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# Volatile square planar $\beta$ -imino carbonyl enolato complexes of Pd(II) and Ni(II) as potential MOCVD precursors

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# ABSTRACT

A series of palladium(II) and nickel(II) [ML<sub>2</sub>] complexes (**1-6**: **1**, Pd, **L<sup>Me</sup>**; **2**, Pd, **L<sup>iBu</sup>**; **3**, Pd, **L<sup>nBu</sup>**; **4**, Pd, **L<sup>nHe</sup>**; **5**, Ni, **L<sup>Me</sup>**; **6**, Ni, **L<sup>iBu</sup>**) has been synthesised by reacting the proper acetato salt with the  $\beta$ -enamino ketoesters (MeCO)(MeOCO)C=C(NH<sub>2</sub>)R (R = Me, *i*-Bu, *n*-Bu, *n*-hexyl). The chain length has practically no effect on the output of the synthetic procedure so that complexes are obtained always in good yields. They are all square planar and the potentially tridentate ligand is coordinated via the N,O donor atoms of the imino and keto groups. Their thermal behaviour has been fully studied and [Ni(**L<sup>Me</sup>**)<sub>2</sub>] demonstrated to be a convenient precursor for the Metal Organic Chemical Vapour Deposition of Ni and NiO thin films.

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#### 1. Introduction

We have recently exploited the potentiality of a general procedure for the synthesis of  $\beta$ -imino carbonyl enolato complexes by reacting the proper metal acetate with β-enaminodiones of the type  $(R'CO)(R''CO)C=C(NH_2)R$  (HL). The nature of the substituents is extremely variable and, for example, R can be an electron-withdrawing (CN [1], CCl<sub>3</sub> [2a], PhCO [2], EtOCO [3], CH<sub>2</sub>CN [4]) or donating group (Me [5], Et [3]). These protonated ligands can be easily synthesised by a method developed in our laboratories involving a metal-catalysed or -promoted reaction of the nitrile RCN with the  $\beta$ -dicarbonyl (R'CO)(R"CO)CH<sub>2</sub> [6–8]. The synthesis of the metal complexes is based on an M(OAc)<sub>2</sub>/2HL exchange process in which the acetate is protonated by the  $\beta$ -enaminodione and liberated in solution as acetic acid. The coordinated  $L^-$  ligand is potentially tridentate through two oxygen and one nitrogen donor atoms, however in the very numerous investigated cases it acts only as bidentate (N,O or O,O). N,O coordination is largely preferred with Ni(II) and Cu(II) metal centres and it is the only one with Pd(II). The obtained complexes are square planar, very stable and volatile, and, as a consequence, interesting as precursors in MOCVD processes [9].

In this paper we have utilized in the reaction with palladium and nickel acetate the  $\beta$ -enaminodiones shown in Chart 1, which are characterised by different lengths of the alkyl chains, in order

to check first of all the effectiveness of the synthetic procedure and secondly how the type of alkyl chain may affect the physicochemical properties of the resulting complexes.

## 2. Experimental

#### 2.1. Reagents and apparatus

The reagents were high purity products and generally used as received. Solvents were dried before use and the reaction apparatus carefully deoxygenated. Reactions were performed under argon and all operations were carried out under an inert atmosphere. The solution <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker 200 AC (200.12 MHz for <sup>1</sup>H and 50.32 MHz for <sup>13</sup>C) or on a Bruker DRX 400 (400.13 MHz for <sup>1</sup>H and 100.63 MHz for <sup>13</sup>C) spectrometer. The chemical shifts are determined by reference to the residual solvent peaks, using tetramethylsilane as internal standard. The solution <sup>1</sup>H-<sup>15</sup>N NMR spectra were recorded on a Bruker Avance 600 (600.13 MHz for <sup>1</sup>H and 60.82 MHz for <sup>15</sup>N) spectrometer. The <sup>1</sup>H and <sup>13</sup>C assignments were performed by means of conventional homonuclear 2D COSY or 2D <sup>1</sup>H–<sup>13</sup>C HETCORR experiments. The <sup>15</sup>N resonances relative to CH<sub>3</sub>NO<sub>2</sub> were detected in the inverse acquisition mode through 2D  ${}^{1}H/{}^{15}N$  correlation via double inept transfer with decoupling during acquisition. The FT IR spectra were recorded on a Biorad FT S7 PC or on Bruker IFS 66 IR spectrophotometers at 2 cm<sup>-1</sup> resolution in KBr disks. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Mass spectra were obtained with a single focus mass spectrometer





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Chart 1.

VG MM16 operating in electron ionisation mode at 70 eV electron beam energy and an ion source temperature of 180 °C. TGS–DSC analysis were performed with a Perkin–Elmer TGS-2, DSC-4 apparatus.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a Perkin–Elmer  $\Phi$  5600ci spectrometer, with monochromatised Al K $\alpha$  radiation (1486.6 eV), calibrated vs. Au4f<sub>7/2</sub> at 83.9 eV [10]. XRD data were collected with a Philips diffractometer with thin film equipment (Cu K $\alpha$ ,  $\lambda$  = 1.54 Å, incident angle 1°).

#### 2.2. Synthesis of the ligands

The  $\beta$ -enaminodiones (MeCO)(MeOCO)C=C(NH<sub>2</sub>)R (R = Me (**HL**<sup>Me</sup>); R = *i*-Bu (**HL**<sup>iBu</sup>); R = *n*-Bu (**HL**<sup>nBu</sup>); R = *n*-hexyl (**HL**<sup>nHe</sup>)), were prepared by reaction of methyl acetoacetate with the appropriate nitrile in the presence of a stoichiometric amount of SnCl<sub>4</sub>, with the same procedure already reported for **HL**<sup>Me</sup> [11,12].

**HL**<sup>nBu</sup>: <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 0.93 (t, 3H, CH<sub>3</sub>), 1.30–1.75 (m, 4H, 2CH<sub>2</sub>), 2.26 (s, 3H, CH<sub>3</sub>CO), 2.45 (m, 2H, CH<sub>2</sub>), 3.76 (s, 3H, CH<sub>3</sub>O-CO), 5.68 (s, 1H, NH), 11.21 (s, 1H, NH). FTIR [cm<sup>-1</sup>, KBr]: 3370 [ν(NH)], 2959–2872 [δ(CH)], 1709 [ν(MeOC=O)], 1603 [ν(C=O)].

**HL**<sup>IBu</sup>: <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta = 0.91$  (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.84 (m, 1H, CH), 2.20 (s, 3H, CH<sub>3</sub>CO), 2.32 (d, 2H, CH<sub>2</sub>), 3.70 (s, 3H, CH<sub>3</sub>O-CO), 6.00 (s, 1H, NH), 11.18 (s, 1H, NH). FTIR [cm<sup>-1</sup>, KBr]: 3364 [v(NH)], 2961–2872 [ $\delta$ (CH)], 1703 [v(MeOC=O)], 1603 [v(C=O)].

**HL**<sup>nHe</sup>: <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 0.87 (m, 3H, CH<sub>3</sub>), 1.20–1.70 (m, 8H, 4CH<sub>2</sub>), 2.24 (s, 3H, CH<sub>3</sub>CO), 2.44 (m, 2H, CH<sub>2</sub>), 3.75 (s, 3H, CH<sub>3</sub>O-CO), 5.64 (s, 1H, NH), 11.21 (s, 1H, NH).

#### 2.3. Synthesis of the complexes

Complexes **1–6** were obtained by reaction of the metal acetate with the appropriate ligand in 1/2 molar ratio, in anhydrous ethanol, at room temperature under argon; the resulting solutions were left under stirring for variable times and the complexes can either precipitate spontaneously from the reaction mixture or be recovered from the solution evaporated to dryness. In many cases the compounds are isolable in different forms, distinguished as **a** or **b**, which exhibit identical composition but different spectroscopic properties; the symbols **a** and **b** indicate only the order in which the complexes have been isolated.

[Pd(L<sup>Me</sup>)<sub>2</sub>] (1a, 1b). [Pd(OAc)<sub>2</sub>] (0.17 g, 0.76 mmol) and HL<sup>Me</sup> (0.25 g, 1.60 mmol) were dissolved in anhydrous ethanol (20 ml) and the resulting solution was stirred for 4 h at room temperature, then filtered. The solid was recrystallised from dichloromethane/ hexane, affording pure (1a) as a bright yellow solid (0.090 g, 27% yield). The yellow alcoholic filtrate was evaporated to small volume under reduced pressure and treated with diethylether (10 ml), giving (1b) as a light vellow solid, which was filtered and dried under vacuum (0.157 g, 47% yield). Anal. Calc. for  $C_{14}H_{20}N_2O_6Pd$  (*MW* = 418.72): C, 40.16; H, 4.81; N, 6.69. Found for (1a): C, 40.28; H, 4.71; N, 6.37. Found for (1b): C, 39.57; H, 4.76; N, 6.68%. (1a). <sup>1</sup>H NMR (in CDCl<sub>3</sub>), two species, labelled a and  $\mathbf{a}'$ , in approximately 2/1 ratio are present in solution:  $\delta$  = 2.09 (s, 3H, CH<sub>3</sub>CO, 1a), 2.16 (s, 3H, CH<sub>3</sub>, 1a), 2.18 and 2.19 (2s, 3H, CH<sub>3</sub>CO and CH<sub>3</sub>, 1a'), 3.76 (s, 4.5H, CH<sub>3</sub>OCO, 1a and 1a'), 6.34 (s, 0.5H, NH, 1a'), 6.79 (s, 1H, NH, 1a). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):

 $\delta$  = 25.6 and 26.7 (CH<sub>3</sub> and CH<sub>3</sub>CO, **1a**), 26.1 and 27.0 (CH<sub>3</sub> and CH<sub>3</sub>CO, 1a'), 51.6 (CH<sub>3</sub>OCO, 1a and 1a'), 106.0 ((CH<sub>3</sub>CO)C, 1a and 1a'), 164.7 (CNH, 1a), 165.4 (CNH, 1a'), 170.9 (CH<sub>3</sub>OCO, 1a'), 171.1 (CH<sub>3</sub>OCO, 1a), 179.5 (CH<sub>3</sub>CO, 1a), 181.4 (CH<sub>3</sub>CO, 1a'). FTIR [cm<sup>-1</sup>, KBr]: 3322 [v(NH)], 1692 [v(MeOC=O)], 1577 [v(C-O)]. FTIR [cm<sup>-1</sup>, CDCl<sub>3</sub>]: 3348, 3316(sh) [v(NH)], 1702 [v(MeOC=O)],  $(\lambda_{max}/nm,$ 1587 [v(C----O)]. UV–Vis CHCl<sub>3</sub>): 328 260 ( $\varepsilon = 21100 \pm 2100 \,\mathrm{dm^3}$  $(\varepsilon = 6400 \pm 500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}),$ mol<sup>-1</sup> cm<sup>-1</sup>). MS-EI: m/z 418 ([Pd( $\mathbf{L}^{Me}$ )<sub>2</sub>]<sup>+</sup>). (1b). <sup>1</sup>H NMR (in  $CDCl_3$ ):  $\delta = 2.15$  (s, 3H,  $CH_3CO$ ), 2.17 (s, 3H,  $CH_3$ ), 3.75 (s, 3H,  $CH_3O$ -CO), 6.80 (s, 1H, NH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 25.9 and 26.7 (CH<sub>3</sub>) and CH<sub>3</sub>CO), 51.6 (CH<sub>3</sub>OCO), 106.0 ((CH<sub>3</sub>CO)C), 165.2 (CNH), 171.0 (CH<sub>3</sub>OCO), 180.7 (CH<sub>3</sub>CO). FTIR [cm<sup>-1</sup>, KBr]: 3325 and 3310 [v(NH)], 1684 and 1675 [v(MeOC=O)], 1584 and 1576 [v(C--O)]. FTIR [cm<sup>-1</sup>, CDCl<sub>2</sub>]: 3348 and 3313 [v(NH)], 1702 [v(MeOC=O)],  $(\lambda_{max}/nm,$ 1576 [v(C...0)].UV-Vis  $CHCl_3$ ): 326  $mol^{-1} cm^{-1}$ ), 260 ( $\varepsilon = 22300 \pm 1600 dm^3$  $(\varepsilon = 7400 \pm 500 \,\mathrm{dm^3})$  $mol^{-1} cm^{-1}$ ). MS-EI: *m/z* 418 ([Pd(**L<sup>Me</sup>**)<sub>2</sub>]<sup>+</sup>). Complex (**1a**) decomposes at 178 °C at atmospheric pressure, while it sublimes at 156 °C at  $4 \times 10^{-2}$  mbar; FTIR analysis reveals that both the sublimate (FTIR: 3321 [v(NH)], 1689 [v(MeOC=O)] and 1576 [v(C--O)]) and the residue are still (1a) (FTIR: 3322 [v(NH)], 1690 [v(MeO-C=O)], 1574 [v(C--O)]). Complex (**1b**) decomposes at 210 °C at atmospheric pressure, while it sublimes at 156 °C at  $4 \times 10^{-2}$  mbar; FTIR analysis reveals that the sublimate is (1a) (FTIR: 3320 [v(NH)], 1688 [v(MeOC=O)] and 1576 [v(C-O)]) while the residue is still (1b) (FTIR: 3323 and 3310 [v(NH)], 1685 and 1673 [v(MeOC=O)], 1574 [v(C---O)]).

[Pd(L<sup>iBu</sup>)<sub>2</sub>] (2a, 2b). [Pd(OAc)<sub>2</sub>] (0.17 g, 0.76 mmol) was dissolved in anhydrous ethanol (15 ml) and the resulting solution was additioned with HL<sup>iBu</sup> (0.30 g, 1.50 mmol, in 15 ml anhydrous ethanol). The reaction mixture was left under stirring for 2 h at room temperature, then evaporated under reduced pressure. The residue was dissolved with dichloromethane (15 ml) and filtered through Celite. The filtrate was again evaporated to small volume and finally, treated with diethylether (20 ml), affording a vellow precipitate (2), which was filtered and dried under vacuum (0.24 g, 63% yield). Anal. Calc. for  $C_{20}H_{32}N_2O_6Pd$  (MW = 502.88): C, 47.77; H, 6.41; N, 5.57. Found: C, 46.96; H, 6.40; N, 5.38%. (2): FTIR [cm<sup>-1</sup>, KBr]: 3297, 3270 and 3248 [v(NH)], 1715 [v(MeOC=O)], 1584 [ $\nu$ (C---O)]. UV–Vis ( $\lambda_{max}/nm$ , CHCl<sub>3</sub>): 330 ( $\varepsilon$  = 6600 ±  $500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 260 ( $\varepsilon = 19000 \pm 1400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). MS-EI: m/z 502 ([Pd( $\mathbf{L}^{i\mathbf{Bu}})_2$ ]<sup>+</sup>). The NMR spectra revealed that the isolated solid was a mixture of two isomers (2a, 2b) in 2.5/1 ratio. (2a). <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta = 0.89$  (d, 6H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>,  ${}^{3}J_{HH} = 6.6 \text{ Hz}$ ), 1.83 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 2.18 (s, 3H, CH<sub>3</sub>CO), 2.37 (d, 2H,  $(CH_3)_2CHCH_2$ ,  ${}^{3}J_{HH} = 7.4 \text{ Hz}$ ), 3.74 (s, 3H,  $CH_3OCO$ ), 6.34 (s, 1H, NH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta = 22.8$  ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 26.6 (CH<sub>3</sub>CO), 28.1 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 49.5 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 52.2 (CH<sub>3</sub>OCO), 106.2 ((CH<sub>3</sub>CO)C), 169.0 (CNH), 171.6 (CH<sub>3</sub>OCO), 181.7 (CH<sub>3</sub>CO). <sup>15</sup> N NMR (in CDCl<sub>3</sub>):  $\delta$  = 145.4. (**2b**). <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta = 0.92$  (d, 6H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), 1.83 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 2.09 (s, 3H, CH<sub>3</sub>CO), 2.33 (d, 2H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>,  ${}^{3}J_{\text{HH}}$  = 7.4 Hz), 3.74 (s, 3H, CH<sub>3</sub>OCO), 6.74 (s, 1H, CNH).  ${}^{13}$ C NMR (in CDCl<sub>3</sub>):  $\delta = 22.9$  ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 26.2 (CH<sub>3</sub>CO), 27.9 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 49.0 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 52.2 (CH<sub>3</sub>OCO), 106.4 ((CH<sub>3</sub>CO)C), 168.0 (CNH), 171.8 (CH<sub>3</sub>OCO), 179.9 (CH<sub>3</sub>CO). <sup>15</sup> N NMR (in CDCl<sub>3</sub>):  $\delta$  = 166.9. Complex (2) decomposes at 195 °C at atmospheric pressure, while it sublimes at 155 °C at  $6 \times 10^{-2}$  mbar; FTIR analysis reveals that the sublimate is (2b) (FTIR [cm<sup>-1</sup>, KBr]: 3270 and 3248 [v(NH)], 1713 [v(MeOC=O)], 1585 [v(C - 0)] while the residue is still a mixture of (2a) and (**2b**) (FTIR: 3298, 3270 and 3248 [v(NH)], 1715 [v(MeOC=O)], 1584 [v(C---O)]).

 $[Pd(L^{nBu})_2]$  (3). A yellow solid was obtained with the same experimental procedure of complex (2) (0.29 g, 77% yield). *Anal.* 

Calc. for C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>Pd (*MW* = 502.88): C, 47.77; H, 6.41; N, 5.57. Found: C, 46.89; H, 6.30; N, 5.41%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 0.87 (t, 3H,  $CH_3(CH_2)_3$ ,  ${}^{3}I_{HH} = 7.2 \text{ Hz}$ , 1.28 (m, 2H,  $CH_3CH_2(CH_2)_2$ ), 1.52 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.14 (s, 3H, CH<sub>3</sub>CO), 2.42 (t, 2H,  $CH_3(CH_2)_2CH_2$ ,  ${}^{3}J_{HH} = 8.0 Hz$ ), 3.72 (s, 3H,  $CH_3OCO$ ), 6.38 (s, 1H, NH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 13.8 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), 22.7 (CH<sub>2</sub>), 25.6 (CH<sub>3</sub>CO), 30.4 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>), 51.7 (CH<sub>3</sub>OCO), 105.7 ((CH<sub>3</sub>CO)C), 168.7 (CNH), 171.1 (CH<sub>3</sub>OCO), 179.3 (CH<sub>3</sub>CO). FTIR [cm<sup>-1</sup>, KBr]: 3295 [v(NH)], 1719 [v(MeOC=O)], 1582 [v(C=O)]. UV–Vis ( $\lambda_{max}$ / 328  $(\varepsilon = 7100 \pm 500 \,\mathrm{dm^3 \, mol^{-1} \, cm^{-1}}),$ nm, CHCl<sub>3</sub>): 260  $(\varepsilon = 20200 \pm 1500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ . MS-EI:  $m/z 503 ([Pd(\mathbf{L}^{nBu})_2]^+)$ . Complex (3) decomposes at 195 °C at atmospheric pressure, while it sublimes at 172 °C at  $4 \times 10^{-2}$  mbar; FTIR analysis reveals that both the sublimate (FTIR: 3293 [v(NH)], 1717 [v(MeOC=O)], 1582 [v(C - O)] and the residue are complex (3) (FTIR: 3293 [v(NH)], 1719 [v(MeOC=0)], 1582 [v(C=0)]).

 $[Pd(L^{nHe})_2]$  (4).  $[Pd(OAc)_2]$  (0.16 g, 0.73 mmol) was dissolved in anhydrous ethanol (15 ml) and the resulting solution was additioned with HL<sup>nHe</sup> (0.33 g, 1.45 mmol) dissolved in anhydrous ethanol (15 ml) and ethyl acetate (1 ml). The reaction mixture was left under stirring for 1 h at room temperature, then evaporated to small volume under reduced pressure. The residue was treated with ethanol (20 ml) under stirring for 1 h and the solvent was removed. The residue was dissolved with dichloromethane (15 ml) and filtered through Celite. The filtrate was again evaporated to small volume and finally treated with diethylether (20 ml), affording a yellow precipitate, which was filtered and dried under vacuum (0.25 g, 61% yield). Anal. Calc. for  $C_{24}H_{40}N_2O_6Pd$ (MW = 558.99): C, 51.57; H, 7.21; N, 5.01. Found: C, 51.61; H, 7.31; N, 4.90%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta = 0.85$  (t, 3H,  $CH_3(CH_2)_5$ ,  ${}^{3}J_{HH} = 6.1 \text{ Hz}$ , 1.25–1.50 (m, 8H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>), 2.15 (s, 3H, CH<sub>3</sub>CO), 2.40 (t, 2H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>,  ${}^{3}J_{HH}$  = 7.3 Hz), 3.72 (s, 3H, CH<sub>3</sub>OCO), 6.19 (s, 1H, NH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 14.0 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>), 22.5 (CH<sub>2</sub>), 25.9 (CH<sub>3</sub>CO), 28.2 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 39.6 (CH<sub>2</sub>), 51.6 (CH<sub>3</sub>OCO), 105.6 ((CH<sub>3</sub>CO)C), 169.0 (CNH), 171.1 (CH<sub>3</sub>OCO), 180.6 (CH<sub>3</sub>CO). FTIR [cm<sup>-1</sup>, KBr]: 3297 [v(NH)], [v(MeOC=O)], 1580 [v(C=O)]. UV-Vis  $(\lambda_{max}/nm,$ 1711 CHCl<sub>3</sub>): 328 ( $\varepsilon = 7600 \pm 500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). 260 ( $\varepsilon = 20100 \pm 100 \text{ cm}^{-1}$ ). 1500 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). MS-EI: m/z 558 ([Pd(**L**<sup>nHe</sup>)<sub>2</sub>]<sup>+</sup>). Complex (4) decomposes at 189 °C at atmospheric pressure, while it sublimes at 180 °C at  $5 \times 10^{-2}$  mbar; FTIR analysis reveals that both the sublimate (FTIR: 3295 [v(NH)], 1713 [v(MeOC=O)], 1582 [v(C - 0)] and the residue (FTIR: 3297 [v(NH)], 1711 [v(MeOC=0)], 1580 [v(C=0)]) are complex (4).

 $[Ni(L^{Me})_2]$  (5). A solution of  $HL^{Me}$  (0.63 g, 4.02 mmol) and [Ni(OAc)<sub>2</sub>]<sup>4</sup>H<sub>2</sub>O (0.50 g, 2.00 mmol) in anhydrous ethanol (20 ml) was stirred for 1 h at room temperature, then evaporated to small volume under reduced pressure. The residue was treated with ethanol (20 ml) and again the solvent was removed. This treatment was continued until the smell of acetic acid disappeared; 3-4 cycles were generally sufficient. Finally, treatment with diethylether (10 ml) gave a light red solid, which was filtered and dried under vacuo (0.47 g, 63%). Anal. Calc. for C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>NiO<sub>6</sub> (MW = 371.03): C, 45.32; H, 5.43; N, 7.55. Found: C, 45.34; H, 5.34; N, 7.58%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 1.95 (s, 3H, CH<sub>3</sub>CO), 2.08 (s, 3H, CH<sub>3</sub>CNH), 3.68 (s, 3H, CH<sub>3</sub>OCO), 5.37 (s, 1H, NH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 25.9 and 27.2 (CH<sub>3</sub>CNH and CH<sub>3</sub>CO), 51.2 (CH<sub>3</sub>OCO), 105.8 ((CH<sub>3</sub>CO)C), 167.7 (CNH), 170.3 (CH<sub>3</sub>OCO), 181.7 (CH<sub>3</sub>CO). FTIR [cm<sup>-1</sup>, KBr]: 3320 [v(NH)], 1688 [v(MeOC=O)], 1570 [v(C-O)]. UV-Vis  $(\lambda_{max}/nm, CHCl_3)$ : 342 ( $\epsilon = 3500 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ),  $(\varepsilon = 30200 \pm 2800 \,\mathrm{dm^3 \,mol^{-1} \, cm^{-1}}), 244 \quad (\varepsilon = 36500 \pm 1000 \,\mathrm{cm^{-1}})$ 272  $3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). MS-EI: *m/z* 370 ([Ni( $L^{Me}$ )<sub>2</sub>]<sup>+</sup>). Complex (**5**) decomposes at 193 °C at atmospheric pressure, while it sublimes at 130 °C at  $4 \times 10^{-2}$  mbar; FTIR analysis reveals that the sublimate is a mixture of (5) and another isomer (FTIR: 3342 and 3320 [v(NH)], 1690 [v(MeOC=O)], 1591 and 1572 [v(C--O)]), while the residue is complex (**5**) (FTIR: 3320 [*v*(NH)], 1688 [*v*(MeOC=O)], 1570 [*v*(C---O)]).

 $[Ni(L^{iBu})_2]$  (6). A solution of HL<sup>iBu</sup> (0.25 g, 1.60 mmol) in anhydrous ethanol (20 ml) was added to a solution of [Ni(OAc)<sub>2</sub>]<sup>2</sup>4H<sub>2</sub>O (0.19 g, 0.78 mmol, in 15 ml anhydrous ethanol). The resulting mixture was stirred for 12 h at room temperature and then evaporated to small volume under reduced pressure. The resulting residue was treated with ethanol (20 ml) under stirring for 1 h and the solvent was again removed. Treatment with diethylether (20 ml) afforded a reddish precipitate, which was filtered and dried under vacuum. The solid was recrystallised from dichloromethane/diethylether, affording pure (6) as a pink solid (0.26 g, 75% yield). Anal. Calc. for C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>NiO<sub>6</sub> (*MW* = 455.19): C, 52.77; H, 7.09; N, 6.15. Found: C, 51.44; H, 7.01; N, 5.98%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 0.90 (d, 6H,  $(CH_3)_2CHCH_2$ ,  ${}^{3}J_{HH} = 6.8 \text{ Hz}$ ), 1.72 (m, 1H,  $(CH_3)_2CHCH_2$ ), 1.94 (s, 3H, CH<sub>3</sub>CO), 2.28 (d, 2H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 3.70 (s, 3H, CH<sub>3</sub>CO<sub>2</sub>), 5.37 (s, 1H, CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 22.8 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 26.7 (CH<sub>3</sub>CO), 27.9 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 49.0 ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 51.8 (CH<sub>3</sub>OCO), 106.1 ((CH<sub>3</sub>CO)C), 170.7 (CNH), 171.1 (CH<sub>3</sub>OCO), 181.5 (CH<sub>3</sub>CO). <sup>15</sup> N NMR (in CDCl<sub>3</sub>):  $\delta$  = 162.7. FTIR [cm<sup>-1</sup>, KBr]: 3279 and 3268 [v(NH)], 1709 [v(MeOC=O)], 1582 [v(C - O)]. UV-Vis ( $\lambda_{max}/nm$ , CHCl<sub>3</sub>): 346 ( $\varepsilon = 3000 \pm$ 200 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 272 ( $\varepsilon = 26300 \pm 1700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 244 ( $\varepsilon = 34600 \pm 2300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). MS-EI: m/z 454 ([Ni- $(\mathbf{L^{iBu}})_2^{\dagger}$ ). Complex (6) decomposes at 180 °C at atmospheric pressure, while it sublimes at 125 °C at 7.5  $\times$  10<sup>-2</sup> mbar; FTIR analysis reveals that both the sublimate (FTIR: 3279 and 3268 [v(NH)], 1707 [v(MeOC=O)], 1582 [v(C-O)] and the residue (FTIR: 3279 and 3268 [v(NH)], 1709 [v(MeOC=O)], 1582 [v(C-O)]) are complex (6).

# 2.4. Vapour deposition of complex $[Ni(L^{Me})_2]$ (5)

All deposition experiments were performed in a cold wall reactor using  $O_2$ ,  $N_2$ ,  $N_2/O_2$  or  $N_2/O_2/H_2O$  mixtures as gas carrier (purity 99.999%). The precursor was sublimed from a small crucible located close to the reactor (for a similar reactor see Ref. [13]).

Deposition on silicon under N<sub>2</sub>: temperature of precursor 132 °C, of substrate 450 °C, total pressure 0.08 mbar, gas flow 8.1 cc min<sup>-1</sup>; deposition on glass under O<sub>2</sub>: temperature of precursor 130 °C, of substrate 450 °C, total pressure 0.08 mbar, gas flow 8.1 cc min<sup>-1</sup>; deposition on silicon under O<sub>2</sub> + H<sub>2</sub>O: temperature of precursor 133 °C, of substrate 450 °C, total pressure 0.03 mbar, gas flow 10 cc min<sup>-1</sup>; deposition on glass under O<sub>2</sub> + H<sub>2</sub>O: temperature of precursor 133 °C, of substrate 450 °C, total pressure 0.03 mbar, gas flow 10 cc min<sup>-1</sup>; deposition on glass under O<sub>2</sub> + H<sub>2</sub>O: temperature of precursor 133 °C, of substrate 450 °C, total pressure 0.03 mbar, gas flow 10 cc min<sup>-1</sup>.

The Si(100) substrate before the deposition was degreased using boiling trichloroethylene and rinsed with isopropyl alcohol.

#### 3. Results and discussion

The results obtained in this study confirm the validity of the procedure for the synthesis of  $\beta$ -imino carbonyl enolato complexes starting from metal(II) acetates and  $\beta$ -enaminodiones (Eq. (1)). The factors governing the success of this exchange reaction have been recently fully

$$\begin{split} \mathsf{M}(\mathsf{OAc})_2 + 2(\mathsf{R}'\mathsf{CO})(\mathsf{R}''\mathsf{CO})\mathsf{C} = \mathsf{C}(\mathsf{NH}_2)\mathsf{R} \\ & \rightarrow [\mathsf{M}((\mathsf{R}'\mathsf{CO})(\mathsf{R}''\mathsf{CO})\mathsf{C}\mathsf{C}(\mathsf{NH})\mathsf{R})_2] + 2\mathsf{HOAc} \end{split} \tag{1}$$

exploited and depend on: (i) the relative stabilities of metal acetates and metal complexes and on (ii) the acidity of the  $\beta$ -enaminodiones compared with that of acetic acid [2a]. The chain length in the series of investigated  $\beta$ -enamino ketoesters (MeCO)(MeOCO)C=C(NH<sub>2</sub>)R (R = Me, *i*-Bu, *n*-Bu, *n*-hexyl) has practically no effect on the output of the synthetic procedure so that complexes [ML<sub>2</sub>] (**1–6: 1**, Pd, **L**<sup>Me</sup>; **2**, Pd, **L<sup>iBu</sup>**; **3**, Pd, **L<sup>nBu</sup>**; **4**, Pd, **L<sup>nHe</sup>**; **5**, Ni, **L<sup>Me</sup>**; **6**, Ni, **L<sup>iBu</sup>**) are obtained always in good yields. In most cases the complexes precipitate spontaneously otherwise the reaction is forced toward the desired products by co-distillation from the reaction mixture of solvent and the acetic acid produced in the ligand exchange process.

The results are coherent with those obtained with the ethyl substituent at the imino group [3]. The potentially tridentate N,O,O ligand acts in all cases as bidentate through the nitrogen and the keto oxygen atoms to give monomeric square planar neutral complexes. These are air and moisture stable solids, which can be stored safely under inert atmosphere; they are soluble in common organic solvents, such as ethanol,  $CH_2Cl_2$ , and  $CHCl_3$ , but mostly insoluble in *n*-hexane or diethylether.

The IR spectra in KBr of all complexes are very similar as the whole, being characterised by: (i) the N–H band approximately around 3300 cm<sup>-1</sup>, (ii) a band at 1570–1585 cm<sup>-1</sup>, which can be easily attributed to the coordinated acetyl carbonyl, (iii) an absorption in the range 1675–1719 cm<sup>-1</sup> due to the C=O stretching vibration of the uncoordinated ester. In fact, the wavenumber values for O,O'-chelation in  $\beta$ -diester complexes are always close to 1600 cm<sup>-1</sup>, as an effect of electronic delocalisation which occurs in the metallocycle ring [14]. These features confirm N,O ligand to metal coordination.

In addition the <sup>1</sup>H and <sup>13</sup>C NMR spectra are consistent with the proposed picture; in particular the ketonic carbonyl C signal (179.3–181.7 ppm) is shifted upfield in comparison with the signal of the corresponding carbon in the free ligand [2b,3]. No information can be gained instead from the chemical shift values of the C=N and C(O)OMe carbons which remain practically unchanged. Preferential coordination of the keto group with respect to the ester one has been widely observed in analogous complexes [1–3].

The palladium complexes (1) and (2) have been isolated in two forms, labelled **a** and **b**, whereas palladium(II) complexes (3) and (4) and the nickel ones (5) and (6) have been isolated only in one form.

This explains some small differences between the NMR spectra of samples (1a) and (1b) or (2a) and (2b). NOE experiments carried out on sample **2a** revealed a strong dipolar interaction between the protons of the *i*-butyl substituent and the imino hydrogen. Moreover a strong dipolar interaction between the hydrogen atoms of the acetyl and methyl ester groups indicates that they are spatially very close to each other (conformation A in Fig. 1). The same experiments carried out on sample (2b), indicate that the oxo and methoxy substituents on (2b) are turned and the methyl ester is preferentially faced toward the *i*-butyl group (conformation **B**). Thus the small differences observed in the solution NMR spectra of (2a) and (2b) can be easily attributed to these conformational changes of the ester substituent of the chelate ring. Similar considerations may apply to the solution chemistry of the palladium complex (1) for which three different sets of signals relative to a, **a**' and **b** are observed. NOE experiments are not conclusive for this complex; in fact a sample of (1b) shows strong dipolar interactions consistent with conformation **B**. However sample (1a) shows two N-H proton signals of different intensity relative to the two species labelled a and a', both correlating only with the corresponding imino methyl substituent, and no other spatial correlations are evi-



Fig. 1. Proposed conformations of complex (2).

dent. The absence of these expected correlations may be due perhaps to a turning away of the methyl oxo. It should be underlined that the position of the N–H signal attributable to the minor species labelled **a**' strongly depends on the type of solvents and, for example, passing from CDCl<sub>3</sub> to anhydrous  $C_6D_6$  moves from 6.34 to 5.10 ppm, thus suggesting the possibility of intermolecular hydrogen bonding. With more sterically demanding groups, like *n*-butyl or *n*-hexyl, only one species has been isolated, thus indicating that the rotation of the ester group is hindered and that acetyl and methyl ester groups are preferentially faced to each other (conformation **A** in Fig. 1)

In the UV–Vis spectra, palladium(II) complexes (1)–(4) show two maxima at ca. 330 and 260 nm of medium and strong intensities respectively. The shortest wavelength absorption at 260 nm may be assignable to  $\pi \to \pi^*$  transition of the ligand, while the absorption at 330 nm ca. may be due to metal-to-ligand charge transfer transitions. The nickel compounds (5) and (6) present a third absorption at 240 nm ca., which is still assigned to a  $\pi \to \pi^*$ transition of the ligand.

The complexes are volatile and remarkably stable as it appears evident from the presence of very intense molecular ions in the mass spectra of all compounds (1)–(6) (see Supplementary Information). The primary fragmentations are the same for both forms (**a** and **b**) and can be divided in two main categories: fragmentations of the ligand moiety anchored to the metal and those of the "free" ligand. The mass spectra of all the complexes are also characterised by the presence of HML<sup>+</sup> ions containing only one coordinated ligand and related fragmentations.

The high stability of this type of complexes is also confirmed by melting point measurements and TGA analysis (Table 1 and Fig. 2). The effect of the length of R chain on the melting point is rather limited, even if a decrease of the value with the lengthening of the chain is observed, probably due to reduced H-bonding interactions. Comparing palladium(II) and nickel(II) complexes it is evident a greater stability of the former ones, as indicated by the somewhat higher melting point values (215–178 °C versus 193–180 °C). TGA studies of the palladium complexes (**1)–(4**) show that they decompose in two steps; the first around 300 °C gives a residue (ca. 30%), which transforms in palladium black upon heating at 950 °C. Also in the case of nickel complexes (**5)–(6**) there are two losses of weight: the major one takes place between 110–350 °C and gives a residue that vaporizes almost completely at temperatures below 750 °C.

DSC measurements show a markedly different behaviour for the two metal centres. Nickel complexes are characterised by a strong endothermic peak (31.3 and 54.3 kJ mol<sup>-1</sup>) at approximately the fusion temperatures 193 (**5**) and 180 (**6**) °C. For the palladium complexes the  $\Delta$ H versus temperature diagram is much more complicated: low energy endothermic peaks (ca. 3 kJ mol<sup>-1</sup>), probably associated to conformational processes, are observed, in addition to very intense peaks in the correspondence of state changes like fusion and evaporation.

The nickel complex (**5**) has been tested under MOCVD conditions to verify its suitability as precursor in the formation of thin films over glass or silicon substrates. Its high volatility allows rather accessible temperatures (130–133 °C) and pressures ( $3 \times 10^{-2}$ – $8 \times 10^{-2}$  mbar), whereas the substrate was kept at 450 °C to ensure fast decomposition of the complex.

The film surface morphology was investigated by SEM (Fig. 3), confirming a uniform substrate coverage, typical of a three-dimensional growing, characterised by well-interconnected agglomerates with mean sizes around 100 nm.

The nature of the thin films depends on the employed carrier gases: use of  $N_2$  and of  $O_2$  gives nickel metal and nickel oxide respectively, whereas a mixture of water with either  $N_2$  or  $O_2$  affords a co-deposition of both. The presence of nickel oxide in the

Table 1	
Thermal data for complexes $(1)-(6)$ and for $[M(L^{Et})_2]$ (M = Pd, N	i).

Complex	m. p.	DSC		TGA	
	(°C)	T (°C)	$\Delta H (kJmol^{-1})$	T (°C) range	Wt.% loss
(1a)	178 (dec.)	93	2.9	70-150	2.2
		129	12.9	150-290	58.66
		194	1.9	290-950	12.15
( <b>1b</b> )	210-220 (dec.)	196	18.2	110-320	68.63
		216	0.6	320-950	10.73
		242	17.4		
$[Pd(\mathbf{L^{Et}})_2]$ form $\mathbf{a}^a$	>250	178–301	142.2	150-440	75.44
				440-915	6.16
$[Pd(\mathbf{L^{Et}})_2]$ form $\mathbf{b}^a$	>250	117	19.9	130-290	68.3
		208-310	101.2	290–935	6.95
(2)	194–199 (dec.)	178	0.4	115-300	78.28
		190	3	300-950	13.68
		220	4.8		
		250	17.2		
(3)	195–200 (dec.)	223	55.3	130-285	71.83
		246	6.9	285-950	9.25
(4)	189 (dec)	148	3.2	185-290	74.95
		212	1.4	290-950	8.79
		220	31.7		
(5)	193	197	31.3	210-350	92.42
				350-950	5.61
[Ni( <b>L<sup>Et</sup></b> ) <sub>2</sub> ] <sup>a</sup>	183	126	17.3	150-280	92.6
		183	31.2	280-900	6.6
		322	95.7		
(6)	178-181 (dec.)	182	54.3	110-310	93.9
				310-950	6.22

<sup>a</sup> The synthesis and characterisation of these complexes have been reported in Ref. [3].



Fig. 2. Comparison of the thermal behaviour (TGA and DSC) of complexes (1a) and (5).

films obtained under nitrogen can not be detected by X-ray technique, even if ESCA analysis indicates the presence of NiO (see further); these results suggest an amorphous phase for NiO [15]. X-rays analysis on the deposited films reveals a preferential



Fig. 3. Selected SEM images of the thin films deposited on glass using  $O_2 + H_2O$  carrier.

Table 2 Superficial composition of films obtained by MOCVD of complex  $[{\rm Ni}(L^{Me})_2]$  (5).

C/% 64.0 21.0 47.7	51.4
0/% 18.3 40.7 26.6	25.4
Ni/% 15.4 32.9 24.7	22.0
N/% 2 0 1	1
Si/% 0 5.0 0	0

orientation (111) for nickel metal and (200) plus (111) for nickel oxide.

The superficial composition determined by ESCA (Table 2) shows in all cases a high carbon content, mostly due to a superficial contamination, and very low quantity of nitrogen derived from ligand decomposition.

Silicon is practically absent in the surface so ensuring a good homogeneity of the deposit. The Ni/O ratio is within the experimental errors close to 1. Analysis of the films deposited in the presence of water reveals two contributions to the O1s peak: the first one at 529.9 eV is attributed to Ni–O bonds in the NiO, whereas the contribution at higher binding energy (531.6 eV) suggest the presence of OH groups present on the NiO surface [16–18]. The Ni2p peaks are found at a value consistent with literature data for NiO with hydroxyl groups on the surface [17]; the NiO (111) faces can be in fact stabilised by hydroxylation [19].

#### 4. Conclusions

In conclusion, the synthesis of  $\beta$ -imino carbonyl enolato complexes of palladium(II) and nickel(II), by reaction of the acetato salt and the required  $\beta$ -enaminodione, appears rather general. The obtained complexes are square planar, stable and volatile, with a limited effect of the imino alkyl chain on their thermal behaviour. The N,O square planar coordination observed also for nickel(II) complexes is particularly interesting, because it makes possible to utilize, for example, [Ni(**L**<sup>Me</sup>)<sub>2</sub>], as convenient MOCVD precursor for the production of Ni or NiO thin films. It should be underlined that O,O coordination to nickel(II), as in  $\beta$ -carbonyl enolato complexes, gives rise to octahedral high melting, non volatile, oligomeric *via* O-bridges structures [20].

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.02.017.

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