



New ionic fluorenylnickel complexes: Synthesis and solid state structure



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ABSTRACT

New fluorenylnickel complexes $[M(\text{THF})_n]^+[\text{Ni}(\eta^5\text{-Flu})(\eta^1\text{-Flu})_2]^-$ ($M = +48 \text{ Li}$, **1** and $M = \text{Na}$, **2**) have been obtained in the reaction of nickel bromide with fluorenyllithium and -sodium. The X-ray molecular structures of **1** (monoclinic; $P2_1/c$) and **2** (orthorhombic; $Fdd2$) reveal that in both complexes two fluorenyl ligands are bonded to the nickel atom by η^1 bond and the third one is bonded to the nickel atom by η^5 bond. Complexes **1** and **2** are the first structurally characterized nickel complexes bearing fluorenyl ligands.

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Introduction

Fluorenyl group is an attractive ligand for organometallic chemistry for several reasons. It can be bonded to the metal atom in various modes. Its complexes exhibit catalytic activity in many polymerization reactions. It is bulky and plane and easily forms free radicals and carbene species. Many transition (Ti [1], Zr [2,3], Hf [3], Nb [2], Cr [4], Mn [5], Mo [6], Fe [7], Os [8], Re [9], Ru [10], Co [11]) and main group (Ba [12], K [13], Li [14], Na [15], Ca [16]) metal complexes, bearing one fluorenyl ligand in η^5 -bonding mode, have been described up to now.

Transition (Mo [17], Fe [18], Co [18], Mn [5,18], Zr [19], Zn [20], Y [21], Re [9], Rh [22], Ti [23], Cu [24], Au [25]) and main group (Na [26], Ga [27], Ge [28], Sn [29], Si [14], Al [30], In [27], Mg [31]) metal complexes, bonded to the fluorenyl ligand in η^1 -bonding mode, are also known. The fluorenyl ligand can also be bonded to metal in η^3 and η^6 modes [32–34] (Fig. 1).

According to our knowledge, transition metal complexes of groups 5–10 with two η^5 -bonded fluorenyl ligands have not been reported up to now. However, $\text{Yb}(\eta^5\text{-Flu})_2(\text{THF})_2$ [35] and $\text{Sm}(\eta^5\text{-Flu})(\eta^3\text{-Flu})(\text{THF})_2$ have been obtained [36]. The other examples of compounds with two fluorenyl ligands bonded to metal in η^5 -

bonding mode have been known for zirconium [37] and barium [38].

Nickel complexes with fluorenyl ligands have not been described up to now. Ferreira de Silva and co-workers carried out a number of gas-phase reactions between fluorene and transition metals [39]. They reported that fluorenylnickel compounds were not formed in these reactions.

In this work we present synthesis and structure of novel fluorenylnickel complexes, in which the nickel atom is bonded to the fluorenyl ligands in η^5 - and σ -bonding modes. As far as we know there are not known analogous complexes of other metals. Examples of complexes bearing one σ - and one η^5 -bonded fluorenyl ligands are known for zirconium [40] and titanium [23]. One σ -fluorenyl and two η^5 -cyclopentadienyl ligands are present in zirconium complex [19]. The ionic complex $[\text{Li}(\text{THF})_4]^+[\text{Cu}(\eta^1\text{-Flu})_2\text{PPh}_3]^-$ was obtained by Wright et al. [24].

Results and discussion

Trifluorenylnickel complexes, $[\text{Li}(\text{THF})_4]^+[\text{Ni}(\eta^5\text{-Flu})(\eta^1\text{-Flu})_2]^-$ **1** and $[\text{Na}(\text{THF})_5]^+[\text{Ni}(\eta^5\text{-Flu})(\eta^1\text{-Flu})_2]^-$ **2**, were obtained in the reactions of $\text{NiBr}_2(\text{DME})$ with fluorenyllithium and -sodium in tetrahydrofuran. Two of the fluorenyl ligands are in the σ -bonding mode, while the third one is η^5 -bonded to the nickel atom. Bis-acetylacetonate nickel reacts with fluorenyllithium in the same

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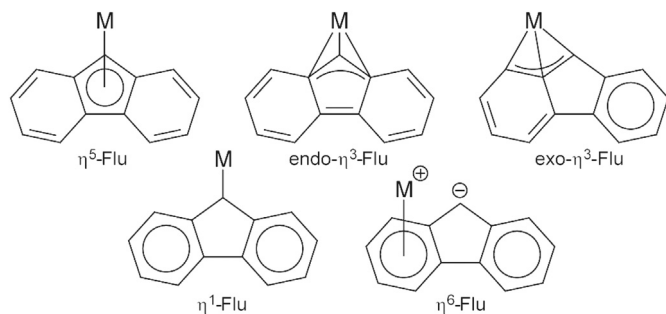


Fig. 1. Bonding modes of the fluorenyl ligand to metals.

manner. On the other hand $\text{NiCl}_2(\text{NH}_3)_6$ does not react with fluorenyllithium and -sodium.

The compounds **1** and **2** can be crystallized from tetrahydrofuran at -78°C forming dark green crystals. They are sensitive towards oxygen and moisture but in an inert atmosphere (argon) are quite stable up to about 40°C , where a slow decomposition begins. **1** and **2** are insoluble in hexane, toluene and acetonitrile. They are soluble in diethyl ether, dichloromethane and dioxane, but solutions are not stable and decompose after few minutes forming black nickel powder and 9,9'-bisfluorenyl. Solutions of **1** and **2** in tetrahydrofuran were stable enough to be characterized by ^1H and ^{13}C NMR.

^1H and ^{13}C NMR spectra of the compounds **1** and **2** are almost identical. The ^1H NMR spectra exhibit only one set of signals from differently bonded fluorenyl ligands: doublet at 7.4 ppm ($^3J_{\text{H-H}} = 8$ Hz) from protons bonded to C-4 and C-5, multiplet at ~ 7 ppm from protons at C-2, C-3, C-6 and C-7 and multiplet at ~ 6.3 ppm from protons at C-1 and C-8. This suggests a fast exchange in hapticity between three fluorenyl groups. Low temperature spectra (at -60°C) did not show any significant change besides some broadening of signals. A further lowering of the temperature to -100°C did not allow us to make a definitive conclusion mainly due to a very low sample concentration. Signals of protons at C-9 were not observed. Signals of complexed tetrahydrofuran molecules were observed at 3.54 and 1.69 ppm. ^{13}C NMR spectra exhibit signals at the range 145–141 ppm for C-8', C-9' and C-4' C-5' carbon atoms, at 123–121 ppm for C-2, C-7 and C-3, C-6, and at 119–118 ppm for C-1, C-8 and C-4, C-5. The signal of C-9 appeared at 50.1 ppm (this signal was observed only for the complex **1**). Signals of complexed tetrahydrofuran molecules were observed at 67.8 and 25.9 ppm.

The molecular structures of the compounds **1** and **2** were determined by X-ray (Figs. 2 and 3). The crystal data and structure refinement parameters for **1** and **2** are collected in Table 1. The compound **1** crystallizes in monoclinic crystal system in space group $P2_1/c$ ($Z = 4$). The compound **2** crystallizes in orthorhombic crystal system, space group $Fdd2$ ($Z = 48$) with three crystallographically independent anions and cations. Dimensions of the unit cell of **2** are: $a = 37.420(9)$ Å; $b = 118.55(3)$ Å; $c = 13.846(3)$ Å. This is a very large unit cell what is unusual for this kind of complexes. The atom numbering scheme for **1** is shown on Fig. 2 and for **2** on Fig. 3. Both complexes have ion-separated structures, where lithium cation is solvated by four THF molecules, and sodium is solvated by five THF molecules.

The compounds **1** and **2** contain the same anion and differences appearing in the Li or Na salt and between the different molecules in the Na salt are not chemically relevant. Therefore, the detailed discussion is concentrated on the anion of the compound **1**.

The Ni–C9 distances between nickel atom and two fluorenyl ligands (FluA and FluB) are Ni(1)–C(9A) 2.013(2) Å and Ni(1)–C(9B)

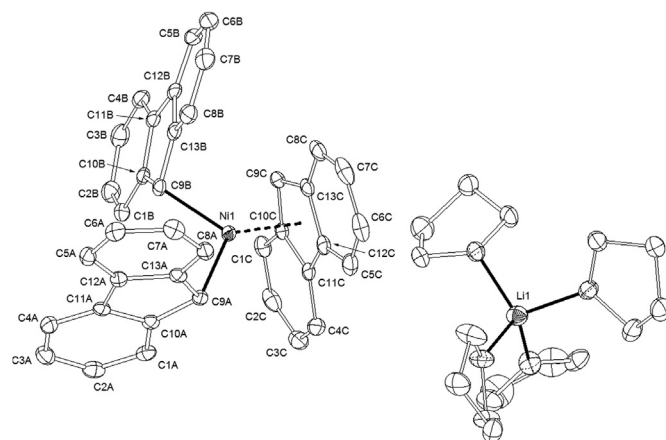


Fig. 2. Molecular structure of $[\text{Li}(\text{THF})_4]^+[\text{Ni}(\eta^5\text{-Flu})(\eta^1\text{-Flu})_2]^-$ **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bonds (Å) and angles ($^\circ$): Ni(1)–C(9A) 2.013(2); Ni(1)–C(9B) 1.996(2); Ni(1)–C(9C) 2.048(2); Ni(1)–C(10C) 2.228(2); Ni(1)–C(11C) 2.346(2); Ni(1)–C(12C) 2.310(2); Ni(1)–C(13C) 2.180(2); Ni(1)–C(9A)–FluA_{cent} 118.3(1); C(9A)–Ni(1)–C(9B) 98.3(1); Ni(1)–C(9B)–FluB_{cent} 117.1(1); C(9B)–Ni(1)–FluC_{cent} 133.5(1); Ni(1)–C(9C)–FluC_{cent} 63.4(1); C(9A)–Ni(1)–FluC_{cent} 128.1(1).

1.996(2) Å. The angles Ni(1)–C(9A)–FluA_{cent} and Ni(1)–C(9B)–FluB_{cent} are $118.3(1)^\circ$ and $117.1(1)^\circ$ respectively, indicating σ -bonding mode of these two ligands.

The two planes drawn through all carbon atoms of FluA and FluB are almost perpendicular with the angle between them $81.2(1)^\circ$ in **1** and $84.1(1)^\circ$ in **2**. Such arrangement of these ligands allowed minimizing repulsion between them.

The average C–C bond lengths of six-membered rings in FluA and FluB are 1.398 Å and 1.396 Å indicating aromatic character of these rings.

Six-membered rings of the FluC ligand are planar. There are unequivocal differences between bond lengths in these rings (Fig. 4). The C(1C)–C(2C), C(3C)–C(4C), C(5C)–C(6C) and C(7C)–C(8C) bonds (av. 1.377 Å) are much shorter than the others (av. 1.416 Å) indicating localized double bonds. The plausible reason of a visible loss of aromatic character of six-membered rings of the FluC ligand is the higher participation of π -electrons of five-membered ring in the bond to the nickel atom. Ni–FluA and Ni–FluB are σ -bonded to nickel, which does not disturb the aromatic nature of the six-membered rings.

Bonds C(9C)–C(10C) and C(9C)–C(13C) (Fig. 4) of FluC five-membered ring are shorter than corresponding bonds in FluA and FluB, bonded to nickel in η^1 -bonding mode. Those differences are in the range 0.029–0.040 Å. This indicates an increase of electron density in five-membered ring of FluC.

The angle Ni(1)–C(9C)–FluC_{cent} equal $63.4(1)^\circ$ what indicates the position of the nickel atom over the five-membered ring and is characteristic for π -bonding mode. The coordination modes of five-membered ring to nickel can be determined by slip-fold distortion [41]. To define a bonding mode of the Ni atom to the fluorenyl ligand FluC, we have calculated the slip parameter $\Delta_{\text{M-C}}$, i.e. the difference between the average Ni1–C distances to C11 and C12 and those to C10 and C13. The value for perfect η^5 coordination should be 0, although values till about 0.2 indicate this type of coordination. For “true” η^3 coordination $\Delta_{\text{M-C}}$ values have been reported of ca. 0.69–0.79 [41]. The value of $\Delta_{\text{M-C}}$ in **1** is ca. 0.12 Å, and ca. 0.09 Å in all three independent molecules of the compound **2**, what indicates η^5 -bonding mode of Ni to the fluorenyl ligand FluC. It seems that fluorenylnickel complexes prefer 18 valence electron (VE) configuration over a possible 16 VE configuration as in

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