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Ni(II) and Pd(II) organometallic and coordination complexes with a new tridentate N,N,O-donor ligand

Cristina Esqueda [b], José C. Alvarado-Monzón [b], Gabriel Andreu-de-Riquer [b], J. Alfredo Gutiérrez [b], Luis M. De León-Rodríguez [b], Oracio Serrano [b], José G. Alvarado-Rodríguez [a], Jorge A. López [b,*]

[a] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Ciudad Universitaria, Km. 4.5 Carretera Pachuca-Tulancingo, Pachuca Hgo., Mexico*
[b] *Departamento de Química, División de Ciencias Naturales y Exactas, Campus Guanajuato, Universidad de Guanajuato, Cerro de la Venada s/n, Col. Pueblito de Rocha. Guanajuato, Gto., C.P. 36040, Mexico*

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ABSTRACT

Nickel and palladium organometallic [M(R)(**NNO**)] (R = $CH_2CMe_2C_6H_5$; M = Pd, **1**, Ni, **2**; R = Me, M = Pd, **3**, Ni, **4**; R = CH_2SiMe_3, M = Ni, **5**) and coordination [MCl(**NNO**)] (M = Pd(II), **6**, Ni(II), **7**), [Ni(**NNO**)$_2$], **8**, complexes containing the potentially tridentate Schiff base **NNO-donor** ligand which is the condensation product of 2-hidroxynaphtaldehyde and *N*-benzylethylenediamine, were prepared and characterized by elemental analysis, IR and NMR spectroscopy. The crystal structure of **8** was determined by single X-ray diffraction measurements. Complexes **1**–**6** had a square planar structure with the ligand being tridentate through the **NNO** atoms. On the other hand compound **7** presented a conformational equilibrium in dissolution at room temperature and a rigid square-planar structure at 220 K. The crystal structure of **8** indicated a monoclinic lattice, with a *P*2(1)/*c* space group, a = 13.1799(8), b = 14.5556(9), c = 17.5018(11) Å, b = 98.0420 (10)°, Z = 4. The central Ni atom in **8** was in a N_4O_2 coordination sphere formed by two **NNO** Schiff base ligands. In this structure two of the Ni–N bonds trans to the oxygen atoms were significantly longer than the other two Ni–N bonds, 2.0175(17), 2.2761(17) versus 2.0070(17), 2.1794(14) Å. The two oxygen phenol atoms of the chelating ligands were cis and the distances of the Ni(II)–O(phenol) bond were 2.0410(14) and 2.0415(14) Å, respectively.

1. Introduction

Nickel and palladium alkyl and halide complexes constitute a classical research area in organometallic and coordination inorganic chemistry [1,2]. Interest in Ni and Pd alkyl and aryl complexes has increased in recent years due to their application in a variety of important processes especially in catalytic applications such as oligomerization or polymerization of alkenes, alkynes and dienes [3], carbonylation of several substrates such as alkyl halides and aryl or alkynes [4] and carbon–carbon bond formation reactions [5]. Some of these processes (e.g. alkoxycarbonylation of alkynes (Reppe reaction) or dimerization of ethylene) can be considered classics in the field of industrial homogeneous catalysis [6]. Most of these transformations use simple Ni or Pd catalysts such as Ni(COD)$_2$, Ni(CO)$_4$, Pd(dba)$_2$, Pd(PR$_3$)$_4$ or salts of these metals. Furthermore, by adding auxiliary ligands it is often possible to adjust the electronic properties and stereo configuration of a catalyst to suit a particular process. On the other hand, Schiff base (**SB**) ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tunable steric and electronic properties and good solubility in common solvents [7–11]. Transition metal complexes with **SBs** containing oxygen and nitrogen donor atoms are of particular interest [12,13] because of their (i) ability to present unusual configurations, (ii) structural lability and (iii) sensitivity to molecular environments [14]. **SB** ligands can also accommodate different metal centers with various coordination modes, thus allowing successful synthesis of homo and heterometallic complexes with varied stereochemistry [15]. Here we report organometallic and coordination complexes containing a new tridentate NNO-donor **SB** ligand.

2. Results and discussion

2.1. Synthesis of *NNO* ligand

The **NNO** ligand, 1-(2-(phenylamino)(phenylimino)methyl) naphthalen-2-ol, was obtained in good yield as yellow crystals by condensation of 2-hidroxy-1-naphthaldehyde with one equivalent of N1-phenylbenzene-1,2-diamine in ethyl ether. The imine and amine protons of the ligand were observed in ^{1}H NMR solution at 8.78 and 1.57 ppm, respectively, while the hydroxyl proton

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* Corresponding author.
E-mail address: albinol@ugto.mx (J.A. López).

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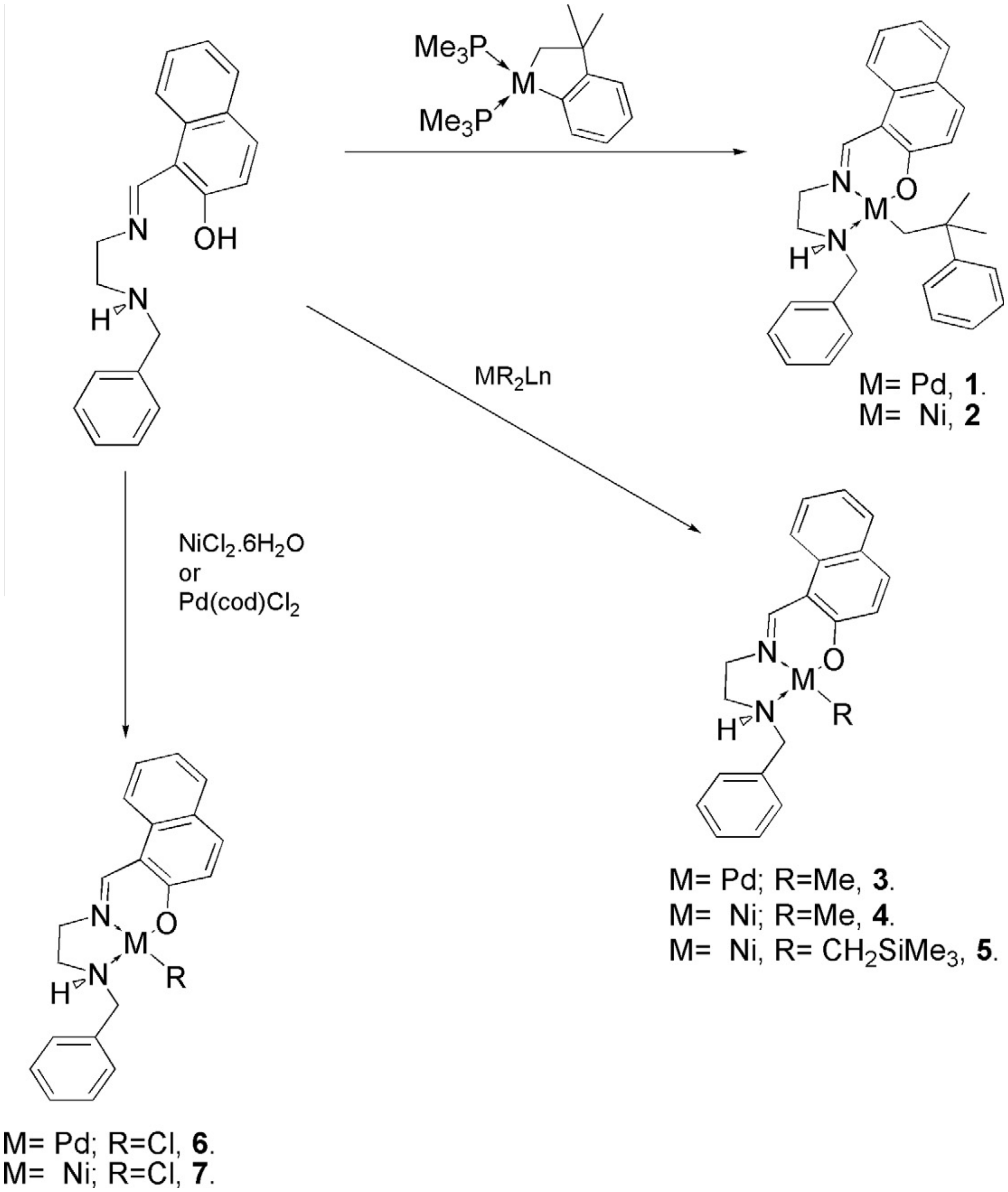
appeared downfield at 14.42 ppm indicating the formation of an intramolecular hydrogen bond. C=N and NH stretching vibration IR bands were observed at 1620 and 3280 cm^{-1}, respectively.

2.2. Preparation and characterization of alkyl complexes

Divalent metal organometallic complexes [M(R)(**NNO**)] (R = $CH_2CMe_2C_6H_5$; M = Pd, **1**, Ni, **2**; R = Me, M = Pd, **3**, Ni, **4**; R = CH_2SiMe_3, M = Ni, **5**) (Scheme 1) were readily prepared in good yield by reaction of metallacycles $\overline{M(CH_2CMe_2\text{-}o\text{-}C}{}_6H_4)(L_2)$ (M = Pd, L_2 = PMe_3; M = Ni, L = PMe_3) or dialkyl complexes [ML_2R_2] {where M = Pd, R = Me, L_2 = TMEDA; M = Ni, L = Py, R = Me; M = Ni, L = PMe_3, R = CH_2SiMe_3} with one equivalent of **NNO** ligand. These compounds were obtained pure as yellow (palladium) or red crystals (nickel), by recrystallization from diethylether.

Complexes **1**–**5** are diamagnetic, which is characteristic of a complex with square planar geometry (Fig. 1). The ^1H NMR spectra of **1**–**5**, showed a similar signal pattern. Furthermore, all signals were sharp which indicates that the structures were static on the NMR timescale. The absence of the phenol proton as well as significant chemical shift changes of some ligand's protons can be observed upon coordination of the ligand to the metal (Table 1). For example, the signal of the $\mathbf{H^5}$ proton which appeared at 8.78 ppm in the free ligand, is shifted to lower or higher fields in the complexes, 8.50, 8.48, 8.81, 8.45 and 8.23 ppm for **1**, **2**, **3**, **4** and **5**, respectively. Furthermore, all methylene signals of the ethylene chain and benzyl group of the ligand appeared as unsymmetric multiplets with the same intensity. This spectral feature can be attributed to the presence of diasterotopic proton pairs within each methylene group, which is the result of the chirality of the nitrogen amino group and the conformational rigidity imposed to the structure upon metal coordination. Take for example complex **1** the



Scheme 1. Synthesis of nickel and palladium complexes.

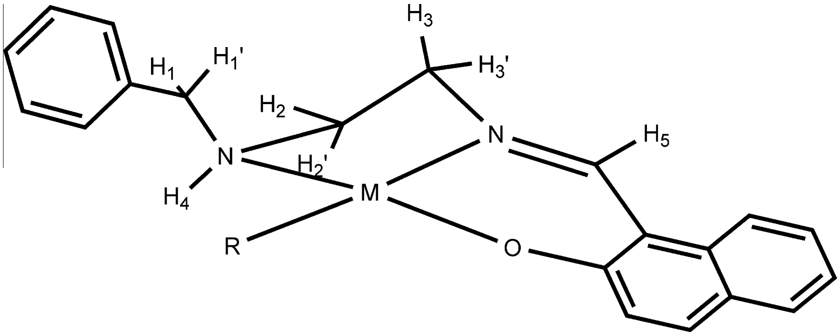


Fig. 1. Structure of the nickel and palladium complexes **1**–**7**.

Table 1
^{1}H NMR values of **NNO** ligand (in $CDCl_3$) and complexes **1**–**6** (in C_6D_6) at 293 K.

Compound	^{1}H NMR					
	H^5	$H^1H^{1\prime}$	$H^2H^{2\prime}$–$H^3H^{3\prime}$	M-CH_2	CH_3	H^4
NNO ligand	8.78 (s)	3.83 (s)	2.97 (t, J_{HH} = 5.6) 3.69 (t, J_{HH} = 5.6)			1.57 (bs)
[Pd($CH_2CMe_2C_6H_5$)(**NNO**)], **1**	8.50 (s)	3.64 (d, $^2J_{HH}$ = 14.3) 3.47 (t, $^2J_{HH}$ = 11.4)	2.89 (t. $^2J_{HH}$ = 12.7) 2.28 (d, $^2J_{HH}$ = 14.0) 1.82 (m)	2.40 (d, $^2J_{HH}$ = 8.6) 1.61 (d, $^2J_{HH}$ = 8.6)	2.02 (s) 1.68 (s)	1.75 (bs)
[Ni($CH_2CMe_2C_6H_5$)(**NNO**)], **2**	8.48 (s)	3.91 (d, $^2J_{HH}$ = 13.4) 3.39 (d, $^2J_{HH}$ = 13.5)	2.06 (t, $^2J_{HH}$ = 13.4) 2.61 (d, $^2J_{HH}$ = 13.3) 1.38 (d, $^2J_{HH}$ = 14.1) 0.95 (t, $^2J_{HH}$ = 14.2)	1.58, 0.72 (dd,$^2J_{HH}$ = 14.2)	2.21 (s) 1.64 (s)	1.18 (bs)
[Pd(CH_3)(**NNO**)], **3**[a]	8.81 (s)	4.62 (d, $^2J_{HH}$ = 13.2) 3.80 (d, $^2J_{HH}$ = 13.1)	3.52 (d, $^2J_{HH}$ = 13.1) 3.40 (t, $^2J_{HH}$ = 13.1) 2.66 (d, $^2J_{HH}$ = 13.8) 2.81 (t, $^2J_{HH}$ = 13.7)		0.40 (s)	6.19 (bs)
[Ni(CH_3)(**NNO**)], **4**	8.45 (s)	3.73 (d, $^2J_{HH}$ = 11.7) 4.24 (d, $^2J_{HH}$ = 11.5)	2.85 (d, $^2J_{HH}$ = 14.2) 2.63 (d, $^2J_{HH}$ = 14.0) 2.48 (t, $^2J_{HH}$ = 14.2) 2.19 (d, $^2J_{HH}$ = 14.1)		0.19 (s)	1.63 (bs)
[Ni(CH_2SiMe_3)(**NNO**)], **5**	8.43(s)	4.21 (d, $^2J_{HH}$ = 13.2) 3.61 (t, $^2J_{HH}$ = 13.2)	2.81 (d, $^2J_{HH}$ = 13.6) 1.88 (t, $^2J_{HH}$ = 13.9) 2.17 (d, $^2J_{HH}$ = 14.1) 1.43 (t, $^2J_{HH}$ = 14.0)	0.06 (d, $^2J_{HH}$ = 13.9) −0.52 (d, $^2J_{HH}$ = 13.8)	0.62 (s)	
[Pd(**NNO**)Cl], **6**[b]	8.45(s)	4.18 (d, $^2J_{HH}$ = 13.2) 4.33 (d, $^2J_{HH}$ = 13.2)	3.83 (t, $^2J_{HH}$ = 13.9) 3.95 (t, $^2J_{HH}$ = 13.9)	2.40 (m)		6.63 (bs)

[a] In $CDCl_3$.
[b] In $DMSO_d$.

diasterotopic proton $\mathbf{H^1}$ of the benzyl group appeared as a doublet at 3.64 ppm ($^2J_{HH}$ = 14.3) due to coupling with $\mathbf{H^{1\prime}}$ and $\mathbf{H^{1\prime}}$ appeared as one virtual triplet at 3.47 ppm ($^2J_{HH}$ = 11.40) due to coupling with $\mathbf{H^1}$ and NH (Fig. 2). On the other hand, protons of the bridge ethylene appeared as partially resolved multiplets at 2.89 (dt, 1H), 2.28 (dd, 1H), 1.81 (m, 1H) and 1.77 (m, 1H) ppm, given the coupling among themselves and with the proton of the amine. The methylene protons of the neophyl group were also diasterotopic and a AX spin system can be observed at 2.40 (d, $^2J_{HH}$ = 8.60, 1H) and 1.61 (d, $^2J_{HH}$ = 8.60, 1H) ppm, while the methyl protons are found as two singlets at 2.02 (s, 3H) and 1.68 (s, 3H) ppm.

$^{13}C\{^1H\}$ and ^{13}C NMR (C_6D_6, 300 MHz) of **1** provided additional information on the structure of the complex. There were four signals in the aliphatic region of the carbon spectra at 29.9, 33.0, 36.7 and 42.3 ppm, which were assigned to the methyl, methylene and quaternary carbons of the neophyl ligand, respectively. The methylene carbons of **NNO** were located at lower field at 53.6 (s, J_{CH} = 140.1, CH_2), 50.3 (s, J_{CH} = 131.3, CH_2) and 53.8 (s, J_{CH} = 133.5, CH_2) ppm. The complete assignment of carbon and protons was carried out using the monodimensional NMR techniques discussed herein together with bidimensional NMR techniques such as ^1H–^1H COSY, ^1H–^{13}C HETCOR and NOESY (see Supplementary information).

Infrared spectroscopy also provides supplementary evidence on the tridentate coordination nature of the NNO ligand. Thus, in complexes **1**–**5** the signal corresponding to C═N stretching vibration was observed at higher energies relative to the free ligand (1623–1632 cm^{-1}), whereas the stretching vibration of the NH group was found between 3150 and 3250 cm^{-1}, in addition the phenolic proton vibration was absent.

As mentioned above alkyl complexes **2**–**5** showed very similar ligand spectroscopic features relative to compound **1** and therefore the former will not be discussed in detail. The ^{1}H and $^{13}C\{^1H\}$ NMR data for these complexes are shown in Tables 1 and 2, respectively. A general observation is that the metal atom provokes a chemical shift displacement of carbons and protons of the ligand in the complex relative to the free ligand, for instance, in the nickel complexes the methylene protons of alkyl groups appeared displaced 0.3 ppm at higher fields, while the other aliphatic protons moved to lower fields.

2.3. Preparation and characterization of Ni(II) and Pd(II) coordination complexes

The coordination complexes of formula [MCl(NNO] (M = Pd(II), **6**; Ni(II), **7**), were prepared by mixing equimolar amounts of

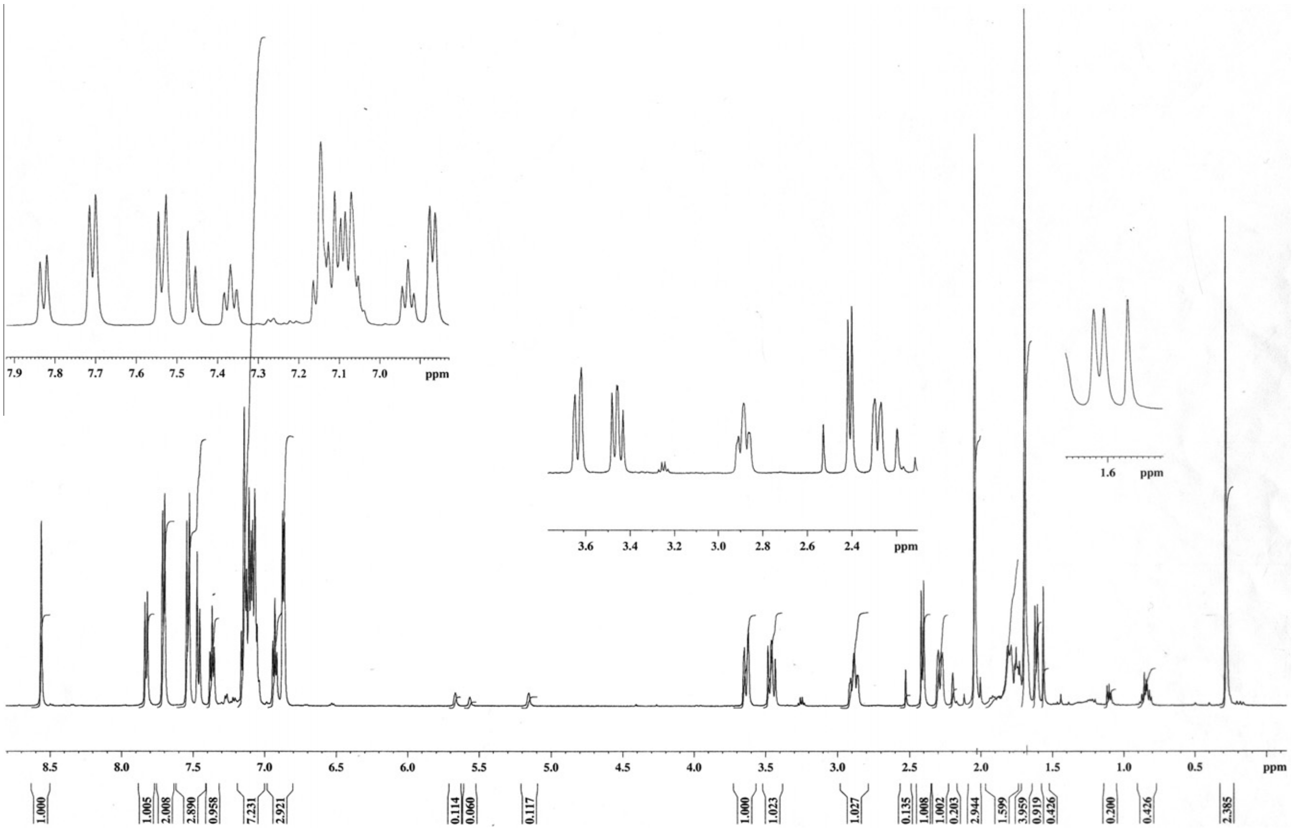


Fig. 2. ^{1}H NMR spectrum (300 MHz, C_6D_6) of [Pd(CH_2CMe_2-*o*-C_6H_5)(**NNO**)], **1**.

Table 2
$^{13}C\{^1H\}$ NMR values of **NNO** ligand (in $CDCl_3$) and complexes **1–6** (in C_6D_6) at 293 K.

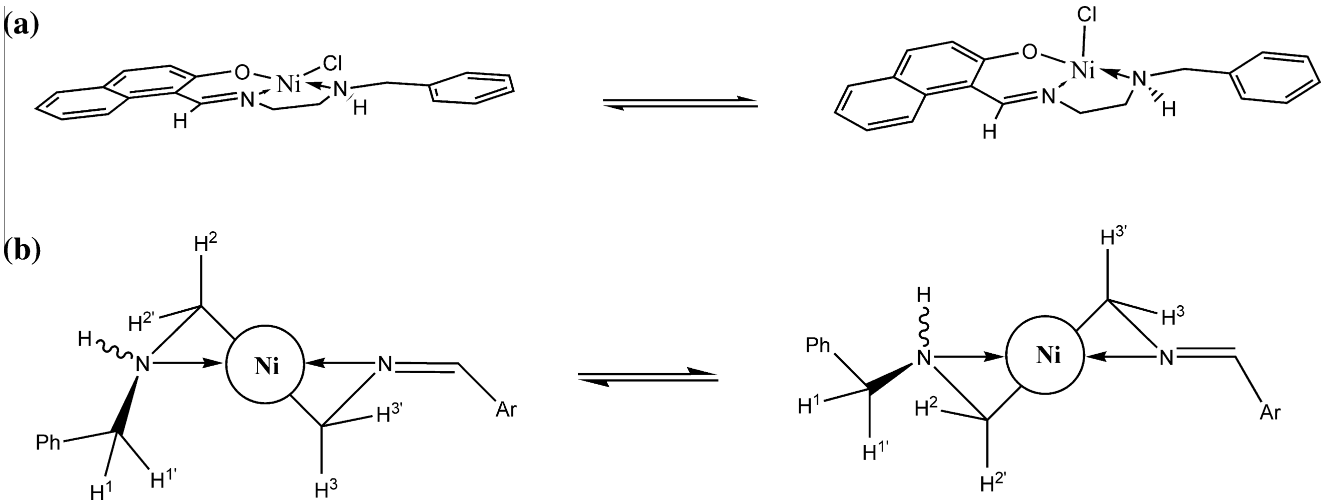
Compound	^{13}C NMR						IR (cm^{-1})	
	<u>HC</u>=N	<u>CH$_2$</u>-Ph	N-<u>CH$_2$-CH$_2$</u>-N	M-<u>CH$_2$</u>	<u>C</u>(CH$_3$)$_2$	<u>CH$_3$</u>	C=N	NH
NNO ligand	158.9	53.6	48.7, 53.8				1620	3280
[Pd($CH_2CMe_2C_6H_5$)(**NNO**)], **1**	169.1	53.6	50.3, 53.8	36.7	42.3	29.9, 33.0	1630	3150
[Ni($CH_2CMe_2C_6H_5$)(**NNO**)], **2**	167.5	50.1	45.9, 50.2	31.9	41.8	29.3, 33.1	1628	3250
[Pd(CH_3)(**NNO**)], **3**[a]	166.0	56.5	53.0, 57.2			−4.0	1623	3220
[Ni(CH_3)(**NNO**)], **4**	166.4	51.9	47.8, 54.1			−7.4	1628	3190
[Ni(CH_2SiMe_3)(**NNO**], **5**	167.9	52.1	47.2, 53.6	-0.9		3.2	1632	3150
[Pd(**NNO**)Cl], **6**[b]	163.9	54.4	50.4, 60.2				1617	3105

[a] In $CDCl_3$.
[b] In DMSOd.

$PdCl_2$(COD) or $NiCl_2{\cdot}6H_2O$ and **NNO** in dichloromethane followed by addition of KOH in excess. The diamagnetic square–planar palladium yellow complex **6** showed very similar spectroscopic features to analogous organometallic compounds, vide supra, particularly with the methyl palladium compound **3** and therefore its spectroscopic features will not be discussed further. The room temperature ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the brown complex **7** exhibited only broad signals between 0 and 10 ppm. When the temperature was progressively lowered, the broad signals progressively sharpened and at 220 K distinct sharp signals appeared for all protons. Seven unsymmetrical multiplets assigned to the methylene $–CH_2CH_2–$ chain, benzyl group and amine protons were observed at 220 K (see Supplementary information). The imine proton H^5 was not observed even at the lowest temperature, but the stretching vibration of the C=N bond was observed at 1621 cm^{-1} by IR spectroscopy.

Given that for some Ni(II) complexes a temperature-dependent equilibrium between diamagnetic square–planar and high-spin tetrahedral structures has been proposed in the literature [16], we first considered that the broad signals in the ^{1}H NMR spectrum of **7** could be attributed to the presence of the paramagnetic Ni(II) species [17,18] (Scheme 2a). However, we measured the magnetic moment of 7 in solution ($CDCl_3$) at 298 K (using Evans' method) as well as in solid state and we found that complex **7** was diamagnetic agreeing with a square–planar structure. This finding is also supported by the fact that there was no color change of the solution of **7** in the studied temperature range (323–250 K). Therefore, we suggest that the dynamic process observed for complex **7** in solution is due to a conformational flexibility of the two chelating rings as depicted in Scheme 2b which has been observed for other Ni(II) complexes [19].

Complex Ni(NNO)$_2$, **8**, was prepared by reaction of any of the alky complex precursors used in this work with two equivalents of **NNO** ligand (Scheme 1). Crystals of 8 suitable for X-ray diffraction were obtained by crystallization in a mixture of Et_2O/petroleum ether at −30 °C. Crystalline complex 8 was quite insoluble



Scheme 2. (a) Representation of the equilibrium between diamagnetic square–planar and high-spin tetrahedral structures of **7**. (b) Proposed conformational rearrangement for **7**, certain atoms have been omitted for clarity proposes.

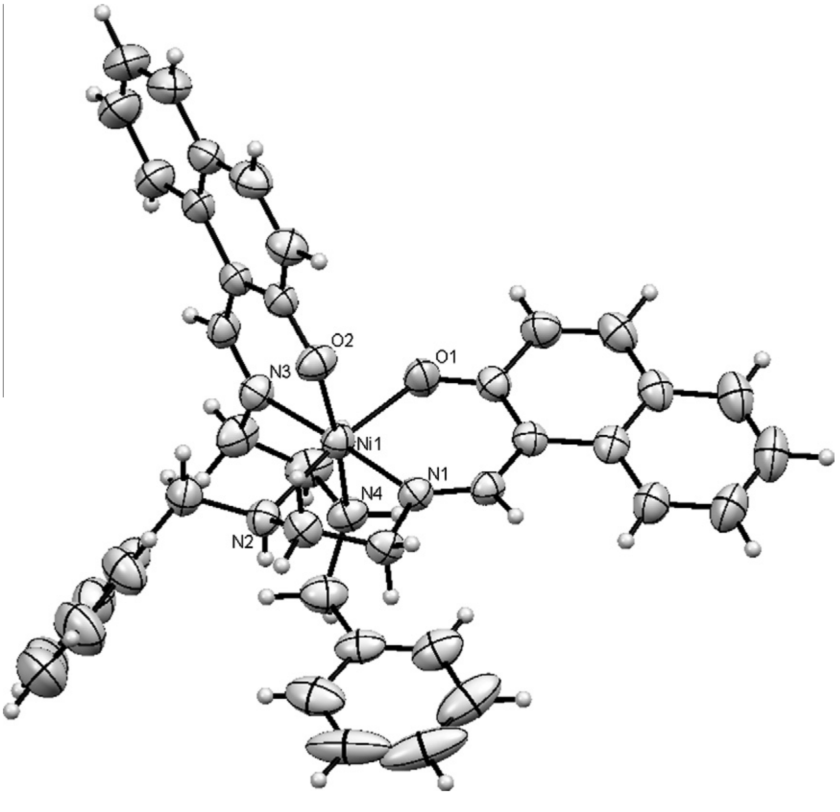


Fig. 3. ORTEP drawing of the molecular structure of [Ni(**NNO**)$_2$], **8**. Selected interatomic distances (Å) and angles (°): Ni(1)–N(1) = 2.0070(17), Ni(1)–N(3) = 2.0175(17), Ni(1)–O(1) = 2.0410(14), Ni(1)–O(2) = 2.0415(14), Ni(1)–N(2) = 2.1794(17), Ni(1)–N(4) = 2.2761(17); N(1)–Ni(1)–N(3) = 177.12(6), N(1)–Ni(1)–O(1) = 88.81(6), N(3)–Ni(1)–O(1) = 93.86(6), N(1)–Ni(1)–O(2) = 93.00(6), N(3)–Ni(1)–O(2) = 87.99(6), O(1)–Ni(1)–O(2) = 92.43(6), N(1)–Ni(1)–N(2) = 81.23(6), N(3)–Ni(1)–N(2) = 96.10(7), O(1)–Ni(1)–N(2) = 170.04(6), O(2)–Ni(1)–N(2) = 88.04(7), N(1)–Ni(1)–N(4) = 97.99(6), N(3)–Ni(1)–N(4) = 81.11(7), O(1)–Ni(1)–N(4) = 86.12(7), O(2)–Ni(1)–N(4) = 168.88(6), N(2)–Ni(1)–N(4) = 95.29(7).

in most common solvents and had high thermal and thermodynamic stability.

Fig. 3 shows a perspective drawing of complex 8 indicating selective atom labels and relevant bond lengths and angles. The Ni(II) ion appeared in a N_4O_2 coordination sphere. Each of the two meridionally spanning ligands (**NNO**) coordinated the metal ion via imine-N, amine-N and deprotonated phenol-O, with the oxygen atoms being in cis position, so each ligand forms two chelate rings of six and five members. A distortion of the NiN_4O_2 pseudo octahedron was clearly evident from the bond distances and angles given in Fig. 3. The crystal structure also shows that the nitrogen atoms of the amine group of the two **NNO** ligands bonded to the metal center are chiral. Interestingly, the H attached to N(4) was pointing towards O(1) while the H bound to N(2) was opposite to O(2), so that the absolute configuration of one amine nitrogen of one ligand is “R” and the amine nitrogen of the other ligand is “S”.

The bond lengths of Ni-N(2) and Ni-N(4) [2.1794(17), 2.2761(17)] were longer than Ni-N(1) and N(3) [2.0070(17), 2.0175(17)] due to bigger trans influence of the oxygen atoms. These data are in agreement to the values found for known six coordinated Ni complexes with nitrogen donor ligands [20]. Moreover, only one of the two phenyl rings of the benzyl group was oriented over the five ring chelate. It should be noted that the six membered chelate rings are almost planar suggesting an aromatic character.

3. Conclusions

In this study, we prepared alkyl and chloro Ni(II) and Pd(II) compounds containing a Schiff base ligand having N_2O donor atoms. The complexes were characterized by analytical, IR and NMR spectroscopic methods. Structural characterization by single-crystal diffraction analysis of one Ni(II) octahedral complex was also discussed where the main feature was that the central Ni(II) ion possesses a distorted octahedral geometry.

4. Experimental

4.1. General procedures

Unless otherwise stated, operations for synthesis of organometallic compounds were carried out under strictly inert atmosphere conditions using standard Schlenk techniques and the solvents were distilled under N_2 atmosphere, employing as drying agents CaH_2(CH_2Cl_2, Hexane), Na/benzophenone (Et_2O, THF, Toluene). The starting materials were reagent grade and were purchased from Aldrich. The $\overline{\mathrm{Pd(CH_2CMe_2\text{-}\mathit{o}\text{-}C}}\mathrm{_6H_4)(cod)}$ [21], $\overline{\mathrm{Ni(CH_2CMe_2\text{-}\mathit{o}\text{-}C}}\mathrm{_6H_4)(PMe_3)_2}$ [22], Pd(cod)(Cl)(Me) [23], Pd(TMEDA)Me_2 [24], Ni$(Py)_2Me_2$ [25] and Ni$(PMe_3)_2(CH_2SiMe_3)_2$ [26], were prepared following reported procedures.

FT-IR spectra were recorded using a Perkin-Elmer 710-B spectrophotometer, in 4000–400 cm^{-1} region. ^1H, ^{13}C and bidimensional NMR experiments were obtained either in an NMR Brucker 300 spectrometer (300 MHz) or a Varian Gemini 200 MHz Unity plus. Chemical shits (δ) are expressed in ppm downfield from TMS at $\delta = 0$ ppm, and coupling constants (J) are expressed in Hz. Elemental Analysis were carried out in the Chemical Research Center at Universidad Autónoma del Edo. Hidalgo and Universidad Autónoma de Morelos. X-ray diffraction data of compound [Ni(**NNO**)$_2$] was obtained at the Chemical Research Center of the Universidad Autónoma del Edo. Hidalgo.

4.2. Synthesis of [NNO] ligand, 1-((2-benzylamino)ethylimino)methyl)naphthalene-2-ol

A solution of 2-hydroxy-1-naphthaldehyde (910 mg, 5 mmol) in 30 ml of dichloromethane was added to a solution of *N*-benzylethylenediamine (751 mg, 5 mmol) in 20 ml of Et_2O. The mixture was allowed to react at room temperature for 1 h, then filtered and washed whit Et_2O (2×5 ml). Yield: 1.49 g, 90%. *Anal.* Calc. for $C_{20}H_{20}N_2O$: C, 78.92; H, 4.82; N, 9.20. Found: C, 78.80; H, 4.80; N, 9.03%. ^1H NMR ($CDCl_3$): 1.57(s, *NH*, 1H), 2.97(t, $J = 5.6$ Hz, HN-CH_2, 2H), 3.69(t, $J = 5.6$ Hz,CN-CH_2, 2H), 3.83(s, CH_2Ph, 2H), 6.91(d, $J = 9.3$ Hz, 1H), 7.20–7.40(m, 5H), 7.40(t, $J = 7.2$ Hz, 1H), 7.59(d, $J = 7.8$ Hz, 1H), 7.67(d, $J = 9.3$ Hz, 1H), 7.82 (d $J = 8.4$ Hz, 1H), 8.78(s, *HC* = N, 1H), 14.42 (sa, *OH*, 1H). ^{13}C NMR ($CDCl_3$):48.7, 53.6, 53.8, 117.8, 122.7, 124.8, 127.2, 128.1, 128.5, 128.8, 129.3, 137.2, 158.9. FAB-MS: *m/z* 304(62%, **NNO**). IR spectrum (selected bands, KBr, cm^{-1}): 3280 (NH), 1620(C=N).

4.3. Synthesis of [Pd(NNO)($CH_2CMe_2C_6H_5$)], $\underline{\mathbf{1}}$

A Schlenk flask containing 504.84 mg (2 mmol) of palladium neophyl metallacycle $\overline{\mathrm{Pd(CH_2CMe_2\text{-}\mathit{o}\text{-}C}}\mathrm{_6H_4)(cod)}$ and 592 mg (2 mmol) of **NNO** ligand was cooled to −78° C, followed by addition of 60 ml of Et_2O. The mixture was stirred for 15 min at this temperature and then 1.5 h at room temperature. The solvent was evaporated to dryness and the residue was extracted with 30 ml of Et_2O, the solute was concentrated by reduced pressure and the product crystallized at −30 °C. The reaction was almost quantitative. *Anal.* Calc. for $C_{30}H_{32}N_2OPd$: C, 66.36, H, 5.94; N, 5.16. Found: C, 66.15; H, 5.71; N, 5.03%. IR spectrum (selected bands, Nujol, cm^{-1}): 3150 (NH), 1630 (C=N). ^1H NMR (C_6D_6): 1.68(s, CH_3, 3H), 2.02 (s, CH_3, 3H), 1.61 (d, $^2J_{HH} = 8.60$ Hz,C_q-CH_2, 1H), 1.77 (m, N-CH_2, 2H), 1.81 (m, N-CH_2, 1H), 2.28 (dd, CN-CH_2, 1H), 2.40 (d, $^2J_{HH} = 8.60$ Hz, C_q-CH_2, 1H), 2.89 (dd, *NH*, 1H), 3.47 (d, $^2J_{HH} = 11.40$ Hz,Ph-CH_2, 1H), 3.64 (d, $^2J_{HH} = 14.26$ Hz,Ph-CH_2, 1H), 6.80–7.80 (m, 16H), 8.50(s, *HC* = N, 1H). ^{13}C NMR (C_6D_6): 29.9 (C_q-$\underline{Me}_2$), 33.0 (C_q-$\underline{Me}_2$), 36.7 (C_q-$\underline{C}H_2$), 42.3 ($\underline{C}_q$-Me_2), 53.6 ($\underline{CH}_2$-Ph), 50.3 ($\underline{C}H_2$NH), 53.8 (s, $\underline{C}H_2$C=N), 109.3 (C_{ar}), 118.0 (CH_{ar}), 121.3 (CH_{ar}), 124.8(CH_{ar}), 125.2 (C_{ar}), 125.7 (CH_{ar}), 126.0–130.0 (C_{ar}), 152.5 (CH_{ar}), 155.8 (C_{ar}), 169.1 ($\underline{C}$=N).

4.4. Synthesis of [Ni(NNO)($CH_2CMe_2C_6H_5$)], $\underline{\mathbf{2}}$

A Schlenk flask containing 399.5 mg (1.16 mmol) of $\overline{\mathrm{Ni(CH_2CMe_2\text{-}\mathit{o}\text{-}C}}\mathrm{_6H_4)(PMe_3)_2}$ and 338.7 mg (1.16 mmol) of **NNO** ligand was cooled to −78 °C and then 50 ml of Et_2O were added. The mixture was continuously stirred for 15 min at −78 °C followed by 1.5 h at room temperature. The solvent was evaporated to dryness. Subsequently, the product was extracted with a minimum amount of Et_2O and then petroleum ether was slowly added until the product began to precipitate as a red solid. Yield: 419 mg (73%). *Anal.* Calc. for $C_{30}H_{32}N_2NiO$: C, 72.75; H, 5.66; N, 6.51. Found: C, 72.65; H, 5.51; N, 6.23%. IR spectrum (selected bands, Nujol, cm^{-1}): 3250 (NH), 1628 (C=N). ^1H NMR (C_6D_6): 1.64 (s, CH_3, 3H), 2.21 (s, CH_3, 3H), 0.72 (d, $^2J_{HH} = 8.05$ Hz,C_q-CH_2, 1H), 0.95 (dd, $^2J_{HH} = 4.69$ Hz, N-CH_2, 1H), 1.18 (sa, *NH*, 1H), 1.38 (m, N-CH_2, $^2J_{HH} = 4.94$ Hz, 1H), 2.06 (t, CN-CH_2, $^2J_{HH} = 13.36$ Hz,1H), 1.58 (d, $^2J_{HH} = 8.05$ Hz, C_q-CH_2, 1H), 2.61 (t, $^2J_{HH} = 14.10$ Hz, CN-CH_2, 1H), 3.39 (d, $^2J_{HH} = 13.37$ Hz,Ph-CH_2, 1H), 3.91 (d, $^2J_{HH} = 14.26$ Hz, Ph-CH_2, 1H), 6.70–7.90 (m, 16H), 8.48 (s, *HC*=N, 1H). ^{13}C NMR ((C_6D_6): 29.3 (C_q-$\underline{Me}_2$), 33.1 (C_q-$\underline{Me}_2$), 31.9 (C_q-$\underline{C}H_2$), 41.8 ($\underline{C}_q$-Me_2), 50.1 ($\underline{CH}_2$-Ph), 45.9 ($\underline{C}H_2$NH), 52.1 (s, $\underline{C}H_2$C = N), 109.7 (C_{ar}), 118.0–136.0 (C_{ar}), 154.5 (CH_{ar}), 156.8 (C_{ar}), 167.5 ($\underline{C}$=N).

4.5. Synthesis of [Pd(NNO)(Me)], **3**

Five hundred and ninety two milligrams (2 mmol) of **NNO** ligand was added to a solution of dialkyl palladium complex, [$PdMe_2$(TMDA)], 504.84 mg (2 mmol) in 30 ml of Et_2O maintained at −30 °C. The mixture was allowed to stir 15 min at this temperature and then 1 h at room temperature. The solvent was evaporated under reduced pressure, the product was extracted with 30 ml of CH_2Cl_2, filtered and the solution was concentrated. The filtrate was stored at −30 °C yielding yellow crystals. Yield: 100 mg (47%). *Anal.* Calc. for $C_{21}H_{22}N_2OPd$: C, 59.37; H, 5.22; N, 6.59. Found: C, 59.15; H, 5.11; N, 6.23. IR spectrum (selected bands, Nujol, cm^{-1}): 3220 (NH), 1623 (C=N). ^1H NMR ($CDCl_3$): 0.40 (s, CH_3, 3H), 2.66 (m, N-CH_2, 1H), 2.81 (m, N-CH_2, 1H), 3.40 (m, CN-CH_2, 1H), 3.52 (m CN-CH_2, 1H), 3.80 (dd, $^2J_{HH} = 11.70$ Hz,Ph-CH_2, 1H), 4.62 (dd, $^2J_{HH} = 11.16$ Hz, Ph-CH_2, 1H), 6.15 (sa, NH, 1H), 7.15–7.75 (m, 11H), 8.81 (s, *HC* = N, 1H). ^{13}C NMR ($CDCl_3$): −4.0 (CH_3), 56.5 ($\underline{C}H_2$-Ph), 53.0 ($\underline{C}H_2$NH), 57.2 (s, $\underline{C}H_2$C=N), 110.5 (C_{ar}), 115.0–140.0 (C_{ar}), 152.5 (CH_{ar}), 166.0 ($\underline{C}$=N).

4.6. Synthesis of [Ni(NNO)(Me)], **4**

A suspension of $NiCl_2Py_4$ (880 mg, 2 mmol) in 50 ml of Et_2O was cooled to −78 °C and 1 ml of pyridine was added. The mixture was allowed to stir 15 min and then 3.5 ml (2 mmol) of a solution LiMe (1.4 M in Et_2O) was added. The mixture was stirred 15 min at −78 °C followed by 1 h at room. Again, the mixture was cooled at −78 °C and 292 mg (1 mmol) of **NNO** ligand was added, stirred 15 min at this temperature and then 1.5 h at room temperature. The solvent was evaporated under reduced pressure and the product was extracted with 50 ml of Et_2O, filtered and concentrated. The concentrated solution was stored at −30 °C yielding orange crystals. Yield: 460 mg (61%). *Anal.* Calc. for $C_{21}H_{22}N_2NiO$: C, 66.88; H, 5.88; N, 7.43. Found: C, 66.53; H, 5.75; N, 7.23%. IR spectrum (selected bands, Nujol, cm^{-1}): 3190 (NH), 1628 (C=N). ^1H NMR (C_6D_6): 0.19 (s, CH_3, 3H), 1.63 (sa, NH, 1H),2.19 (m, N-CH_2, 1H), 2.48 (m, N-CH_2, 1H), 2.63 (sa, CN-CH_2, 1H), 2.85 (m CN-CH_2, 1H), 3.73 (dd,Ph-CH_2, 1H), 4.24 (dd, Ph-CH_2, 1H), 7.00–8.00 (m, 11H), 8.45 (s, *HC*=N, 1H). ^{13}C NMR (C_6D_6): -7.4 (CH_3), 47.8 ($\underline{C}H_2$-Ph), 51.9 ($\underline{C}H_2$NH), 54.1 (s, $\underline{C}H_2$C=N), 108.5 (C_{ar}), 115.0–140.0 (C_{ar}), 152.5 (CH_{ar}), 166.4 ($\underline{C}$ = N).

4.7. Synthesis of [Ni(NNO)(CH_2SiMe_3)], **5**

Two hundred and ninety two milligrams (1 mmol) of ligand **NNO** was added to a solution of $[Ni(PMe_3)_2(CH_2SiMe_3)_2]$ (383 mg, 1 mmol) in 50 ml of Et_2O which was kept at −78 °C The mixture was stirred for 15 min at −78 °C and then 1.5 h at room temperature. The solution color changed from orange to yellow. The reaction mixture was filtered and the solvent evaporated giving a red oil which was dissolved in petroleum ether and concentrated by reduced pressure until an orange precipitate appeared. Yield: 359.2 (80%). *Anal.* Calc. for $C_{24}H_{38}N_2NiOSi$: C, 64.16; H, 6.73; N, 6.24. Found: C, 66.03; H, 6.20; N, 6.12%. IR spectrum (selected bands, Nujol, cm^{-1}): 3150 (NH), 1632 (C=N). ^1H NMR (C_6D_6): 0.62 (s, CH_3, 9H), 1.81 (sa, NH, 1H), -0.52 (m, $^2J_{HH}$ = 10.60 Hz, Si-CH_2, 1H), 0.06 (m, $^2J_{HH}$ = 10.60 Hz, Si-CH_2, 1H),1.43 (dd, $^2J_{HH}$ = 5.97 Hz,N-CH_2, 1H), 2.17 (m, $^2J_{HH}$ = 13.90 Hz, N-CH_2, 1H), 1.88 (dd, $^2J_{HH}$ = 6.37 Hz,CN-CH_2, 1H), 2.81 (t, $^2J_{HH}$ = 14.30 Hz, CN-CH_2, 1H), 3.61 (t, $^2J_{HH}$ = 1.70 Hz,,Ph-CH_2, 1H), 4.21 (d, $^2J_{HH}$ = 13.18 Hz, Ph-CH_2, 1H), 6.80–8.00 (m, 11H), 8.43 (s, *HC* = N, 1H). ^{13}C NMR (C_6D_6): -0.9 ($\underline{C}H_2$-Si), 3.2 (CH_3), 51.9 ($\underline{C}H_2$-Ph), 47.8 ($\underline{C}H_2$NH), 53.6 (s, $\underline{C}H_2$C=N), 110.3 (C_{ar}), 115.0–140.0 (C_{ar}), 153.1 (CH_{ar}), 167.9 ($\underline{C}$=N).

4.8. Synthesis of [Pd(NNO)Cl], **6**

$PdCl_2$(cod) (285 mg, 1 mmol) was added to a suspension of **NNO** (304 mg, 1 mmol) in 30 ml of EtOH. The mixture was allowed to react at room temperature for 1 h giving a yellow precipitate. The solid was filtered and washed with cold EtOH (2 times/10 ml). Yield: 393 mg (88.0%). *Anal.* Calc. for $C_{20}H_{19}ClN_2OPd$: C, 53.95; H, 4.30; N, 6.29. Found: C, 53.87; H, 4.22; N, 6.21. IR spectrum (selected bands, KBr, cm^{-1}): 3105 (NH), 1617 (C=N). ^1H NMR (DMSOd): 2.30–2.50 (m, N-CH_2, 2H), 3.83 (t, CN-CH_2, 1H), 3.95 (t, CN-CH_2, 1H), 4.18 (dd, Ph-CH_2, 1H), 4.33 (dd, Ph-CH_2, 1H), 6.63 (ta, NH, 1H), 7.00–8.00 (m, 11H), 8.45 (s, *HC*=N, 1H). ^{13}C NMR (C_6D_6): 54.4 ($\underline{C}H_2$-Ph), 50.4 ($\underline{C}H_2$NH), 60.2 (s, $\underline{C}H_2$C=N), 109.5 (C_{ar}), 120.0–140.0 (C_{ar} and CH_{ar}), 153.0 (CH_{ar}), 163.9 ($\underline{C}$=N).

4.9. Synthesis of [Ni(NNO)Cl], **7**

This compound was obtained as a brown solid following the same route used in the preparation of complex **6**. Yield: 286.5 mg (73.0%). *Anal.* Calc. for $C_{20}H_{19}ClN_2NiO$: C, 60.43; H, 4.82; N, 7.05. Found: C, 60.27; H, 4.66; N, 6.88%. IR spectrum (selected bands, KBr, cm^{-1}): 3285 (NH), 1621 (C=N). ^1H NMR ($CDCl_3$, 220 K): 1.61 (d, N-CH_2, 2H), 3.02 (d, N-CH_2, 2H), 3.33 (t, CN-CH_2, 1H), 3.60 (t, CN-CH_2, 1H), 3.98 (t, Ph-CH_2, 1H), 4.76 (d, Ph-CH_2, 1H), 4.75 (sa, NH, 1H), 6.50–7.50 (m, 12H).

4.10. Synthesis of [Ni($NNO)_2$], **8**

This compound can be obtained by double protonation of any dialkyl nickel complex with two equivalents of **NNO** ligand. i.e. 152 mg (0.5 mmol) of **NNO** ligand was added to a solution of [**Ni(NNO)CH$_3$**] 188 mg (0.5 mmol) in 30 ml of Et_2O and the reaction mixture was stirred 1 h at room temperature. The solution was concentrated to half of its original volume under reduced pressure. The product crystallized as dark red crystals by diffusion with petroleum ether after 72 h at −30 °C. *Anal.* Calc. for $C_{40}H_{38}N_4NiO_2$: C, 72.20; H, 5.76; N, 8.42. Found: C, 71.98; H, 5.68; N, 8.25%. IR spectrum (selected bands, KBr, cm^{-1}): 1621 (C=N).

4.11. X-ray structure analyses for compound 8

An X-ray-quality red crystal was glued onto the tip of a glass fiber, and reflections were collected on a Bruker-SMART 5000 CCD based diffractometer, using ω scans and a rotating anode with Mo Kα radiation (λ = 0.71073 Å) at room temperature. The frames were integrated with the SAINT software package[27], using a narrow-frame algorithm, and the structure was solved by direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures with SHELXTL 5.1 [28]. The structure was checked with PLATON [29] or SXGRAPH included in the WINGX VI.6 [30] crystallographic software package. Non-H atoms were refined with anisotropic thermal parameters.

Table 3
Crystal Data and Structure Refinement Details for Compound **8**.

Formula	$C_{40}H_{38}N_4NiO_2$
Molecular weight	665.45
Temperature (K)	291(2)
Color	red
Crystal size (mm)	.55 × 0.60 × 0.60
Symmetry, space group	monoclinic, *P*2(1)/*c*
a, (Å)	13.1799(8)
b (Å)	14.5556(9)
c (Å)	17.5018(11)
α (°)	90
β (°)	98.0420 (10)
γ (°)	90
V (Å^3)	3324.5(4)
Z	4,
D_{calc} (g cm^{-3})	1.330
Diffractometer	Bruker SMART 5000 CCD
λ (Mo Kα) (Å)	0.71073
Monochromator	graphite
Scan type	ω scan
Theta range for data collection (°)	1.56–24.01
Limiting indices	$-14 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 16$, $-13 \leqslant l \leqslant 20$
Number of data collected	18119
Number of unique data (R_{int})	5223 (0.0502)
Number of parameters/restraints	557/0
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0371, wR_2 = 0.0886
R indices (all data)	R_1 = 0.0459, wR_2 = 0.0938
Extinction coefficient	0.0233 (10)
Largest difference in peak and hole (e A^{-3})	0.325 and −0.330

Hydrogen atoms were treated as idealized contributions. Pertinent crystallographic data are collected in Table 3.

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Appendix A. Supplementary data

CIF file giving details for the crystal structure determinations of **8** and figures giving a ^{1}H NMR ^{13}C{^{1}H}, COSY, HETCOR and NOESY spectra for compound **1**, as well as ^{1}H NMR of temperature variable of **7**. CCDC 855860 contains the supplementary crystallographic data for [Ni(**NNO**)$_2$], **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.04.002.

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