



NOTE

Synthesis and Characterization of Mononuclear Nickel Complexes with Dithiolate Ligands

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Treatment of the mononuclear nickel complex (dppf)NiCl₂ (**1**) [dppf = 1,1'-bis(diphenylphosphino)ferrocene] with HSCH₂CH₂SH or HSCHMeCHMeSH in the presence of Et₃N in CH₂Cl₂ afforded the corresponding nickel dithiolate complexes (dppf)Ni(SCH₂CH₂S) (**2**) and (dppf)Ni(SCHMeCHMeS) (**3**) in 44 and 59 % yields, respectively. The new complexes **2** and **3** were structurally characterized by ¹H NMR, ³¹P{¹H} NMR and ¹³C{¹H} NMR spectroscopy.

Keywords: Nickel complex, Ethanedithiolate, Synthesis, dppf.

The transition metal complexes with dithiolate ligands have been received considerable attention due to their potential applications in catalytic reactions¹⁻⁶. Recently, the mononuclear nickel complexes with chelating *N*-substituted bis(diphenylphosphanyl)amine and dithiolate ligands were prepared by the condensation reaction of the precursors (Ph₂PNRPPH₂)NiCl₂ with dithiols in the presence of Et₃N⁷. In a continuation of our studies of the nickel complex⁸, we have obtained the mononuclear nickel complexes **2** and **3** with chelating 1,1'-bis(diphenylphosphino)ferrocene (dppf) and dithiolate ligands by the condensation reactions of (dppf)NiCl₂ with HSCH₂CH₂SH or HSCHMeC-HMeSH in the presence of Et₃N. In this paper, we describe the synthesis and characterization of the mononuclear nickel complexes with dppf and ethane dithiolate ligands.

(dppf)NiCl₂, HSCH₂CH₂SH and HSCHMeCHMeSH were available commercially and used as received. ¹H (³¹P{¹H}, ¹³C{¹H}) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

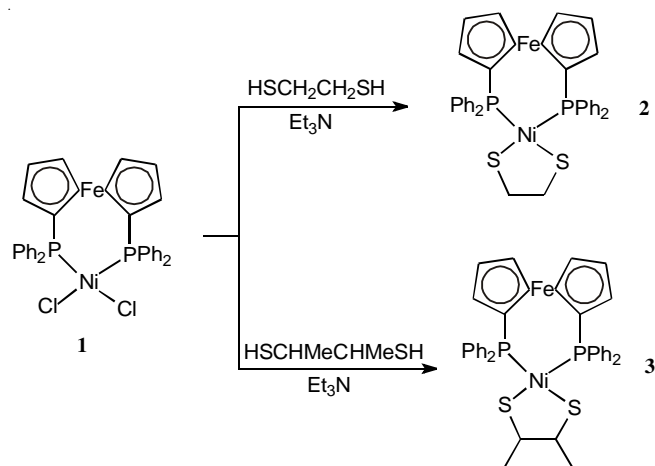
Synthesis of complex 2: To a solution of (dppf)NiCl₂ (0.137 g, 0.2 mmol) and HSCH₂CH₂SH (0.017 mL, 0.2 mmol) in CH₂Cl₂ (30 mL) was added Et₃N (0.060 mL, 0.4 mmol) and the new mixture was stirred for 1 h at room temperature. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH₂Cl₂ as eluent. From the main brown band afforded 0.062 g (44 %) of complex **2** as a brown solid. ¹H NMR (500 MHz, CDCl₃): 7.91 (q, *J* = 7.0 Hz, 8H, *o*-PhH), 7.44 (t, *J* = 7.2 Hz, 4H, *p*-PhH), 7.36 (t, *J* = 7.5 Hz, 8H, *m*-PhH), 4.28 (s, 4H, CpH), 4.16 (s, 4H, CpH), 2.70 (s, 4H, 2SCH₂) ppm. ³¹P{¹H} NMR (200 MHz, CDCl₃, 85 % H₃PO₄): 26.48 (s) ppm.

Synthesis of complex 3: To a solution of (dppf)NiCl₂ (0.137 g, 0.2 mmol) and HSCHMeCHMeSH (0.025 mL, 0.2 mmol) in CH₂Cl₂ (30 mL) was added Et₃N (0.060 mL, 0.4 mmol) and the new mixture was stirred for 1 h at room temperature. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH₂Cl₂ as eluent. From the main red band afforded 0.087 g (59 %) of complex **3** as a red solid. ¹H NMR (500 MHz, CDCl₃): 7.59-7.39 (m, 20H, PhH), 4.70-4.56 (m, 4H, CpH), 4.32-4.16 (m, 4H, CpH), 4.07-3.97 (m, 2H, 2SCH), 1.62, 1.25 (2s, 6H, 2CH₃) ppm. ³¹P{¹H} NMR (200 MHz, CDCl₃, 85 % H₃PO₄): 28.05 (s) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): 134.30, 133.43, 131.65, 131.54, 131.84, 131.29, 128.33, 128.23 (PhC), 74.88, 74.79, 74.27, 74.18, 74.04, 73.96, 73.50, 73.41 (CpC), 53.44 (CH), 20.44 (CH₃) ppm.

As shown in **Scheme-I**, treatment of (dppf)NiCl₂ with **1** equivalent of HSCH₂CH₂SH or HSCHMeCHMeSH in the presence of Et₃N in CH₂Cl₂ resulted in the formation of the mononuclear nickel complexes **2** and **3** in 44 and 59 % yields, respectively. The new complexes **2** and **3** were air-stable brown solids, which have been characterized by ¹H NMR, ³¹P{¹H} NMR and ¹³C{¹H} NMR spectroscopy.

¹H NMR spectrum: The ¹H NMR spectrum of complex **2** displayed a quadruplet at δ 7.91 ppm and two triplets at δ 7.44 and 7.36 ppm for the phenyl protons and two singlets at δ 4.28 and 4.16 ppm for the cyclopentadienyl protons. The ¹H NMR spectrum of **3** displayed a multiplet at δ 7.59-7.39 ppm for the phenyl protons and two multiplets at δ 4.70-4.56 and 4.32-4.16 ppm for the cyclopentadienyl protons.

³¹P{¹H} NMR spectrum: The ³¹P{¹H} NMR spectrum of complexes **2** and **3** exhibited a singlet at δ 26.48 and 28.05

Scheme-I: Synthesis of complexes **2** and **3**

ppm, respectively, for the two symmetrical phosphorus atoms of dppf chelated to the nickel atom.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum: The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **3** demonstrated eight signals in the range of δ 134.30–128.23 ppm for the phenyl carbons and eight signals in the range of δ 74.88–73.41 ppm for the cyclopentadienyl carbons.

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