

# Synthesis, spectroscopic and thermal studies of bis(pentafluorophenyl)nickel(II) complexes with $\beta$ -ketoiminate ligands

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## Abstract

The hydroxo-complex  $[\text{NBu}_4]_2[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]$  reacts with  $\beta$ -ketoimines in a 1:2 molar ratio to give the mononuclear anionic nickel (II) derivatives of general formula  $[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{R}_\gamma\text{COCHC}(=\text{NR})\text{Me}\}]$  ( $\text{R}_\gamma = \text{Me}$ ,  $\text{R} = \text{Ph}$ ,  $p\text{-ClC}_6\text{H}_4$ ,  $p\text{-BrC}_6\text{H}_4$ ,  $o\text{-MeC}_6\text{H}_4$ ,  $p\text{-MeC}_6\text{H}_4$ ,  $o\text{-MeOC}_6\text{H}_4$ ,  $p\text{-MeOC}_6\text{H}_4$ ;  $\text{R}_\gamma = \text{Ph}$ ,  $\text{R} = \text{Ph}$ ,  $p\text{-ClC}_6\text{H}_4$ ,  $p\text{-BrC}_6\text{H}_4$ ,  $o\text{-MeC}_6\text{H}_4$ ,  $p\text{-MeC}_6\text{H}_4$ ,  $o\text{-MeOC}_6\text{H}_4$ ,  $p\text{-MeOC}_6\text{H}_4$ ). All the complexes have been characterized by partial elemental analyses, conductance measurements, thermal analysis (thermogravimetry, differential thermogravimetry and differential scanning calorimetry) and spectroscopic (IR, Vis–UV, and  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR) methods. © 1997 Elsevier Science S.A.

**Keywords:** Chelate complexes; Pentafluorophenyl-nickel complexes; Thermal studies

## 1. Introduction

The synthesis of di- $\mu$ -hydroxo-complexes of general formula  $[\text{NBu}_4]_2[\{\text{M}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]$  ( $\text{M} = \text{Ni}$ ,  $\text{Pd}$ ,  $\text{Pt}$ ) [1–3] has been reported. Their use as precursors in synthetic work is based on the considerable nucleophilicity of the bridging OH groups, which is consistent with their high-field proton resonances. Thus, these hydroxo-complexes react with weak protic acids (HL) to give binuclear complexes  $[\{\text{M}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})(\mu\text{-L})\}_2]^{2-}$  and  $[\{\text{M}(\text{C}_6\text{F}_5)_2(\mu\text{-L})\}_2]^{2-}$  ( $\text{L} = \text{azolate}$  and  $\text{thiolate}$  ligand) [1,4]. Mononuclear anionic complexes are obtained by reaction of the hydroxo-complex  $[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]^{2-}$  with protic electrophiles  $\text{H}(\text{LL})$  ( $\text{LL} = \beta\text{-diketonate}$  [5], heterocyclic-2-thiolate [5], salicylaldimines [6], thiols [4], and phenols [7]), and deprotonation of amines or alcohols by the hydroxo-complex in the presence of carbon disulfide leads to the formation of the corresponding dithiocarbamate or xanthate complexes respectively [8]. Moreover, the reaction of the hydroxo-bridged nickel complex with malononitrile leads to the formation of an unprecedented dicyanomethanide-bridged anionic complex [9].

We have now used the hydroxo-complex  $[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]^{2-}$  in an unusual route to the synthesis of  $\beta$ -ketoimine complexes of nickel(II) with the pentafluorophenyl group.

The complexes have been characterized by partial elemental analyses, thermal analysis and spectroscopic (IR, Vis–UV, and  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR) methods.

## 2. Experimental

### 2.1. Physical measurements and materials

C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyser. IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. NMR data were recorded on a Bruker AC 200E ( $^1\text{H}$ ) or a Varian Unity 300 ( $^{19}\text{F}$ ) spectrometer. Conductance measurements were performed with a Crison 525 conductimeter (in acetone;  $c = 10^{-3}$  M). The electronic spectra were recorded on a Hitachi 2000U spectrophotometer. Thermal-analysis studies were carried out on a Mettler TA-3000 system provided with a Mettler TG-50 thermobalance and DSC-20 differential scanning calorimeter. The thermogravimetry (TG) and differential scanning calorimetry (DSC) curves were obtained at a heating rate of  $5^\circ\text{C min}^{-1}$  in flowing air ( $100 \text{ ml min}^{-1}$ ) over the temperature range  $30\text{--}700^\circ\text{C}$  for TG and  $30\text{--}500^\circ\text{C}$  for DSC.

The precursor  $[\text{NBu}_4]_2[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]$  was prepared as described elsewhere [1]. The  $\beta$ -ketoimines were prepared according to literature procedures [10] and all the solvents were dried by standard methods before use.

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## 2.2. Preparation of the complexes

The complexes were obtained by treating  $[\text{NBu}_4]_2[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})_2]$  with the corresponding  $\beta$ -ketoimine (molar ratio 1:2) in methanol according to the following general method. To a methanol (5 ml) solution of  $[\text{NBu}_4]_2[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})_2]$  (0.15 g, 0.115 mmol) was added the  $\beta$ -ketoimine (0.23 mmol), and the solution was stirred at reflux temperature for 1 h. Water added to precipitate the yellow solid the complexes, which were filtered off, washed with *n*-hexane and air-dried.

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = Ph) (**1**) was obtained in 66% yield. Anal. Calcd. for  $\text{C}_{39}\text{F}_{10}\text{H}_{48}\text{N}_2\text{ONi}$ : C, 57.9; H, 5.9; N, 3.5. Found: C, 58.1; H, 5.9; N, 3.4%.  $A_M = 99 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1565 (C=O str), 1510 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 550 (684).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{ClC}_6\text{H}_4$ ) (**2**) was obtained in 83% yield. Anal. Calcd. for  $\text{C}_{39}\text{ClF}_{10}\text{H}_{47}\text{N}_2\text{ONi}$ : C, 55.5; H, 5.6; N, 3.3. Found: C, 55.5; H, 6.0; N, 3.2%.  $A_M = 102 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1570 (C=O str), 1515 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 420 (642).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{BrC}_6\text{H}_4$ ) (**3**) was obtained in 66% yield. Anal. Calcd. for  $\text{C}_{39}\text{BrF}_{10}\text{H}_{47}\text{N}_2\text{ONi}$ : C, 52.7; H, 5.3; N, 3.1. Found: C, 52.3; H, 5.4; N, 2.9%.  $A_M = 92 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1565 (C=O str), 1510 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 640 (628).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = *o*- $\text{MeC}_6\text{H}_4$ ) (**4**) was obtained in 75% yield. Anal. Calcd. for  $\text{C}_{40}\text{F}_{10}\text{H}_{50}\text{N}_2\text{ONi}$ : C, 58.3; H, 6.1; N, 3.4. Found: C, 58.1; H, 6.3; N, 3.2%.  $A_M = 110 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1570 (C=O str), 1510 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 310 (656).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{MeC}_6\text{H}_4$ ) (**5**) was obtained in 68% yield. Anal. Calcd. for  $\text{C}_{40}\text{F}_{10}\text{H}_{50}\text{N}_2\text{ONi}$ : C, 58.3; H, 6.1; N, 3.4. Found: C, 58.5; H, 5.9; N, 3.6%.  $A_M = 97 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1570 (C=O str), 1515 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 640 (554).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = *o*- $\text{MeOC}_6\text{H}_4$ ) (**6**) was obtained in 62% yield. Anal. Calcd. for  $\text{C}_{40}\text{F}_{10}\text{H}_{50}\text{N}_2\text{O}_2\text{Ni}$ : C, 57.2; H, 6.0; N, 3.3. Found: C, 57.0; H, 6.2; N, 3.1%.  $A_M = 110 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1565 (C=O str), 1505 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 100 (526).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{MeCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{MeOC}_6\text{H}_4$ ) (**7**) was obtained in 74% yield. Anal. Calcd. for  $\text{C}_{40}\text{F}_{10}\text{H}_{50}\text{N}_2\text{O}_2\text{Ni}$ : C, 57.2; H, 6.0; N, 3.3. Found: C, 57.3; H, 6.3; N, 3.1%.  $A_M = 105 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1560 (C=O str), 1515 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 23 470 (528).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = Ph) (**8**) was obtained in 80% yield. Anal. Calcd. for  $\text{C}_{44}\text{F}_{10}\text{H}_{50}\text{N}_2\text{ONi}$ : C, 60.6; H, 5.7; N, 3.2. Found: C, 60.4; H,

5.9; N, 3.2%.  $A_M = 96 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1565 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 570 (1768).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{ClC}_6\text{H}_4$ ) (**9**) was obtained in 84% yield. Anal. Calcd. for  $\text{C}_{44}\text{F}_{10}\text{ClH}_{49}\text{N}_2\text{ONi}$ : C, 58.3; H, 5.4; N, 3.1. Found: C, 58.1; H, 5.5; N, 3.1%.  $A_M = 99 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1550 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 470 (1708).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{BrC}_6\text{H}_4$ ) (**10**) was obtained in 63% yield. Anal. Calcd. for  $\text{C}_{44}\text{F}_{10}\text{BrH}_{49}\text{N}_2\text{ONi}$ : C, 55.6; H, 5.2; N, 2.9. Found: C, 55.3; H, 5.4; N, 3.0%.  $A_M = 101 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1550 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 170 (2034).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = *o*- $\text{MeC}_6\text{H}_4$ ) (**11**) was obtained in 79% yield. Anal. Calcd. for  $\text{C}_{45}\text{F}_{10}\text{H}_{52}\text{N}_2\text{ONi}$ : C, 61.0; H, 5.9; N, 3.2. Found: C, 60.7; H, 6.1; N, 2.9%.  $A_M = 97 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1560 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 470 (1784).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{MeC}_6\text{H}_4$ ) (**12**) was obtained in 76% yield. Anal. Calcd. for  $\text{C}_{45}\text{F}_{10}\text{H}_{52}\text{N}_2\text{ONi}$ : C, 61.0; H, 5.9; N, 3.2. Found: C, 61.1; H, 6.0; N, 3.0%.  $A_M = 104 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1560 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 120 (2392).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = *o*- $\text{MeOC}_6\text{H}_4$ ) (**13**) was obtained in 80% yield. Anal. Calcd. for  $\text{C}_{45}\text{F}_{10}\text{H}_{52}\text{N}_2\text{O}_2\text{Ni}$ : C, 59.9; H, 5.8; N, 3.1. Found: C, 59.6; H, 6.0; N, 2.9%.  $A_M = 90 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1560 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 470 (1866).

$[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2\{\text{PhCOCHC}(=\text{NR})\text{Me}\}]$  (R = *p*- $\text{MeC}_6\text{H}_4$ ) (**13**) was obtained in 79% yield. Anal. Calcd. for  $\text{C}_{45}\text{F}_{10}\text{H}_{52}\text{N}_2\text{O}_2\text{Ni}$ : C, 59.9; H, 5.8; N, 3.1. Found: C, 59.4; H, 5.9; N, 3.0%.  $A_M = 95 \Omega^{-1} \text{ cm mol}^{-1}$ . IR ( $\text{cm}^{-1}$ ): 1560 (C=O str), 1500 (C=C str). Vis-UV [ $\text{cm}^{-1} (\epsilon_{\text{max}})$ ]: 22 520 (1962).

## 3. Results and discussion

In methanol,  $[\text{NBu}_4]_2[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})_2]$  reacts with  $\beta$ -ketoimines (molar ratio 1:2) to give the mononuclear anionic complexes  $[\text{Ni}(\text{C}_6\text{F}_5)_2(\beta\text{-ketoiminate})]^-$ , according to Eq. (1) (as tetrabutylammonium salts).

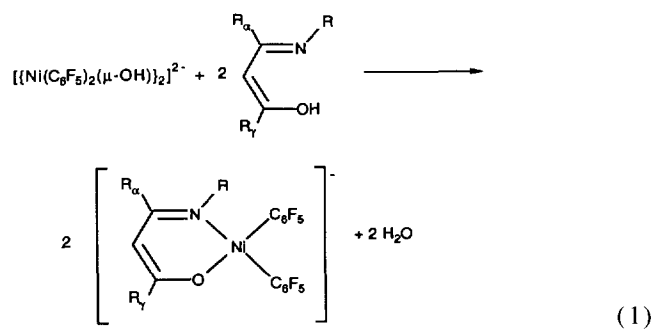


Table 1  
<sup>1</sup>H- and <sup>19</sup>F-NMR data for the nickel complexes <sup>a</sup>

Compound	R <sub>γ</sub>	R	<sup>1</sup> H δ (ppm) (SiMe <sub>4</sub> )	<sup>19</sup> F δ (ppm) (CFCl <sub>3</sub> )
1	Me	Ph	1.39 (s, 3H, γ-Me)	-114.4 (2 F <sub>o</sub> )
			1.60 (s, 3H, α-Me)	-116.0 (2 F <sub>o</sub> )
			4.88 (s, 1H, β-H)	-167.4 (1 F <sub>p</sub> )
			6.66 (m, 3H, Ph)	-167.7 (1 F <sub>p</sub> )
			6.84 (m, 2H, Ph)	-168.0 (2 F <sub>m</sub> )
2	Me	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	1.41 (s, 3H, γ-Me)	-114.4 (2 F <sub>o</sub> )
			1.60 (s, 3H, α-Me)	-116.1 (2 F <sub>o</sub> )
			4.91 (s, 1H, β-H)	-167.2 (1 F <sub>p</sub> )
			6.62 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-167.4 (1 F <sub>p</sub> )
			6.86 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-168.1 (4 F <sub>m</sub> )
3	Me	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	1.42 (s, 3H, γ-Me)	-114.4 (2 F <sub>o</sub> )
			1.60 (s, 3H, α-Me)	-116.4 (2 F <sub>o</sub> )
			4.91 (s, 1H, β-H)	-166.9 (1 F <sub>p</sub> )
			6.57 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-167.2 (1 F <sub>p</sub> )
			7.00 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-167.9 (4 F <sub>m</sub> )
4	Me	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	1.33 (s, 3H, γ-Me)	-113.1 (1 F <sub>o</sub> )
			1.60 (s, 3H, α-Me)	-114.3 (1 F <sub>o</sub> )
			2.50 (s, 3H, <i>o</i> -Me)	-115.6 (1 F <sub>o</sub> )
			4.91 (s, 1H, β-H)	-116.7 (1 F <sub>o</sub> )
			6.59 (m, 4H, C <sub>6</sub> H <sub>4</sub> )	-167.4 (1 F <sub>p</sub> )
5	Me	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	1.39 (s, 3H, γ-Me)	-114.4 (2 F <sub>o</sub> )
			1.57 (s, 3H, α-Me)	-115.9 (2 F <sub>o</sub> )
			2.03 (s, 3H, <i>p</i> -Me)	-167.4 (1 F <sub>p</sub> )
			4.85 (s, 1H, β-H)	-168.4 (4 F <sub>m</sub> + 1 F <sub>p</sub> )
			6.47 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	
6	Me	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	1.37 (s, 3H, γ-Me)	-113.2 (1 F <sub>o</sub> )
			1.59 (s, 3H, α-Me)	-115.1 (1 F <sub>o</sub> )
			3.71 (s, 3H, <i>o</i> -MeO)	-116.1 (2 F <sub>o</sub> )
			4.88 (s, 1H, β-H)	-168.0 (1 F <sub>p</sub> )
			6.44 (m, 2H, C <sub>6</sub> H <sub>4</sub> )	-168.7 (4 F <sub>m</sub> + 1 F <sub>p</sub> )
7	Me	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	1.42 (s, 3H, γ-Me)	-114.8 (2 F <sub>o</sub> )
			1.60 (s, 3H, α-Me)	-116.4 (2 F <sub>o</sub> )
			3.58 (s, 3 H, <i>p</i> -MeO)	-167.8 (1 F <sub>p</sub> )
			4.87 (s, 1H, β-H)	-168.7 (4 F <sub>m</sub> + 1 F <sub>p</sub> )
			6.42 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	
8	Ph	Ph	1.56 (s, 3H, α-Me)	-114.4 (2F <sub>o</sub> )
			5.71 (s, 1H, β-H)	-116.2 (2F <sub>o</sub> )
			6.72 (m, 3H, Ph)	-167.1 (1F <sub>p</sub> )
			6.86 (d, 2H, Ph)	-167.5 (1F <sub>p</sub> )
			7.22 (m, 3H, γ-Ph)	-167.8 (2F <sub>m</sub> )
9	Ph	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	7.55 (d, 2H, γ-Ph)	-168.3 (2F <sub>m</sub> )
			1.59 (s, 3H, α-Me)	-114.3 (2F <sub>o</sub> )
			5.75 (s, 1H, β-H)	-116.4 (2F <sub>o</sub> )
			6.70 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-166.9 (1F <sub>p</sub> )
			6.91 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-167.2 (1F <sub>p</sub> )
10	Ph	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	7.24 (m, 3H, γ-Ph)	-167.9 (4F <sub>m</sub> )
			7.55 (d, 2H, γ-Ph)	
			1.59 (s, 3H, α-Me)	-114.3 (2F <sub>o</sub> )
			5.74 (s, 1H, β-H)	-116.4 (2F <sub>o</sub> )
			6.64 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-166.9 (1F <sub>p</sub> )
			7.05 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-167.2 (1F <sub>p</sub> )
			7.24 (m, 3H, γ-Ph)	-167.9 (4F <sub>m</sub> )
			7.55 (d, 2H, γ-Ph)	

(continued)

Table 1 (continued)

Compound	R <sub>γ</sub>	R	<sup>1</sup> H δ (ppm) (SiMe <sub>4</sub> )	<sup>19</sup> F δ (ppm) (CFCl <sub>3</sub> )
11	Ph	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	1.51 (s, 3H, α-Me)	-113.0 (1F <sub>o</sub> )
			2.54 (s, 3H, Me)	-114.2 (1F <sub>o</sub> )
			5.76 (s, 1H, β-H)	-116.0 (1F <sub>o</sub> )
			6.71 (m, 4H, C <sub>6</sub> H <sub>4</sub> )	-116.9 (1F <sub>o</sub> )
			7.23 (m, 3H, γ-Ph)	-167.1 (1F <sub>p</sub> )
			7.57 (d, 2H, γ-Ph)	-167.7 (1F <sub>p</sub> )
12	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	1.57 (s, 3H, α-Me)	-168.1 (4F <sub>m</sub> )
			2.08 (s, 3H, <i>p</i> -Me)	-114.8 (2F <sub>o</sub> )
			5.70 (s, 1H, β-H)	-116.6 (2F <sub>o</sub> )
			6.56 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-167.60 (1F <sub>p</sub> )
			6.69 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-168.31 (2F <sub>m</sub> )
			7.21 (m, 3H, Ph)	-168.60 (1F <sub>p</sub> )
			7.55 (d, 2H, Ph)	-168.91 (2F <sub>m</sub> )
13	Ph	<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub>	1.54 (s, 3H, α-Me)	-112.8 (1F <sub>o</sub> )
			3.73 (s, 3H, MeO)	-114.6 (1F <sub>o</sub> )
			5.71 (s, 1H, β-H)	-116.0 (2F <sub>o</sub> )
			6.61 (m, 4H, C <sub>6</sub> H <sub>4</sub> )	-167.3 (1F <sub>p</sub> )
			7.22 (m, 3H, γ-Ph)	-168.0 (4F <sub>m</sub> + 1F <sub>p</sub> )
			7.55 (m, 2H, γ-Ph)	
14	Ph	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	1.58 (s, 3H, α-Me)	-114.3 (2F <sub>o</sub> )
			3.01 (s, 3H, MeO)	-116.2 (2F <sub>o</sub> )
			5.70 (s, 1H, β-H)	-167.1 (1F <sub>p</sub> )
			6.45 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	-168.1 (4F <sub>m</sub> + 1F <sub>p</sub> )
			6.59 (d, 2H, C <sub>6</sub> H <sub>4</sub> )	
			7.20 (m, 3H, γ-Ph)	
			7.55 (m, 2H, γ-Ph)	

<sup>a</sup> Solvent: acetone-d<sub>6</sub>.

The new pentafluorophenyl-nickel derivatives are air-stable yellow solids, and their acetone solutions exhibit conductance values corresponding to 1:1 electrolytes [11]. The IR spectra show the absorptions attributed to the C<sub>6</sub>F<sub>5</sub> group [12] at ca. 1630 (m), 1490 (vs), 1050 (s) and 950 (vs) cm<sup>-1</sup>, as well as a broad or split band at 780 cm<sup>-1</sup> for the so-called 'X-sensitive' mode of C<sub>6</sub>F<sub>5</sub> which is characteristic of the *cis*-Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> fragment [13].

The most significant absorption bands of the β-ketoimine complexes appear in the 1600–1500 cm<sup>-1</sup> region, thus the IR spectra of the complexes show two strong bands at ca. 1560 and 1510 cm<sup>-1</sup> attributed to C=O and C=C stretching vibrations [14]. All the complexes give an absorption band in their electronic spectra overlapped with a charge-transfer band which may be assigned to the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2g</sub> transition in a square-planar ligand field [15].

The <sup>1</sup>H- and <sup>19</sup>F-NMR data are listed in Table 1. The <sup>1</sup>H spectra show the expected patterns for the β-ketoimine ligands. The β-ketoimine complexes exhibited three different <sup>19</sup>F-NMR patterns (Table 1). The <sup>19</sup>F spectra of the complexes 1–3, 5, 7, 8–10, 12 and 14 give two resonance signals (relative intensities 2:2) in the *o*-fluorine region indicating that there are two inequivalent C<sub>6</sub>F<sub>5</sub> groups, one trans to O and one trans to N. The same result was previously observed for other N,O-donor bidentate ligands [5,6]. However, when the substituents on the nitrogen atom are *o*-methoxyphenyl (6 and 13) or *o*-tolyl (4 and 11) the spectra show the effect

of frozen rotation of the *ortho*-substituents around the C–N bond and the resulting anisotropy produces three (intensity ratio 1:1:2) or four (intensity ratio 1:1:1:1) signals for the *o*-fluorines.

The TG curves in flowing air exhibit a two-stage decomposition pattern but stable intermediate products were not found. In all the complexes, the final pyrolysis product corresponds to nickel(II) oxide. The DSC curves (also in flowing air) show one endothermic peak due to melting of the sample and two exothermic peaks for the simultaneous decomposition and combustion of the evolved gas. The values of the melting enthalpies, calculated by integration of DSC endothermic peaks were in the range 29.0–50.0 kJ mol<sup>-1</sup>.

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