), 119 ( $\text{C}_9\text{H}_{11}^+$ , 13%). EI HR MS: Observed: 538.16614, Calculated for  $\text{C}_{32}\text{H}_{38}^{58}\text{Ni}_2$ : 538.16805.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): 19, 11,  $-82$  and  $-108$  (broad signals). Magnetic moment in toluene solution at 295 K was 2.786  $\mu_{\text{B}}$ .

##### 4.2. Reaction of pentamethylcyclopentadienylnickelacetylacetonate with (*E*)-1-lithio-1-phenyl-2-(2'-lithiophenyl)ethene

(*E*)-1-lithio-1-phenyl-2-(2'-lithiophenyl)ethene (1.5 g, 3.32 mmol) and 70 cm<sup>3</sup> of diethyl ether were placed in a Schlenk flask and cooled to  $-30\text{ }^\circ\text{C}$ . The solution of pentamethylcyclopentadienylnickelacetylacetonate (1.95 g, 6.68 mmol) in 20 cm<sup>3</sup> of diethyl ether was added. The reaction was stirred for 1 h at  $-30\text{ }^\circ\text{C}$ , and then at room temperature overnight. After the reaction was completed, the solvent was removed and the residue was extracted with 60 cm<sup>3</sup> of toluene. Extract was filtered through the alumina layer and then the solvent was evaporated. The residue was dissolved in 10 cm<sup>3</sup> of hexane and chromatographed on neutral alumina (deactivated with 5% of water). One brown band was collected (hexane/toluene 10:1). The solvent was removed and brown solid compound **2** was obtained (0.16 g, 0.27 mmol, 16%). Crystals appropriate for X-ray measurements were grown from hexane solution. EIMS (70 eV) *m/e* (rel. int.) ( $^{58}\text{Ni}$ ): 592 ( $\text{M}^+$ , 100%), 456 ( $\text{C}_{26}\text{H}_{28}\text{Ni}_2^+$ , 58%), 384 ( $\text{C}_{20}\text{H}_{28}\text{Ni}_2^+$ , 21%), 324 ( $\text{C}_{16}\text{H}_{16}\text{Ni}_2^+$ , 13%), 266 ( $\text{C}_{16}\text{H}_{16}\text{Ni}^+$ , 16%), 191 ( $\text{C}_{10}\text{H}_{13}\text{Ni}^+$ , 20%), 133 ( $\text{C}_{10}\text{H}_{13}^+$ , 12%), 119 ( $\text{C}_9\text{H}_{11}^+$ , 16%). EI HR MS: Observed 592.21373, Calculated for  $\text{C}_{36}\text{H}_{44}^{58}\text{Ni}_2$ : 592.21500.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  (ppm): 14, 13, 8,  $-28$ ,  $-38$ ,  $-42$  and  $-53$  (broad signals). Magnetic moment in toluene solution at 293 K is 3.85  $\mu_{\text{B}}$ .

##### 4.3. Crystal structure determination of **1**

The crystal was sealed in a glass capillary under nitrogen stream. Unit cell from 6768 reflections  $2.91^\circ < \theta < 27.48^\circ$ . X-ray data were collected on a Nonius KappaCCD diffractometer. Data collected with subsequent  $\varphi$  and  $\omega$  scans (213 frames, rotation per frame  $1.5^\circ$ , exposure per frame 60 s) 43,084 reflections collected, 6493 unique, 4797 above threshold [ $I > 2\sigma(I)$ ]. Diffractometer control program COLLECT [14], unit cell parameters and data reduction with Denzo and Scalepak [15], structure solved by direct methods SHELXS-97 [16] and refined on  $F^2$  by full-matrix least-squares with SHELXL-97 [17]. Two independent molecules were found in asymmetric unit, each molecule lies on crystallographic mirror plane. In molecule B one of the pentamethylcyclopentadiene ligands is highly disordered at several positions and it was extremely difficult to find appropriate model for it. Due to the above difficulties only carbon atoms with approximate s.o.f. and isotropic thermal

displacement parameters at the peaks  $>1 \text{ e} \text{ \AA}^{-3}$  in Fourier difference maps were introduced into final refinement. No attempt was made to attach hydrogen atoms to the methyl groups in this ligand. All the reminding hydrogen atoms were placed in calculated positions and refined using a riding model. Three methyl groups C(12a), C(16a) and C(10b) appeared to be disordered in two positions due to the crystallographic mirror plane. Final  $R = 0.046$  (0.071 for all reflections),  $wR = 0.117$  (0.126 for all reflections).

#### 4.4. Crystal structure determination of 2

The crystal was sealed in a glass capillary under nitrogen stream. Unit cell from 10,777 reflections  $2.91^\circ < \theta < 27.48^\circ$ . X-ray data were collected on a Nonius KappaCCD diffractometer. Data collected with  $\varphi$  scans (121 frames, rotation per frame  $1.5^\circ$ , exposure per frame 45 s) 36,054 reflections collected, 13,442 unique, 7242 above threshold [ $I > 2\sigma(I)$ ]. Diffractometer control program COLLECT [14], unit cell parameters and data reduction with Denzo and Scalepak [15], structure solved by direct methods SHELXS-97 [16] and refined on  $F^2$  by full-matrix least-squares with SHELXL-97 [17]. All the hydrogen atoms were placed in calculated positions and refined using a riding model. Final  $R = 0.053$ ,  $wR = 0.094$ .

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#### Appendix A. Supplementary data

Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre Nos. CCDC 600976 and 600977. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, (fax +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.06.013](https://doi.org/10.1016/j.jorganchem.2006.06.013).

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