



Novel, axially chiral analogues of nickelocene with nickeladibenzofluorenyl ligand



Piotr Buchalski ^{a,*}, Roman Pacholski ^a, Aleksander Shkurenko ^b, Kinga Suwińska ^c

^a Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland

^b Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

^c Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University in Warsaw, K. Wóycickiego 1/3, 01-938 Warszawa, Poland

ARTICLE INFO

Article history:

Received 26 November 2014

Received in revised form

13 February 2015

Accepted 16 February 2015

Available online 26 February 2015

Keywords:

Nickel

Lithium

Cyclopentadienyl ligands

Chirality

X-ray diffraction

ABSTRACT

In this paper we describe the syntheses and characterization of novel axially chiral metallacyclic complexes. Contrary to previously described synthesis of 9-nickelafluorenyllithium complexes, reaction of dilithium ligand afforded nickelacyclic analogue of nickelocene. Similar compounds were obtained after replacing nickelocene with pentamethylcyclopentadienyl nickel and cobalt acetylacetonates. Structural characterization proved to be difficult since all of these compounds exhibit paramagnetic behaviour. Crystal and molecular structures of products were determined by single-crystal X-ray analysis. Electronic properties were investigated using Evans method and DFT calculations.

© 2015 Elsevier B.V. All rights reserved.

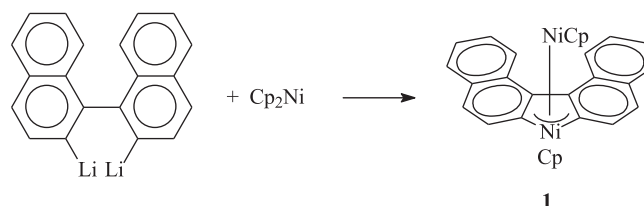
Introduction

We have reported the synthesis of 9-nickelafluorenyllithium complexes [1], novel metallafluorenyl-alkali metal compounds that contain a transition metal in the five-membered metallacyclic ring. Such compounds proved to be very useful in the synthesis of metallametalocenes. Metallametalocenes are the compounds in which one or two cyclopentadienyl groups of metallocene is replaced by a metallacyclopentadienyl ring [2]. In previous papers we described the synthesis of new nickelametalocenes [3] which possessed one nickelaindenyl or nickel-afluorenyl ring [4]. More recently we have employed 9-nickelafluorenyllithium [1], in the synthesis of the first analogues of nickelocene and cobaltocene with two nickelafluorenyl rings [5].

In this paper we report the reactions between (1,1'-binaphthalene-2,2'-diyl)dilithium with nickelocene, pentamethylcyclopentadienylnickel acetylacetonate and with pentamethylcyclopentadienylcobalt acetylacetonate and the influence of the binaphthyl ligand on the formation of metallacycles.

Results

The reactions of (1,1'-binaphthalene-2,2'-diyl)dilithium with nickelocene has been carried out in a diethyl ether at temperatures ranging from $-50\text{ }^{\circ}\text{C}$ to room temperature. The products were extracted with toluene. Attempts to purify the products by column chromatography on neutral alumina deactivated with 5% of water failed because the compounds were unstable and decomposed during chromatography. The product was crystallized from acetonitrile and black powder of **1** $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-}[(\text{C}_5\text{H}_5)\text{NiC}_{20}\text{H}_{12}]\}]$ was obtained.



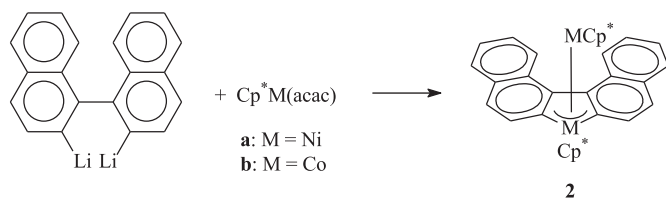
EIMS spectrum of **1** showed the parent ion at m/e 498 (^{58}Ni calc.) with an isotopic pattern characteristic for two nickel atoms in the molecule. This was confirmed by the HR EI MS $m/$

* Corresponding author. Tel.: +48 22 234 78 59; fax: +48 22 234 54 62.
E-mail address: pjb@ch.pw.edu.pl (P. Buchalski).

$e = 4,98,04,092$ which well fitted the formula $C_{30}H_{22}^{58}Ni_2$. In 1H NMR spectrum of **1** there were no signals in the range between 0 and 10 ppm. Magnetic moment of **1** in toluene solution at 293 K is $2.60 \mu_B$, what indicates that the compound is paramagnetic. The total number of valence electrons and the value of the magnetic moment suggested that there are 2 unpaired electrons per molecule which is close to the “spin only value” for two unpaired electrons. There were also no signals in EPR spectrum of **1** at room temperature in the solid state. Several attempts to obtain crystals of **1** good for X-ray measurements failed. Even if we were unable to grow crystals suitable for x-ray measurements, it seems plausible to assume that its structure is similar to that determined for **2a**.

In order to fully characterize nickelacyclic and cobaltacyclic compounds containing binaphthyl ligand we decided to react pentamethylcyclopentadienylnickel acetylacetonate and pentamethylcyclopentadienylcobalt acetylacetonate with (1,1'-binaphthalene-2,2'-diyl)dilithium.

Pentamethylcyclopentadienylnickel acetylacetonate was reacted with (1,1'-binaphthalene-2,2'-diyl)dilithium in diethyl ether at $-50^\circ C$ for 1 h and then at room temperature overnight. The reaction mixture was chromatographed on neutral alumina deactivated with 5% of water. Only one black fraction was collected which after evaporation of solvents gave black solid characterised as **2a** [$Ni(\eta^5-C_5Me_5)\{\eta^3-[(C_5Me_5)NiC_{20}H_{12}]\}$] (yield 30%).



EIMS spectrum of **2a** showed the parent ion at m/e 638 (^{58}Ni calc.) with an isotopic pattern characteristic for two nickel atoms in the molecule. This was confirmed by the HR EI MS $m/e = 6,38,19,743$ which well fitted the formula $C_{40}H_{42}^{58}Ni_2$. 1H NMR (C_6D_6) spectrum of **2a** revealed broad signals at 157 ppm, 31 ppm, 24 ppm, -35 ppm, -37 ppm and -57 ppm (approx. ratio 3:2:2:1:1:1). Magnetic moment of **2a** in toluene solution at 290 K is $3.75 \mu_B$, at 313 K is $3.67 \mu_B$ and at 331 K is $3.63 \mu_B$ what indicates that the compound is paramagnetic with two unpaired electrons per molecule. This is consistent with Russell–Saunders coupling value for two unpaired electrons. As apical nickel atom in **2a** exhibits slightly distorted tetrahedral geometry it can be described as d^8 system with two unpaired electrons ($e^4t_2^4$), which leads to the spin angular momentum $S = 1$ and orbital angular momentum $L = 3$. With neglected spin–orbit coupling, magnetic moment should equal $4.47 \mu_B$ [6,7]. With measured magnetic moment at 290 K of $3.75 \mu_B$ it can be concluded that orbital angular momentum is partially quenched. This is close to the calculated value with effective orbital angular momentum $L = 2$, which is $3.74 \mu_B$. There were no signals in EPR spectrum of **2a** at room temperature in the solid state.

Crystals of **2a** appropriate for X-ray diffraction studies were grown from hexane-acetonitrile solution. The molecular structure of **2a** is presented in Fig. 1. Crystal data, data collection and refinement parameters are given in Table 1. The compound crystallises in a monoclinic crystal system. There are two independent molecules (A and B) in an asymmetric unit cell. Molecules A and B are atropisomeric. The Ni–Ni bond (2.4 Å) is within the range of nickel–nickel single bonds. Carbon atoms (C1, C10, C11, C20) and nickel atom (Ni1) form a five-membered heterocyclic ring which is not planar. The nickel atom is deviated by 0.50 Å (molecule A) and

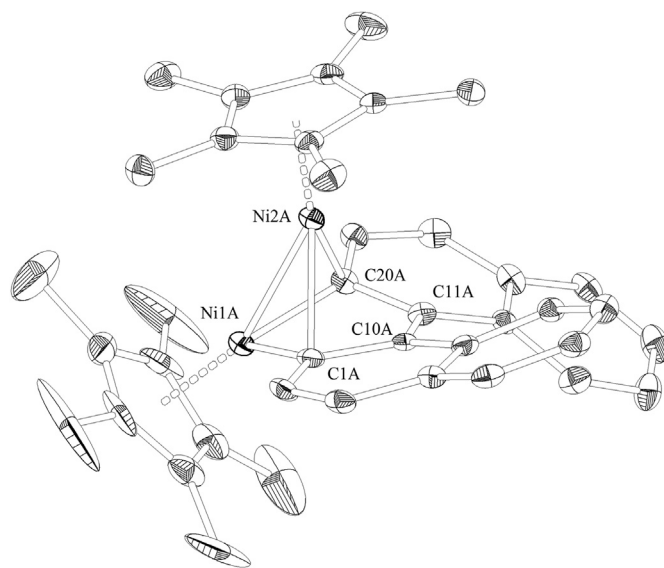
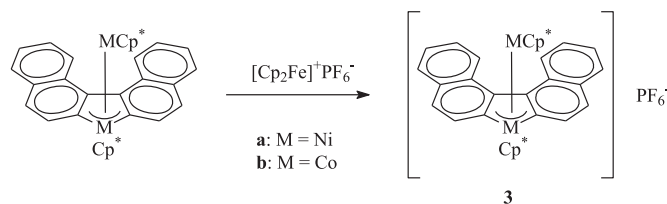


Fig. 1. ORTEP view of the molecular structure of **2a** showing atom numbering scheme. Thermal ellipsoids drawn at 30% probability level. Selected distances [Å] and angles [$^\circ$]: Ni1A–Ni2A 2.422 (1), Ni1A–C1A 1.904 (8), Ni1A–C20A 1.935 (7), Ni2A–C1A 2.145 (7), Ni2A–C20A 2.068 (7), Ni2A–C10A 2.335 (7), Ni2A–C11A 2.463 (7); C1A–Ni1A–C20A 84.1 (3), C20A–Ni2A–C1A 75.2 (3).

0.54 Å (molecule B) from the plane formed by four carbon atoms. The hinge angle, defined as the dihedral angle between the planes C1–C10–C11–C20 and C1–Ni1–C20 is 21.0° in molecule A and 22.4° in molecule B. The central nickel atom (Ni2) is bonded to the pentamethylcyclopentadienyl ring and to three atoms (C1, C20, Ni1) of the nickelacyclic ring.

Pentamethylcyclopentadienylcobalt acetylacetonate was reacted with (1,1'-binaphthalene-2,2'-diyl)dilithium in diethyl ether at $-50^\circ C$ for 1 h and then at room temperature overnight. The compounds were unstable and decomposed during chromatography. Crystallization from hexane afforded 67% of compound **2b** [$Co(\eta^5-C_5Me_5)\{\eta^3-[(C_5Me_5)CoC_{20}H_{12}]\}$] as black powder. EIMS spectrum of **2b** showed the parent ion at m/e 640. This was confirmed by the HR EI MS $m/e = 6,40,19,293$ which well fitted the formula $C_{30}H_{22}^{59}Co_2$. In 1H NMR spectrum of **2b** there were no signals in the range between 0 and 10 ppm. Only very broad signals of low intensity at +26 ppm and -12 ppm (approx. ratio 4:1) were observed. Magnetic moment of **2b** in toluene solution at 290 K is $3.68 \mu_B$, at 313 K is $3.64 \mu_B$ and at 331 K is $3.60 \mu_B$ what indicates that the compound is paramagnetic. These values are close to the “spin only value” for three unpaired electrons. There were also no signals in EPR spectrum of **2b** at room temperature in the solid state.

Compounds **2a** and **2b** were oxidised chemically by $[Cp_2Fe]^+PF_6^-$ to form the monocation complexes **3a** [$Ni(\eta^5-C_5Me_5)\{\eta^4-[(C_5Me_5)NiC_{20}H_{12}]\}^+PF_6^-$] and **3b** [$Co(\eta^5-C_5Me_5)\{\eta^3-[(C_5Me_5)CoC_{20}H_{12}]\}^+PF_6^-$], respectively.



Both compounds are paramagnetic and they do not show any signals in 1H NMR spectra in the range between 0 and 10 ppm. In **3a**

Download English Version:

<https://daneshyari.com/en/article/1320987>

Download Persian Version:

<https://daneshyari.com/article/1320987>

[Daneshyari.com](https://daneshyari.com)