

# Novel complexes of nickel with N-heterocyclic ligands and the hemilabile [2-(dimethylamino)ethyl]cyclopentadienyl group

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## Abstract

Starting out from  $[\text{Cp}^{\text{N}}\text{Ni}]$  (**1**), three new derivatives with polar  $\sigma(\text{Ni}-\text{N})$  bonds of the type  $[\text{Cp}^{\text{N}}\text{NiL}]$  ( $\text{Cp}^{\text{N}} = [2-(N,N\text{-dimethylamino)eth-1-yl}]$ cyclopentadienyl; L = carbazolato, **3**; maleimidato, **4**; phthalimidato, **5**) were synthesized by salt elimination. The new compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy, elemental analysis, mass spectrometry and, in the case of **3** and **5**, by single crystal X-ray diffraction studies. The presence of electron withdrawing groups R at the negatively polarized N-atom, allowing for charge delocalization strongly contribute to the stability of amido and/or imidato complexes at the  $\text{Cp}^{\text{N}}\text{Ni}$  fragment.

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## 1. Introduction

Late transition metal complexes with nitrogen-containing anionic ligands are important intermediates in various industrial [1,2] and biological processes [3]. Nickel complexes represent a typical case in this respect, allowing various applications in stoichiometric and catalytic reactions [4–8]. Metal–nitrogen as well as metal–oxygen bonds in late transition metal alkoxides and amides are quite strongly polarized in the ground state and thus they react readily with electrophilic organic substrates by direct interaction of the M–X moiety (e.g. amido) with the incoming reagent [9]. This qualitatively follows the concept of hard and soft acids and bases (HSAB) that predicts a rather polarized bond between a hard anionic ligand (like N) and a soft metal center with a rather low charge (i.e. low oxidation state, like  $d^8\text{-Ni(II)}$ ). MO theory assigns the enhanced reactivity to destabilizing interactions between filled orbitals on the metal and on the ligands [10,11]. However, a more con-

sistent picture was derived within the E-C model involving ionic and covalent  $\sigma$ -interactions only. In this respect, cyclopentadienyl Ni complexes of the general formula  $[\text{Cp}^*\text{Ni}(\text{PET}_3)\text{X}]$  (X = Br, O(*p*-C<sub>6</sub>H<sub>4</sub>Me), NH(*p*-C<sub>6</sub>H<sub>4</sub>Me), S(*p*-C<sub>6</sub>H<sub>4</sub>Me), OCH<sub>3</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, Me, H and PET<sub>3</sub>) have been the subjects of a detailed investigation of distortions and *trans*-influences in cyclopentadienyl complexes and the thermodynamics of reactions interconverting  $[\text{Cp}^*\text{Ni}(\text{PET}_3)\text{X}] + \text{HX}'$  to  $[\text{Cp}^*\text{Ni}(\text{PET}_3)\text{X}'] + \text{HX}$  were explored. The correlation between H–X and M–X bond energies shows a marked preference for nickel binding to more electronegative ligands [12]. It was argued, that the greater electrostatic character of the Ni–X bond (relative to the H–X bond) is sufficient to explain the observed thermodynamic trends in ligand exchange reactions, without the inclusion of  $\pi$ -effects (repulsion).

We have been active in the field of related cyclopentadienyl-nickel and platinum complexes for a while in particular looking at the hemilabile properties of the [2-(dimethylamino)ethyl]cyclopentadienyl ligand nickel complexes [13]. Here we wish to present our results on the synthesis, characterization and structural properties of some new complexes with nickel–nitrogen bonds of the general type  $[\text{Cp}^{\text{N}}\text{NiL}]$  (L = carbazolato, **3**; maleimidato, **4**; phthalimidato, **5**).

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the strongest shifts. The resonances in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** does not bear any unusual features and is typical of this class of substances [13]. In contrast to **3**, the resolution of the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **4** and **5** suffer probably from paramagnetic species being present as minor components in equilibrium, quite similar as observed for the complex  $[\text{Cp}^{\text{N}}\text{Ni}(\text{acac})]$  [13c]. All signals in the  $^1\text{H}$  NMR spectrum are very broad and are shifted towards lower field in comparison to the resonances reported for  $[(1\text{-Me-Ind})\text{Ni}(\text{PPh}_3)\text{L}]$  (L = maleimidato, phthalimidato) [14]. The proton shifts of the  $\text{Cp}^{\text{N}}$  ligand are very similar in **4** and **5** and resemble those found for  $[\text{Me}_3\text{SiCp}^{\text{N}}\text{NiI}]$  as reference compound [13c]. Most resonances in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are missing entirely even with high scan numbers. It should be noted that even with variation of the temperature ( $-80$  to  $25$  °C) the NMR measurements of **4** and **5** gave no better resolved spectra. The detailed reason of the presumed paramagnetic species is unclear and probably warrants a detailed quantum-chemical study, which is beyond the scope of this work here.

The frequency of the  $\nu_{\text{CO}}$  vibration of the imidato ligand was found to be  $1645\text{ cm}^{-1}$  for **4** and  $1650\text{ cm}^{-1}$  for **5** being halfway between the typical values found for ionic (ca.  $1600\text{ cm}^{-1}$ ) and covalent (ca.  $1720\text{ cm}^{-1}$ ) phthalimidate derivatives. Vibrational frequencies for the CO group in related  $\text{d}^8$ -imidato complexes like  $[(\text{PR}_3)_2\text{Pd}(\text{Ph})(\text{imidato})]$  (phthalimidato:  $1640\text{--}1620\text{ cm}^{-1}$ ; succinimidato:  $1615\text{--}1605\text{ cm}^{-1}$ ) and  $[\text{trans}(\text{PPh}_3)_2\text{M}(\text{CO})(\text{imidato})]$  (M = Rh,

Ir; phthalimidato:  $1640\text{--}1630\text{ cm}^{-1}$ ; succinimidato:  $1620\text{--}1610\text{ cm}^{-1}$ ) are observed at only slightly lower frequencies [15].

Typical features of the mass spectra (FAB, positive ions) of **3–5** are the splitting off the N-heterocyclic ligands releasing  $[\text{Cp}^{\text{N}}\text{Ni}^+]$  at  $m/z = 197$  with about 10%,  $[\text{Cp}^{\text{N}+}]$  at  $m/z = 136$  with about 70% and  $[\text{CH}_2\text{N}(\text{CH}_3)_2^+]$  at  $m/z = 58$  being the base peak. The molecular ions  $[\text{M}^+]$  of **3–5** were observed with low relative intensity of 5–10%.

### 2.3. Structural characterization of **3** and **5**

Complexes **3** and **5** crystallized from saturated toluene solutions at  $-30$  °C in the monoclinic space group  $P2(1)/c$  with two molecules of toluene in the unit cell of  $[\text{Cp}^{\text{N}}\text{Ni}(\text{carbazolato})]$  (**3**) and in the triclinic space group  $P\bar{1}$  space group with one molecule of toluene in the unit cell of  $[\text{Cp}^{\text{N}}\text{Ni}(\text{phthalimidato})]$  (**5**), respectively (see Table 1). Figs. 1 and 2 show the molecular structure of **3** and **5**, respectively.

The molecular structures of **3** and **5** are rather similar. In both compounds, the dimethylaminoethyl side chain of the  $\text{Cp}^{\text{N}}$ -ligand is coordinated to the Ni center as already expected from the NMR spectra, with a Ni–N distance of about  $1.97\text{ \AA}$ , being a bit shorter than in the reference compounds  $[\text{Cp}^{\text{N}}\text{NiI}]$ ,  $[\text{Me}_3\text{SiCp}^{\text{N}}\text{NiI}]$  and  $[\text{Cp}^{\text{N}}\text{Ni}(\text{PPh}_3)]\text{PF}_6$  with related Ni–N donor acceptor bonds around  $2.01\text{--}2.02\text{ \AA}$  [13]. The polar Ni–N bond of the amido and imidato ligands with tri-coordinate  $\text{sp}^2$ -hybridized N-atom

Table 1  
Crystallographic data of compounds **3** and **5**

Compound	<b>3</b>	<b>5</b>
Empirical formula	$\text{C}_{24.5}\text{H}_{26}\text{N}_2\text{Ni}$ (0.5 $\text{C}_7\text{H}_8$ included)	$\text{C}_{20.5}\text{H}_{22}\text{N}_2\text{NiO}_2$ (0.5 $\text{C}_7\text{H}_8$ included)
Formula weight	407.19	387.1
Temperature (K)	203(2)	203(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
<i>a</i> (Å)	18.725(5)	8.1181(12)
<i>b</i> (Å)	13.378(4)	10.5226(15)
<i>c</i> (Å)	17.213(6)	11.6356(17)
$\alpha$ (°)	90	85.066(3)90
$\beta$ (°)	90.59(3)	70.187(2)
$\gamma$ (°)	90	74.809(3)
<i>V</i> (Å <sup>3</sup> )	4312(2)	902.4(2)
<i>Z</i>	8	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.255	1.425
Absorption coefficient (mm <sup>-1</sup> )	0.910	1.091
<i>F</i> (000)	1720	406
Crystal size (mm)	0.40 × 0.12 × 0.06	0.45 × 0.40 × 0.30
$\theta$ Range (°)	1.87–25.22	1.86–25.04
Index ranges	$-22 \leq h \leq 14$ , $-15 \leq k \leq 15$ , $-20 \leq l \leq 20$	$-9 \leq h \leq 9$ , $-7 \leq k \leq 12$ , $-13 \leq l \leq 13$
Reflections collected	22268	4709
Independent reflections [ $I > 2\sigma(I)$ ]	7655	3147
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restrain/parameter	7655/6/503	3147/0/246
Goodness-of-fit on $F^2$	1.016	1.000
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0748$ , $wR_2 = 0.2139$	$R_1 = 0.0533$ , $wR_2 = 0.1229$
<i>R</i> indices (all data)	$R_1 = 0.1266$ , $wR_2 = 0.2511$	$R_1 = 0.0769$ , $wR_2 = 0.1358$
Largest difference in peak and hole (e Å <sup>-3</sup> )	2.286 and $-0.493$	0.581 and $-0.560$

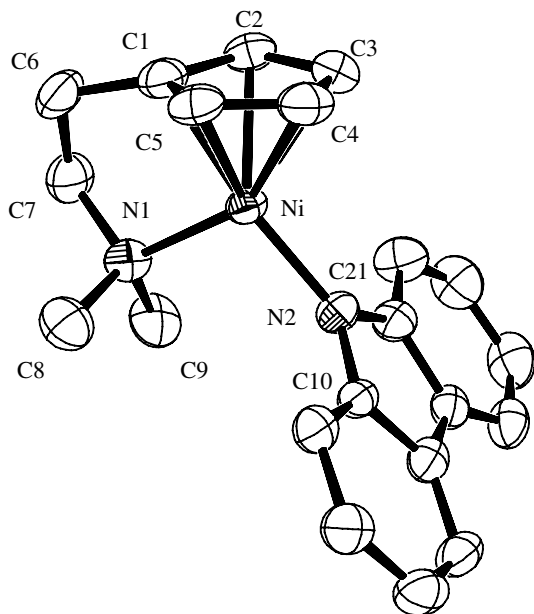


Fig. 1. Molecular structure of  $[\text{Cp}^{\text{N}}\text{Ni}(\text{carbazolato})]$  (**3**) in the solid state (ORTEP drawing using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles ( $^{\circ}$ ), [a] denotes the center of the cyclopentadienyl ring: Ni–N1, 1.965(5); Ni–N2, 1.898(5); Ni–Cp<sup>[a]</sup>, 1.734; Ni–C1, 2.021(6); Ni–C2, 2.139(6); Ni–C3, 2.135(7); Ni–C4, 2.136(6); Ni–C5, 2.139(6); N–C7, 1.489(8); N–C8, 1.485(9); N–C9, 1.500(8); C1–C2, 1.432(10); C2–C3, 1.392(9); C3–C4, 1.434(9); C4–C5, 1.373(9); C5–C1, 1.454(9); Cp<sup>[a]</sup>–Ni–N2, 137.0; C1–C6–C7, 107.5(5); N2–Ni–N1, 100.8(2); C6–C7–N1, 109.2(5); N1–Ni–Cp<sup>[a]</sup>, 122.2; Ni–N2–C10 124.6(4); Cp<sup>[a]</sup>–C1–C6, 169.4; Ni–N2–C21, 129.6(4).

rather than the  $\text{sp}^3$ -type N-donor of the side chain are shorter amounting to 1.90 Å. The coordination mode of the  $\text{Cp}^{\text{N}}$ -ligands is also rather similar. The distance Ni–Cp<sub>centroid</sub> of the cyclopentadienyl ring of about 1.73 Å are equal within the accuracy of the structure determination in both structures.

The coordination of the  $\text{Cp}^{\text{N}}$ -rings are almost symmetric without a significant *trans*-influence of the N-heterocyclic ligand. The same is true for the angles around the nickel atom. However, the diene distortion of the Cp ring, that seems to be absent or only weak in  $[\text{Cp}^{\text{N}}\text{Ni}(\text{phthalimidato})]$  (**5**), is a bit more pronounced in  $[\text{Cp}^{\text{N}}\text{Ni}(\text{carbazolato})]$  (**3**) (the distances between C2 and C3 (1.39 Å) and between C4 and C5 (1.37 Å) are considerably shorter than the other C–C distances being around 1.44 Å). The similarity of the Ni–N2 bonds of **3** and **5** (1.90 Å) match with the corresponding distances in related indenyl and Cp<sup>\*</sup>-substituted imidato and amido complexes of nickel like  $[(1\text{-Me-Ind})\text{Ni}(\text{PPh}_3)(\text{phthalimidato})]$  [14] and  $[\text{Cp}^*\text{Ni}(\text{PET}_3)(\text{NH-Tol})]$  [12]. The Ni–N distances in dimeric compounds such as  $[\text{Cp}^*\text{Ni}(\text{NHR})]_2$  (R = *p*-tolyl, phenyl, 2,6-xylyl, <sup>t</sup>Bu) are somewhat longer and range from 1.93 to 1.98 Å [12].

One interesting feature of the compounds **3** and **5** is certainly the orientation of the planar N-heterocycle (i.e. the plane defined by N2, C10 and C21 for **3** and N2, C10 and C17 for **5**) with respect to the principal plane of the bent  $[\text{Cp}^{\text{N}}\text{Ni}]$  half sandwich fragment of idealized  $\text{C}_s$  symmetry

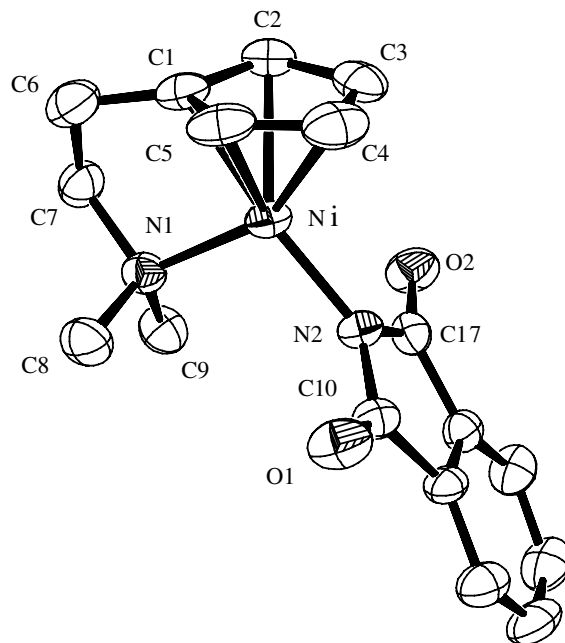


Fig. 2. Molecular structure of  $[\text{Cp}^{\text{N}}\text{Ni}(\text{phthalimidato})]$  (**5**) in the solid state (ORTEP drawing using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles ( $^{\circ}$ ), [a] denotes the center of the cyclopentadienyl ring: Ni–N1, 1.970(3); Ni–N2, 1.907(3); Ni–Cp<sup>[a]</sup>, 1.731; Ni–C1, 2.007(4); Ni–C2, 2.128(4); Ni–C3, 2.136(4); Ni–C4, 2.128(4); Ni–C5, 2.130(4); C1–C2, 1.427(6); C2–C3, 1.381(6); C3–C4, 1.443(7); C4–C5, 1.395(7); C5–C1, 1.415(6); N2–C10, 1.372(5); N2–C17, 1.377(5); N–C7, 1.496(5); N–C8, 1.485(5); C10–O1, 1.213(5); C17–O2, 1.220(5); Cp<sup>[a]</sup>–Ni–N2, 137.2; N2–Ni–N1, 100.33(14); N1–Ni–Cp<sup>[a]</sup>, 122.5; Cp<sup>[a]</sup>–C1–C6, 170.3; C1–C6–C7, 106.9(4); C6–C7–N1, 111.2(4); Ni–N2–C10, 125.9(3); Ni–N2–C17, 123.2(3).

defined by *N,Ni* and Cp<sub>centroid</sub>. Thus, the amido and imidato ligand planes are almost perpendicular to the principal plane of the  $\text{Cp}^{\text{N}}\text{Ni}$  fragment. Bergman et al. reported on the hindered rotation along the Ni–N bond in  $[\text{Cp}^*\text{Ni}(\text{PET}_3)\{\text{HN}(p\text{-C}_6\text{H}_4\text{Me})\}]$  ( $\Delta G = \text{ca. } 11 \text{ kcal/mol}$ ) [12]. Steric reasons were suggested to predominantly account for that barrier but electronic  $\pi$ -interactions seem to play a role as well. A freely rotating amido or imidato ligand would experience destabilizing  $p_{\pi}\text{-d}_{\pi} \text{N} \rightarrow \text{Ni}$ -interactions when the N-heterocycle is parallel to the main plane of the complex. A rotation out of this plane reduces these interaction and has been discussed in various imidato complexes similar to **5**, e.g. the solid state structure of  $[(1\text{-Me-indenyl})\text{Ni}(\text{PPh}_3)(\text{phthalimidato})]$  shows a rotation of  $76^{\circ}$  [14] and the square-planar  $\text{d}^8$ -complexes like  $[\text{Ir}(\text{CO})(\text{PPh}_3)(\text{maleinimidato})]$  adopt comparable spatial arrangements [16].

Consequently, one reason for the enhanced chemical stability, or better to say reduced reactivity (which accounts for the successful isolation) of **3–5** may be the possibility of a Ni  $\rightarrow$  N back bonding which appears feasible by taking into account a certainly low-lying  $\pi^*$  orbital of the ligands due to the presence of delocalizing and  $\pi$ -electron withdrawing substituents. Such stabilizing  $\pi$ -back bonding would contribute to a higher degree of covalency of the Ni–N bond (charge delocalization) and thus would reduce reactivity in polar reactions. The shift in  $\nu_{\text{CO}}$  fre-

quencies of the  $d^6$ -complex  $[\text{CpFe}(\text{CO})\text{L}(\text{phthalimidato})]$  supports this idea to some extent: an increase in back donation when replacing a rather poor  $\sigma$ -donor ligand with a stronger donor ligand causes the frequency to drop from  $1660\text{ cm}^{-1}$  for  $\text{L} = \text{CO}$  to  $1640\text{ cm}^{-1}$  for  $\text{L} = \text{PPh}_3$  [17]. The observed orientation of the N-heterocycles of **3** and **5** is likely to favor such  $\text{Ni} \rightarrow \text{N}$  back donation interaction. The reactivity of late transition metal amides is generally linked to the lability of the Ni–N bond as both the HSAB concept and the expected destabilizing  $\pi$ -interactions between the amide ligand and filled orbitals of the low-valent, electron-rich metal center [18]. Another model describes the character of the M–X-bond in terms of an electrostatic versus a covalent bonding model balancing ionic and covalent  $\sigma$ -interactions and neglecting  $\pi$ -effects [19]. In this context Bergman et al. published an in-depth study of the thermodynamics of various metathesis reactions between  $[\text{Cp}^*\text{Ni}(\text{PEt}_3)\text{X}]$  and  $\text{HX}'$  or  $[\text{Cp}^*\text{Ni}(\text{PEt}_3)\text{X}']$  and  $\text{HX}$  ( $\text{X}, \text{X}' = \text{halogene}, \text{NHR}, \text{OR}, \text{SR}, \text{etc.}$ ) already mentioned in the introduction [12]. According to this, the Ni–X bond exhibits a strong electrostatic component and the stability of the various species depends strongly on the stabilization of the negative charge on X. This explains the experimental observation that Ni–OR species are more stable in comparison to Ni–NR<sub>2</sub> species (a fact that, in turn, is not covered by the arguments that are based on  $p_\pi$ – $d_\pi$  destabilizing interactions only).

### 3. Conclusion

Three new complexes of the type  $[\text{Cp}^{\text{N}}\text{NiL}]$  with the N-heterocyclic ligands carbazolato (**3**), maleimidato (**4**) and phthalimidato (**5**) have been synthesized and characterized. The hemilabile 2-(dimethylamino)ethyl side chain of the substituted  $\text{Cp}^{\text{N}}$  ligand was found to coordinate to the Ni center in solution (ambient conditions) and as well in the solid state. The N-heterocyclic (anionic) ligands bear electron-withdrawing groups and exhibit a planar spatial arrangement around the nitrogen which allows for an efficient delocalization of the lone pair at the N-atom. Thus, repulsive interactions with  $d^8$  transition metal fragments are presumably reduced. In parallel  $\text{Ni} \rightarrow \text{L}$  back donation is favoured, as indicated by the perpendicular arrangement of the main plane of the  $\text{Cp}^{\text{N}}\text{Ni}$  fragment and the main plane of the N-heterocycles.

### 4. Experimental

#### 4.1. General remarks

All reactions and manipulations were carried out under argon atmosphere utilizing standard Schlenk and glovebox techniques. All solvents apart from diethylamine were dried over sodium/paraffine suspension, distilled and stored over molecular sieves (Merck, 4 Å) under inert conditions. Diethylamine was dried and stored over sodium/paraffine suspension and condensed into the reaction vessel

when used. NMR spectra were recorded on Bruker DPX 250 and Bruker DRX 400 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts were referred to the remaining proton signals of the deuterated solvents and referenced to TMS. The NMR solvents were dried over sodium/potassium alloy as mentioned above and degassed prior to use. The mass spectra were performed on a Varian MAT CH5 by FAB ionization and elemental analysis was provided by the Microanalytical Laboratory of the Ruhr-Universität Bochum employing a CHN-Analyser of the type CHN-O-Rapid (Heraeus).

The abbreviations used in this section are  $\text{Cp}^{\text{N}} = \eta^5\text{-C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{NMe}_2)$  and  $\text{Me} = \text{CH}_3$ . [2-(*N,N*-dimethylamino)ethyl]cyclopentadiene ( $\text{Cp}^{\text{N}}\text{H}$ ) was prepared according to the literature procedures [20]. An improved synthesis of [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl-nickel(II)-iodide ( $\text{Cp}^{\text{N}}\text{NiI}$ ) (**1**) has been reported earlier [13,15]. Phthalimide and carbazole were purchased from Merck, maleimide was purchased from Lancaster and all chemicals were recrystallized twice before use.

#### 4.2. $\{(\text{Carbazolato})[2-(N,N\text{-dimethylamino})\text{ethyl}]cyclopentadienyl\}$ -nickel(II) (**3**)

200 mg of [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl-nickel(II)-iodide (0.62 mmol) were dissolved in 20 mL of THF and cooled to  $-78^\circ\text{C}$ . A solution of lithiumcarbazolate (made from 120 mg of carbazole (0.72 mmol) and 0.45 mL of a solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.72 mmol) in 10 mL THF at  $0^\circ\text{C}$ ) was added slowly and the reaction mixture was allowed to warm to room temperature. After stirring for another hour the solvents were removed in vacuo and the residue was extracted with 10 mL of toluene. Filtration and concentration of the solution gave 160 mg dark-green **3** (0.44 mmol) after a storage of 12 h at  $-30^\circ\text{C}$  in 71% yield.  $^1\text{H}$  NMR (250.132 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = 0.73$  (t, 2H,  $\text{NCH}_2\text{CH}_2$ ); 1.63 (t, 2H,  $\text{NCH}_2\text{CH}_2$ ); 1.67 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ); 4.23, 6.10 (s, 4H,  $\text{C}_5\text{H}_4$ ); 7.48 (2m, 2H, H4 and H7); 7.96 (2m, 2H, H3 and H8); 8.49 (2d, 2H, H2 and H9); 8.86 (2d, 2H, H5 and H6).  $^{13}\text{C}\{^1\text{H}\}$  NMR (62.903 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = 25.3$  ( $\text{NCH}_2\text{CH}_2$ ); 51.9 ( $\text{N}(\text{CH}_3)_2$ ); 72.9 ( $\text{NCH}_2\text{CH}_2$ ); 86.6 (*o*- $\text{C}_5\text{H}_4$ ); 94.5 (*i*- $\text{C}_5\text{H}_4$ ); 100.7 (*m*- $\text{C}_5\text{H}_4$ ); 111.0 (C2 and C9); 115.9 (C5a and C5b); 119.8 (C3 and C8); 120.8 (C5 and C6); 124.2 (C4 and C7); 125.8 (C1a and C9a). MS(FAB):  $m/z$  (%): 360 (7) [ $\text{M}^+$ ], 330 (27) [ $\text{M}^+ - 2\text{CH}_3$ ], 194 (19) [ $\text{Cp}^{\text{N}}\text{Ni}^+$ ], 167 (35) [ $\text{C}_{12}\text{H}_8\text{N}^+$ ], 136 (25) [ $\text{Cp}^{\text{N}+}$ ], 58 (100) [ $\text{CH}_2\text{N}(\text{CH}_3)_2^+$ ]. Elem. Anal. Calc. for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{Ni}$  (361.11): C, 69.85; H, 6.14; N, 7.76. Found: C, 70.01; H, 6.00; N, 7.74%.

#### 4.3. $\{[2-(N,N\text{-Dimethylamino})\text{ethyl}]cyclopentadienyl(\text{maleimidato})\}$ -nickel(II) (**4**)

##### 4.3.1. Procedure A

250 mg of [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl-nickel(II)-iodide (0.78 mmol) were dissolved in 20 mL

of THF and cooled to  $-78^{\circ}\text{C}$ . A solution of maleimidatolithium (made from 78 mg maleimide (0.80 mmol) and 0.5 mL of a solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.80 mmol) in 10 mL THF at  $0^{\circ}\text{C}$ ) was added dropwise, the reaction mixture was allowed to warm to room temperature and stirred for another hour. After removing the solvents in vacuo, the residue was extracted with 10 mL of toluene, filtered and concentrated. Storing the solution for 12 h at  $-20^{\circ}\text{C}$  yielded 200 mg **4** (0.69 mmol) as a light-brown powder in 89% yield.

#### 4.3.2. Procedure B

300 mg of [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl-nickel(II)-iodide (0.93 mmol) and 91 mg maleimide (0.93 mmol) were mixed and 30 mL diethylamine were condensed into the reaction vessel. After warming to room temperature, the reaction mixture was stirred for 48 h at ambient temperature. The solvent was removed in vacuo, the remaining solid was washed twice with 20 mL *n*-pentane and extracted twice with 20 mL toluene. Removal of the solvent gave 250 mg **4** (0.86 mmol) as a light-brown solid in 92% yield.  $^1\text{H}$  NMR (250.132 MHz,  $\text{C}_6\text{D}_6$ ,  $25^{\circ}\text{C}$ ):  $\delta = 1.44$  (t, 2H,  $\text{NCH}_2\text{CH}_2$ ); 2.23 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ); 2.98 (t, 2H,  $\text{NCH}_2\text{CH}_2$ ); 4.90 (s, 4H,  $\text{C}_5\text{H}_4$ ); 6.20, 6.48 (2d, 2H,  $-\text{CH}=\text{CH}-$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (62.903 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^{\circ}\text{C}$ ):  $\delta = 21.8$  ( $\text{NCH}_2\text{CH}_2$ ); 41.8 ( $\text{N}(\text{CH}_3)_2$ ); 138.1 ( $-\text{CH}=\text{CH}-$ ); no further signals detected. IR ( $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$ ), THF): 1645 (CO). MS(FAB):  $m/z$  (%): 290 (6) [ $\text{M}^+$ ], 194 (9) [ $\text{Cp}^{\text{N}}\text{Ni}^+$ ], 136 (50) [ $\text{Cp}^{\text{N}+}$ ], 96 (27) [ $\text{C}_4\text{H}_2\text{NO}_2^+$ ], 58 (100) [ $\text{CH}_2\text{N}(\text{CH}_3)_2^+$ ]. Elem. Anal. Calc. for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{NiO}_2$  (290.97): C, 48.66; H, 5.54; N, 9.63. Found: C, 48.36; H, 5.31; N, 10.00%.

#### 4.4. {[2-(*N,N*-Dimethylamino)ethyl]cyclopentadienyl(phthalimidato)}nickel(II) (**5**)

200 mg of [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl-nickel(II)-iodide (0.62 mmol) and 120 mg phthalimide (0.81 mmol) were mixed and 20 mL diethylamine were condensed into the reaction vessel. The mixture was allowed to warm to room temperature, heated to  $40^{\circ}\text{C}$  and stirred for 1 h. The solvent was removed in vacuo, the residue washed twice with 20 mL *n*-pentane and extracted with 20 mL toluene. Concentration to a volume of about 10 mL and storing the solution for 12 h at  $-30^{\circ}\text{C}$  gave 170 mg **5** (0.50 mmol) as a light-brown powder in 81% yield.  $^1\text{H}$  NMR (250.132 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^{\circ}\text{C}$ ):  $\delta = 1.31$  (t, 2H,  $\text{NCH}_2\text{CH}_2$ ); 2.39 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ); 2.91 (t, 2H,  $\text{NCH}_2\text{CH}_2$ ); 5.37 (s, 4H,  $\text{C}_5\text{H}_4$ ); 7.26, 7.86 (2m, 4H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (62.903 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^{\circ}\text{C}$ ):  $\delta = 123.8$  (C3, C6 of the phthalimidato ligand); 128.5 (C4, C5 of the phthalimidato ligand); 134.7 (C2a, C6a of the phthalimidato ligand); 170.0 (CO); no further signals detected. IR ( $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$ ), THF): 1650 (CO). MS(FAB):  $m/z$  (%): 341 (5) [ $\text{M}^+$ ], 327 (4) [ $\text{M}^+ - \text{CH}$ ], 281 (8) [ $\text{M}^+ - \text{CH}_2\text{N}(\text{CH}_3)_2$ ], 194 (7) [ $\text{Cp}^{\text{N}}\text{Ni}^+$ ], 136 (73) [ $\text{Cp}^{\text{N}+}$ ], 58 (100) [ $\text{CH}_2\text{N}(\text{CH}_3)_2^+$ ]. Elem. Anal. Calc. for

$\text{C}_{17}\text{H}_{18}\text{N}_2\text{NiO}_2$  (341.03): C, 59.87; H, 5.32; N, 8.21. Found: C, 57.87; H, 5.38; N, 8.30%.

#### 4.5. Crystal structure determination

Selected crystallographic data and parameters of the structure solution of compounds **2** and **4** are listed in Table 1. Crystals of **3** and **5** were mounted on a goniometer using perfluoroether oil and subsequent cooling ( $T = 203\text{ K}$ ). Intensity data were collected with a Bruker-AXS-SMART diffractometer (Mo  $\text{K}\alpha$  radiation  $\lambda = 0.71073\text{ \AA}$ , graphite monochromator,  $\omega$ -scan). Empirical absorption corrections (SADABS) were applied. The structure solution was done with direct methods [21] and the structure refinement (full-matrix least-squares against  $F^2$ ) was undertaken with anisotropic structural parameters for all non-hydrogen atoms [22]. The thermal reliability index  $wR_2$  is defined as  $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ . The ethylene bridge in the crystal structure of compound **3** was disordered, which could be modelled in the refinement quite similarly to related compounds which structure determination have been discussed and published previously [13]. Both structures contained disordered solvent molecules (toluene) which were refined isotropically. The rather high remaining electron densities in the structure of **3** are explained by that disorder of the solvent molecules.

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#### Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-167-302 (**3**) and CCDC-167-301 (**5**). Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (int. code) +44 1223 336 001; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.016.

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