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Synthesis of dialkyl, diaryl and metallacyclic complexes of Ni and Pd containing pyridine, α -diimines and other nitrogen ligands

Crystal structures of the complexes *cis*-NiR₂py₂ (R = benzyl, mesityl)

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Abstract

The alkylation of NiCl₂py₄ or PdCl₂py₂ with organomagnesium or organolithium reagents affords dialkyl complexes *cis*-MR₂py₂ (R = Me, CH₂SiMe₃, CH₂Ph, CH₂CMe₂Ph, 2,4,6-C₆H₂Me₃). The methyl and trimethylsilyl derivatives undergo ligand exchange reactions with chelating nitrogen ligands (α -diimines or 2-imidoylpyridines), yielding the corresponding dialkyl derivatives in good to excellent yields. A catalytic amount of PMe₃ induces the transformation of the nickel complex Ni(CH₂CMe₂Ph)₂py₂ into the metallacyclic derivative NiCH₂CMe₂-*o*-C₆H₄(py)₂. The latter, and the related palladacycle Pd(CH₂CMe₂-*o*-C₆H₄)(cod), also undergo facile ligand exchange reactions.

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1. Introduction

Nickel alkyl complexes play a central role in several catalytic transformations of great economic importance, such as ethylene dimerization or oligomerization [1]. In these processes, the insertion of two or more ethylene molecules into a nickel hydride or alkyl bond, followed by a chain transfer reaction (either β -hydride elimination or direct chain transfer to the monomer), leads to the formation of α -olefins. The molecular weight of the products is determined by the relative rates of the olefin insertion and chain transfer steps, which in turn are influenced by the reaction pressure and temperature and by the structure of the catalyst.

As shown by Brookhart and co-workers [2], nitrogen ligands containing bulky substituents (e.g. α -diimines

decrease the rate of chain transfer, leading to high molecular weight polymers. This pioneer work has triggered a wide interest in the use of late transition metal catalysts for olefin polymerization [3]. Although MAO or related aluminium alkyls [2,4] may be used as co-catalysts, alkyl derivatives of Ni(II) and Pd(II) can be employed directly as catalyst precursors [3,5], an alternative that becomes specially useful in co-polymerization reactions of ethylene and polar monomers [6].

Although the chemistry of nickel and palladium alkyl complexes that contain phosphine ligands is well developed [7], the preparation of similar derivatives stabilized by hard nitrogen ligands (other than bipyridyl and its derivatives) frequently poses important difficulties. Compared with phosphines, amine or imine ligands usually possess a lower stabilizing influence [8], and the corresponding alkyl derivatives can display low thermal stability and high sensitivity to oxygen and moisture. Another potential problem is the reactivity of some nitrogen ligands, such as the imines, to the Li or Mg

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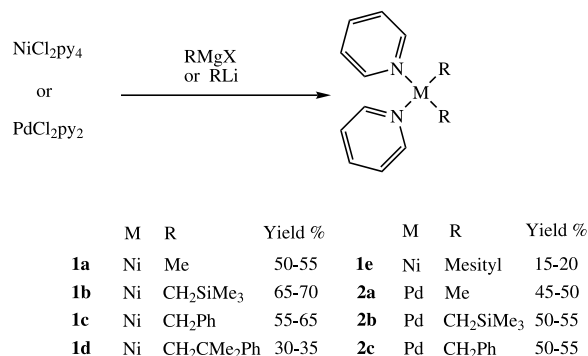
reagents used to transfer the alkyl groups to the metal center. For instance, the alkylation of the α -diimine nickel dibromide complexes $\text{Ni}(\text{N}-\text{N})\text{Br}_2$ with MeLi or $\text{Mg}(\text{CH}_2\text{SiMe}_3)\text{Cl}$, reported by Brookhart and co-workers [2] and Okuda and co-workers [9] respectively, leads to the desired alkyl complexes in low yields, usually below 30%. This can represent a serious drawback for the use of alkyl complexes in catalyst screening protocols. In contrast, ligand exchange reactions, starting from suitable precursors of the type $\text{MR}_2\text{L}'_2$, provide a smooth and selective method for the preparation of the desired Ni and Pd alkyl complexes. In order to be synthetically useful, the precursor must contain labile L' ligands, and at the same time, it should be readily available and display a reasonable stability. Several complexes of Ni and Pd have been used as precursors in the synthesis of alkyl compounds. Thus, the dimethyl derivatives $\text{MMe}_2(\text{tmed})$ ($\text{M} = \text{Ni}$ [10], Pd [11]; $\text{tmed} = \text{N,N,N',N'}$ -tetramethylethylenediamine) display good thermal stability, and the tmed is readily displaced by stronger ligands, such as phosphines or bipyridyl. Cauty has proposed the dimethyl complexes $[\text{PdMe}_2(\text{C}_4\text{H}_4\text{N}_2)_2]_2$ and $\text{PdMe}_2(\text{SMe})_2$ for the preparation of various dimethylpalladium derivatives containing chelating nitrogen donors [12].

Some years ago, our research group reported the synthesis of the nickel bis(trimethylsilyl) complex $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2\text{py}_2$, (**1b**), which contains labile pyridine as the only stabilizing ligand [13]. Compound **1b** is obtained in good yields from the readily available complex NiCl_2py_4 , and undergoes facile ligand displacement reactions with phosphine, bipyridyl, tmed , etc. Therefore, it constitutes a useful starting material for ligand exchange reactions. More recently, we have found that the air stable palladium metallacycle $\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)(\text{cod})$, (**14**), undergoes facile ligand substitution reactions [14]. In this contribution, we extend these previous results, and report the synthesis of a series of complexes of composition MR_2py_2 ($\text{M} = \text{Ni}$, Pd), including the nickelacycle $\text{NiCH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4(\text{py})_2$, (**4**). In addition, we describe the use of these compounds for the preparation of dialkyl and metallacyclic complexes that contain nitrogen-based ligands, such as α -diimines and 2-imidoylpyridines that are relevant in polymerization catalysis.

2. Results and discussion

2.1. Dialkyl complexes MR_2py_2

The alkylation of NiCl_2py_4 with organomagnesium reagents in the presence of an excess of pyridine is known to lead to dialkyl derivatives of composition NiR_2py_2 . Two compounds of this type, $\text{R} = \text{CH}_2\text{SiMe}_3$,



Scheme 1.

1b [13] and $\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-Me}$ [15], have been previously isolated and characterized. As shown in Scheme 1, the same general procedure allows for the preparation of the related complexes **1a–e** (Ni) and **2a–c** (Pd). In most cases organomagnesium reagents were used as alkylating reagents, but the methyl derivatives were prepared from LiMe . The new compounds were isolated as crystalline solids, soluble in hydrocarbon solvents and very sensitive to oxygen. Although the products were isolated in spectroscopically pure form (as seen by NMR), only in some cases (**1e** and **2b**) it has been possible to obtain accurate analytical data, probably because of the relatively low thermal stability of these complexes. Thus, most MR_2py_2 compounds decompose slowly in solution at room temperature in the absence of added pyridine.

While the Pd complexes **2** are in general somewhat more stable than their Ni counterparts, **1**, the thermal stability of these compounds is mainly determined by the nature of the group R. Thus, the mesityl **1e** and the trimethylsilyl derivatives **1b** and **2b** are fairly stable in solution and can be stored in solid form for several weeks at 0°C . On the contrary, the dimethyl complexes **1a** and **2a** decompose slowly at room temperature both in solution and in the solid state. As found previously [16,17], the bis(neophyl) complex **1d** is very unstable and decays in solution within a few hours at room temperature (vide infra). Despite this, we have succeeded in isolating it as a red crystalline solid, and its identity has been confirmed by its transformation into the known compound $\text{Ni}(\text{CH}_2\text{CMe}_2\text{Ph})_2(\text{bipy})$ [13] (see Section 4).

Compounds **1** and **2** exist in solution as a single isomer. Their NMR spectra consist of a single set of signals for the pyridine ligands and another for the alkyl groups, whose relative intensities agree with the composition MR_2py_2 . The signals corresponding to the pyridine protons appear broad in the ^1H -NMR spectra of the nickel complexes **1a–e** and the palladium derivative **2a**, presumably due to a fast, associative exchange with traces of the free ligand, that may result from the partial, irreversible decomposition of the complexes. From the readiness with which this process occurs, the following

order of stability can be proposed: $R = \text{CH}_2\text{CMe}_2\text{Ph} < \text{Me} < \text{CH}_2\text{Ph} < \text{CH}_2\text{SiMe}_3 < \text{mesityl}$. The exchange process is very fast, and for the dimethyl complexes **1a** and **2a**, the NMR signals of the pyridine ligands are broad even at -80°C . Although the configuration of these complexes cannot be deduced from the NMR data, the known compound **1b** exhibits a *cis* disposition in the solid state [13], and the same configuration is observed in the crystal structure of the nickel benzyl complex (**1c**), shown in Fig. 1. Therefore, it seems reasonable that all these MR_2py_2 complexes display a *cis* geometry, avoiding in this way the mutual *trans* influence of the two alkyl groups.

The reaction of $\text{Mg}(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)\text{Br}$ with NiCl_2py_4 in the presence of an excess of pyridine is somewhat more complex since, in addition to the expected complex **1e**, smaller amounts of two other species, **1e'** and **3** are also formed (approximate ratio **1e**:**1e'**:**3** of 6:1:1.5, Scheme 2). The main product, **1e**, and the sparingly soluble **3** have been isolated by fractional crystallization. However, it has not proved possible to isolate a pure sample of **1e'**, since it always co-crystallizes with variable amounts of **1e**. In the absence of added pyridine, the formation of **1e'** is suppressed, and the isolated yield of **1e** is improved (ca. 50%).

Analytical and NMR data for compound **3** demonstrate that it is the monoaryl complex *trans*- $\text{Ni}(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)\text{Br}(\text{py})_2$, resulting from the partial arylation of NiCl_2py_4 by the bulky organomagnesium reagent. Thus, the $^1\text{H-NMR}$ spectrum of **3** reveals the presence of one mesityl group and two equivalent pyridine ligands (Table 4). Naturally, the pyridine ligands appear equivalent in the $^{13}\text{C}\{^1\text{H}\}$ spectrum. Complex **3** can be selectively prepared by reacting **1e** with one equivalent of $\text{HNEt}_3^+\text{Br}^-$.

NMR studies of the **1e** plus **1e'** mixtures reveal their isomeric nature. Each isomer displays characteristic signals for the mesityl and pyridine ligands in a 1:1 ratio. Apart from the different chemical shifts of their related signals (e.g. the *o*- and *p*-Me groups give rise to

resonances at δ 3.29 and 2.27 ppm for **1e**, and 3.34 and 2.28 ppm for **1e'**), the spectra show broad pyridine signals in the case of **1e** but sharp, well defined resonances for **1e'**, indicating that the ligand exchange is slower in the latter. Pure samples of **1e** in C_6D_6 show no indication of isomerization after 24 h at 20°C .

The identity of the major product, **1e**, has been ascertained by an X-ray diffraction study (vide infra) that reveals that this compound has a *cis* geometry. Hence it can be assumed that compound **1e'** corresponds to the *trans* isomer. The relative slowness of the pyridine exchange process for the latter compound could be attributed to the absence of the *trans* labilizing effect that the aryl groups exert in the *cis* isomer.

2.2. Crystal structure of compounds **1c** and **1e**

Figs. 1 and 2 show the crystal structures of the benzyl and mesityl complexes **1c** and **1e**. Selected bond distances and angles are collected in Tables 2 and 3. Complex **1c** crystallizes in the monoclinic system, space group $C2/c$, and the unit cell contains four equivalent molecules. These display a slightly distorted square planar geometry with the pyridine and benzyl ligands arranged in a *cis* fashion. In order to minimize steric interactions, the benzyl groups project themselves in opposite directions, resulting in a general disposition that is reminiscent of the previously reported compound **1b** [13]. As observed in the latter, the pyridine rings are tilted by 51.3° with respect to the coordination plane. The benzyl ligands display a η^1 coordination mode. Although some η^1 -benzyl complexes of Ni can display small $\text{Ni-CH}_2\text{-Ph}$ angles [18] ($< 100^\circ$), these are 109.5 and 116.1° in **1c**, close to the ideal tetrahedral values. The remaining metric parameters of this molecule are as expected, and merit no further discussion.

Crystals of **1e** are orthorhombic, space group $P2_12_12_1$, and contain two crystallographically inequivalent molecules. The crystal packing leaves wide channels along the *a* axis, that are occupied by disordered molecules of solvent. The two molecules adopt a *cis* configuration, and have a similar fourfold propeller shape (Fig. 2), although they display significant differences in the relative orientation of the pyridine and mesityl ligands. A comparison of the structure of the two molecules is also shown in Fig. 2. In the molecule termed 1, the two pyridine ligands lay in planes with a different inclination relative to the coordination plane (65.1 and 48.0°), while in the other the py rings exhibit a more regular disposition, with values of inclination of 54.4 and 51.3° , that are similar to those found in **1c**. The disposition of the mesityl units follow a similar trend, and they are tilted by disparate angles in molecule 1 (72.2 and 67.0° relative to the coordination plane), and more alike in molecule 2 (73.2 and 71.9°).

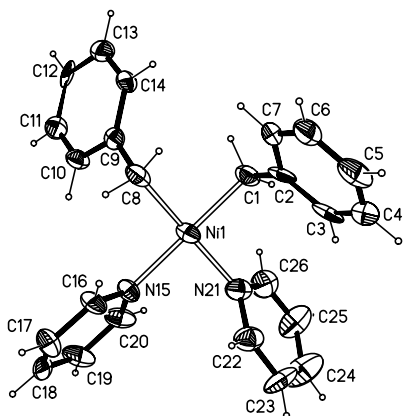
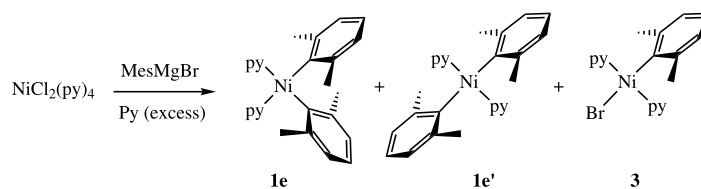


Fig. 1. ORTEP view of compound **1c**.



Scheme 2.

Table 1

Crystal and refinement data for compounds **1e** and **1e'**

	1e	1e' (as 1e · <i>solv</i>) ^a
Empirical formula	C ₂₄ H ₂₄ N ₂ Ni	C ₂₈ H ₃₂ N ₂ Ni
Formula weight	399.16	455.27
Temperature (K)	153(2)	213(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 2 ₁ 2 ₁ (no. 19)
Unit cell dimensions		
<i>a</i> (Å)	24.360(4)	8.092(6)
<i>b</i> (Å)	9.606(2)	23.238(14)
<i>c</i> (Å)	20.128(4)	20.128(4)
α (°)	90	90
β (°)	118.118(3)	90
γ (°)	90	90
<i>V</i> (Å ³)	4154.0(13)	5294(6)
<i>Z</i>	8	8
<i>D</i> _{calc} (g cm ⁻³)	1.276	1.142
Absorption coefficient (mm ⁻¹)	0.944	0.748
<i>F</i> (000)	1680	1936
Crystal size (mm)	0.2 × 0.2 × 0.1	0.6 × 0.4 × 0.08
θ Range (°)	2.78–23.32	1.92–27.00
Index ranges	–22 ≤ <i>h</i> ≤ 22, –29 ≤ <i>k</i> ≤ 29, –6 ≤ <i>l</i> ≤ 22	–11 ≤ <i>h</i> ≤ 11, –29 ≤ <i>k</i> ≤ 29, –32 ≤ <i>l</i> ≤ 32
Reflections collected	3941	64 656
Independent reflections	2045 (<i>R</i> _{int} = 0.0619)	11 555 (<i>R</i> _{int} = 0.0451)
Absorption correction	SADABS	SADABS
Data/restraints/parameters	2045/0/244	11 555/0/571
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0631, <i>wR</i> ₂ = 0.1108	<i>R</i> ₁ = 0.0317, <i>wR</i> ₂ = 0.0674
Goodness-of-fit on <i>F</i> ²	1.015	1.003
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1190, <i>wR</i> ₂ = 0.1272	<i>R</i> ₁ = 0.0399, <i>wR</i> ₂ = 0.0705
Largest difference peak and hole (e Å ⁻³)	0.56 and –0.409	0.32 and –0.15

One of the most salient features of this structure is the presence of short contacts between the metal center and the two of the hydrogen atoms of the *ortho* methyl groups that can be observed in both molecules. The vectors defined by each of these Ni···H interactions project themselves above and below the coordination plane, completing a distorted pseudo-octahedral coordination environment for the Ni atoms. The Ni···H distances are 2.529 (Ni1–H7b) and 2.513 Å (Ni1–H16b) in molecule **1**, somewhat shorter than in the more symmetric molecule **2**, where the Ni2–H35b and Ni2–H44b distances amount to 2.608 and 2.563 Å, respec-

tively. Similar interactions have been found in the nickel and palladium mesityl complexes M(Mes)₂(bipy) (M = Ni [19], Pd [20]) and [Li(THF)₄]⁺[NiMes₃][–] [21], but are absent in other palladium [22] and platinum [23] bis(mesityl) derivatives. The approach of the Ni and H atoms demands a noticeable distortion of the geometry of the metal bound *C*_{ipso} atoms that allows the aryl group to tilt towards the axial position. The Ni–*C*_{ipso}–*C*_{ortho} angles consistently display two different values in each mesityl ligand, ca. 116 and 127°. It is very likely that the Ni···H contacts represent true bonding ('remote agostic' [24]) interactions that compensate for the energetically unfavorable distortion of the Ni-mesityl linkage.

2.3. Formation of the metallacycle **4**

Although metallacyclic complexes can be regarded as a special class of dialkyl complexes, their higher stability [25] makes them especially attractive as starting materials. Thus, we have recently shown that the metallacycles PdCH₂CMe₂-*o*-C₆H₄(cod) and PdCH₂CMe₂-*o*-C₆H₄(Py)₂, (**4**), are readily available, air stable materials that undergo facile ligand exchange reactions [14]. The related nickelacycle NiCH₂CMe₂-*o*-C₆H₄(PMe₃)₂ [16] is also known to exchange PMe₃ by bipyridyl or phenantroline, but the phosphine ligands are partially displaced by α -diimines [26]. Thus, we set out to synthesize the complex **4**, the corresponding pyridine-containing complex.

Nickel [16,27] and platinum [28] bis(neophyl) complexes are known to experience a thermally induced intramolecular δ -H abstraction processes leading to the corresponding cyclometallated products with concomitant elimination of PhCMe₃. In the case of nickel, this reaction seems to be limited to phosphine-containing neophyl complexes, while the decomposition of the bipyridyl or other nitrogen-donor derivatives is more complex and does not allow the isolation of metallacyclic products [16,17].

Workup of the mother liquors from the crystallization of **1d** allows in some instances the isolation of small amounts (<10% yield) of an orange crystalline material, that has been identified as the metallacycle **4**. The metallation of the neophyl ligand is evidenced by the observation in the ¹³C{¹H}-NMR spectrum of this compound of two quaternary (161.5 and 170.5 ppm)

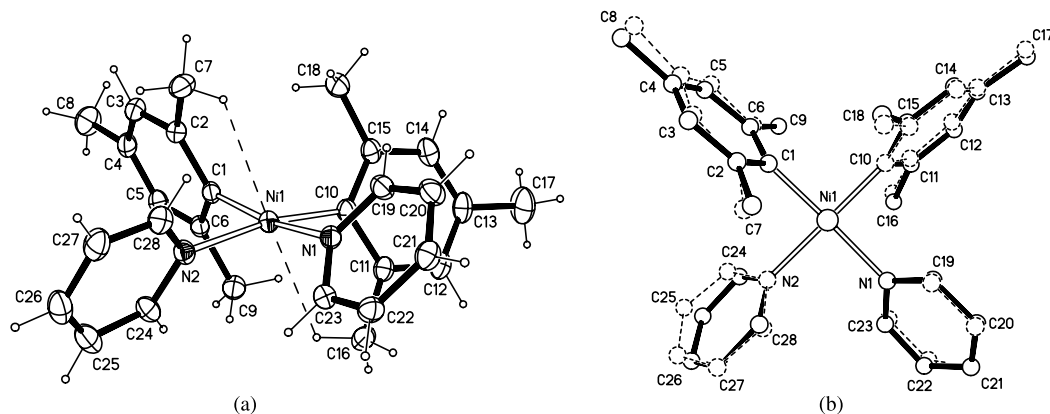


Fig. 2. Crystal structure of compound **1e**. (a) ORTEP view of molecule **1**. (b) Comparison of the two inequivalent molecules found in the solid state (molecule **1** full lines, molecule **2** broken lines).

Table 2
Selected bond lengths (Å) and angles (°) for compound **1c**

Bond lengths			
Ni(1)–C(1)	1.973(6)	Ni(1)–N(15)	1.978(5)
Ni(1)–C(8)	1.926(7)	C(1)–C(2)	1.478(11)
Ni(1)–N(21)	1.966(7)	C(8)–C(9)	1.472(10)
Bond angles			
C(1)–Ni(1)–C(8)	88.0(3)	C(1)–Ni(1)–N(15)	179.3(3)
C(8)–Ni(1)–N(15)	92.3(3)	C(8)–Ni(1)–N(21)	178.6(3)
N(15)–Ni(1)–N(21)	88.2(3)	Ni(1)–C(8)–C(9)	116.1(5)
N(21)–Ni(1)–C(1)	91.6(3)	Ni(1)–C(1)–C(2)	109.5(5)

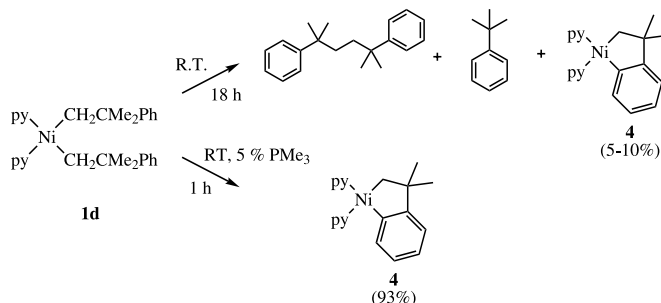
Table 3
Selected bond lengths (Å) and angles (°) for compound **1e** (as **1e·solv**)

	Molecule 1	Molecule 2
Bond lengths		
Ni(1)–C(1)	1.920(2)	1.928(2)
Ni(1)–C(10)	1.913(2)	1.921(2)
Ni(1)–N(1)	1.993(2)	1.993(2)
Ni(1)–N(2)	1.975(2)	1.995(2)
Ni(1)–H(7b)	2.529	2.608
Ni(1)–H(16b)	2.513	2.563
Bond angles		
C(1)–Ni(1)–C(10)	92.3(1)	90.7(1)
C(1)–Ni(1)–N(2)	89.6(1)	89.7(1)
C(10)–Ni(1)–N(1)	90.3(1)	89.5(1)
N(1)–Ni(1)–N(2)	89.5(1)	90.9(1)
C(1)–Ni(1)–N(1)	169.8(1)	171.9(1)
C(10)–Ni(1)–N(2)	169.9(1)	174.0(1)
Ni(1)–C(1)–C(2)	116.5(2)	116.1(2)
Ni(1)–C(1)–C(6)	126.8(2)	126.9(2)
Ni(1)–C(10)–C(11)	115.1(2)	116.7(2)
Ni(1)–C(10)–C(15)	127.6(2)	127.0(2)

and four methyne resonances (137.2, 123.2, 122.7 and 121.2 ppm), corresponding to the *o*-phenylene group. The low symmetry of the metallacyclic fragment causes the inequivalence of the two pyridine ligands, that

originate two independent sets of signals. These display normal line widths at room temperature, indicating that the intermolecular ligand exchange is slow in the NMR time scale. This behaviour contrasts with that of the Ni *cis*-dialkyls **1a–e**, and suggests that **4** does not undergo pyridine-releasing decomposition processes in solution, under ambient conditions.

Contrary to our expectations, the yield of compound **4** does not significantly improve when **1d** is allowed to stand at room temperature for prolonged periods of time. Monitoring the decomposition of the latter compound by ¹H-NMR in C₆D₆ at room temperature for 18 h revealed the formation of the coupling product, 2,5-dimethyl-2,5-diphenylhexane, together with *t*-butylbenzene and minor amounts of **4** (Scheme 3). Therefore, the decomposition of **1d** is dominated by reductive elimination, whereas cyclometallation represents a minor path. The addition of a catalytic amount (ca. 5 mol%) of PMe₃ to **1d** significantly alters this mechanistic scheme, leading to the quantitative formation of **4** in less than 1 h (Scheme 3). In the practice, the preparation of **4** does not require the isolation of pure samples of **1d**, since the addition of a small amount of PMe₃ to a crude extract of the latter in hexane affords the metallacycle as an orange microcrystalline precipitate (ca. 40% yield), that can be used for synthetic purposes without further purification steps. This compound is very stable and can



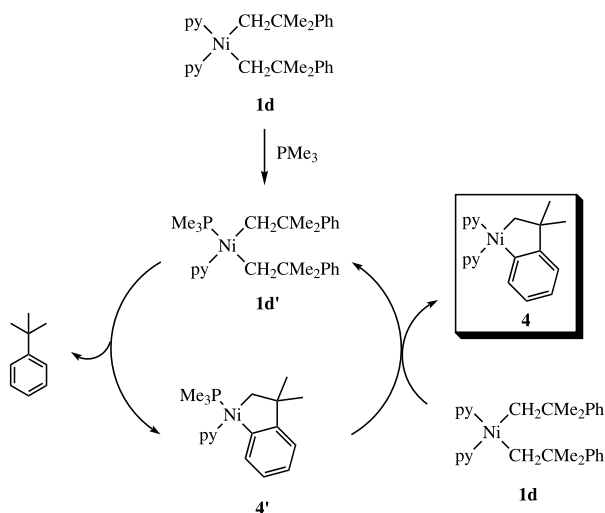
Scheme 3.

be stored for weeks as a solid at 0 °C without signs of decomposition.

The catalytic action of PMe_3 on complex **1d** can be explained on the basis of the known ability of phosphine ligands to promote the δ -H abstraction process in nickel bis-neophyl complexes [16]. As shown on Scheme 4, the displacement of a pyridine ligand of **1d** by PMe_3 leads to the unstable species **1d'**, that immediately decomposes to the known metallacycle **4'** [16]. Since Ni(II) complexes undergo very fast ligand exchange reactions, the phosphine can readily shift from **4'** to the remaining amount of the starting dialkyl **1d**, regenerating **1d'**.

2.4. Synthesis of dialkyl and metallacyclic complexes containing bidentate nitrogen ligands

Brookhart and co-workers [2] and Okuda and co-workers [9] have reported that the alkylation of nickel and palladium halocomplexes containing α -diimine ligands with organomagnesium reagents leads to the formation of the corresponding dialkyl derivatives. In this way, these authors have prepared the dimethyl and bis(trimethylsilylmethyl)nickel complexes (**7a–7d** and **8a–8d**, see Scheme 5), albeit in low yield. We have investigated the reaction of some of the nickel and palladium complexes **1** and **2** with the α -diimines **5a–5d** and the 2-imidoylpyridines **6a, b**. As shown in Scheme 5, the α -diimine ligands displace the pyridine from the nickel dimethyl complex **1a**, affording the blue products **7a–d** in greater than 90% isolated yield. Similarly, complex **1b** reacts cleanly with the α -diimine ligands affording the corresponding trimethylsilylmethyl derivatives **8a–c** as green crystalline solids in ca. 90% isolated yield. Therefore, this reaction provides an improved method for the synthesis of this type of nickel complexes. Full spectroscopic and analytical data have been collected for the seven derivatives.



Scheme 4.

The reaction of **1b** with the bulkiest of the α -diimines employed, **5d**, does not proceed to completion. The analysis of the reaction mixture by $^1\text{H-NMR}$ allowed the identification of the expected product, **8d**, but this could not be separated from the unreacted starting materials. It has to be noted, however, that this compound has been prepared in ca. 18% yield by reacting $\text{NiBr}_2 \cdot \mathbf{5d}$ with $\text{Me}_3\text{SiCH}_2\text{MgCl}$ [9]. Incomplete displacement of pyridine was also observed when the palladium methyl and trimethylsilyl complexes **2a** and **2b** were reacted with the α -diimine **5c**. The dimethyl palladium derivative **9a** could be isolated in analytically pure form in 65% yield, but in the case of the trimethylsilyl complex, incomplete conversion, and similar solubility properties of reagents and products prevented isolation of a pure sample of compound **9b**.

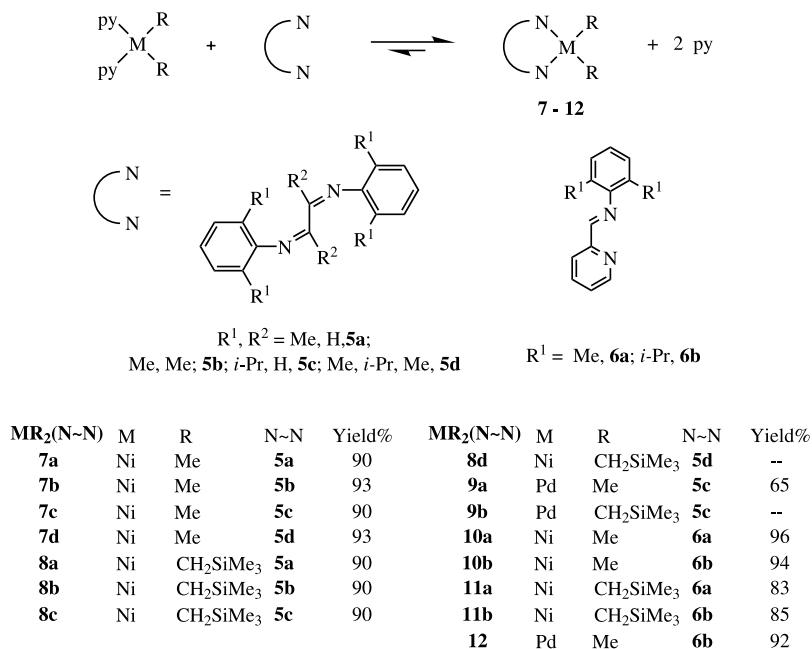
The behaviour of the nickel benzyl complex **1c** differs from that of **1a** and **1b**, since its reaction with the α -diimines **5c** or **5d** leads to dark red solutions from which no products could be isolated. Nevertheless, it provides the known compound **13** [29] when it is allowed to react with *N,N,N,N*-tetramethylethylenediamine (Scheme 6).

The reaction of the nickel metallacycle **4** with the α -diimines **5a** and **5c** affords the substitution products **15a** and **15b** in high yield (Scheme 7). The NMR spectra of **15b** display, in addition to the expected resonances, an additional group of signals that are identical to those of a pure sample of the ligand **5c**. The analytical data for this compound confirm the existence of half a molecule of the mentioned ligand. This crystalline adduct is obtained independently of the reagent ratio employed in its synthesis, and therefore an excess of **5c** must be used in order to complete the pyridine displacement reaction. When a stoichiometric (1:1) reagent ratio is used, the co-crystallization of **15b** and **5c** removes the latter from the equilibrium mixture, leading to decreased yields of the product.

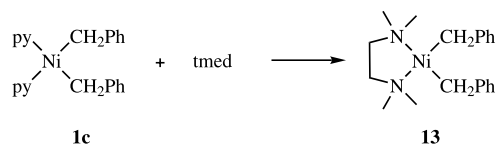
The palladium analogue of **4** has also been reported recently [14], but since it is prepared from the more reactive 1,5-dicyclooctadiene derivative, **14**, we chose to examine the ligand displacement reactions of the latter compound. As shown on Scheme 7, the cyclooctadiene ligand is readily replaced by the α -diimine ligand **5a–d**, affording the corresponding metallacycles in nearly quantitative yields as red or brown solids.

The Ni complexes of 2-imidoylpyridine have been recently shown to induce good levels of activity in the oligomerization of ethylene [30]. These ligands can be considered to occupy an intermediate position between the α -diimines and 2,2'-bipyridyl. Our results are in consonance with this trend, since **6a** and **6b** react with MR_2py_2 ($\text{M} = \text{Ni}$ or Pd), and with the metallacycles **4** and **14**, affording the corresponding organometallic derivatives in quantitative yields (Schemes 5 and 7).

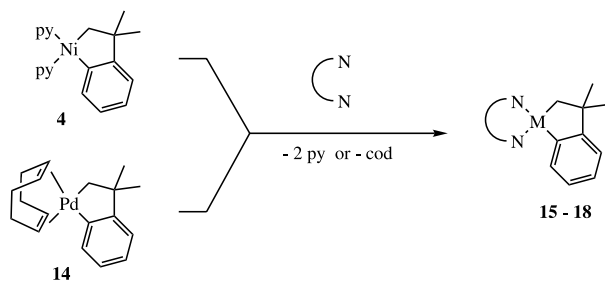
The properties of the dark green (Ni) or red (Pd) complexes of 2-imidoylpyridines are similar to those of



Scheme 5.



Scheme 6.



M(C-C)(N~N)	M	N~N	Yield%	M(C-C)(N~N)	M	N~N	Yield%
15a	Ni	5a	87	16c	Pd	5c	100
15b-0.5 5c	Ni	5c	90	16d	Pd	5d	100
16a	Pd	5a	100	17	Ni	6b	68
16b	Pd	5b	100	18a	Pd	6a	83
				18b	Pd	6b	93

Scheme 7.

their α -diimine counterparts, displaying comparable sensitivity toward atmospheric agents and similar solubility in hydrocarbon or ethereal solvents, from which they can be crystallized. The NMR spectra of the dialkyl derivatives of ligands **6a** and **6b** show many analogies with those of α -diimine complexes. For instance, in spite of their relatively lower steric encumbrance, the aryl

substituents of the imino nitrogen atom can not rotate freely, as deduced from the diastereotopic character of the isopropyl methyl groups of the complexes that contain the ligand **6b**. However, the lower symmetry of the 2-imidoylpyridine ligands causes the inequivalence of the two alkyl ligands. The complexes that contain the unsymmetrical metallacyclic unit exist in solution as a mixture of isomers. As the isomer ratio is found to be approximately constant from one sample to another, these isomers exist in solution as equilibrium mixtures, their mutual interconversion process being slow in the NMR timescale. A combined study of their 2D-NOESY and COSY spectra, as well as bidimensional H-C heterocorrelations has allowed full assignment of the ¹H- and ¹³C{¹H}-NMR signals of each isomer. The relative disposition of the ligands has been determined on the basis of the NOE relationships found in the NOESY spectra, as sketched on Fig. 3.

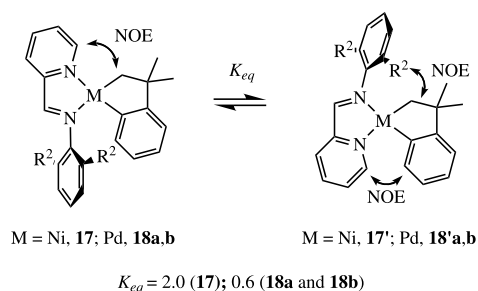


Fig. 3.

3. Conclusions

The reactions of NiCl₂py₄ or PdCl₂py₂ with organomagnesium or organolithium reagents allow the synthesis of dialkyl complexes of composition *cis*-MR₂py₂ (M = Ni, **1**; Pd, **2**). In general, these compounds are very sensitive to oxygen and display limited thermal stability, but can be handled at room temperature for limited periods of time. The nickel neophyl derivative **1d** can be readily converted into the metallacyclic species **4** by the action of catalytic amounts of PMe₃. Complex **4** is considerably more stable than the open-chain dialkyl compounds, and can be stored for longer periods of time.

Chelating nitrogen ligands can displace the pyridine ligands of the Ni complexes, allowing the direct, high yield preparation of dialkyl and metallacyclic derivatives stabilized by relatively poor donors such as the α -diimines. However, this methodology finds some limitations, as a combination of bulky alkyl and α -diimine ligands can lead to incomplete reactions. The displacement of the pyridine ligands by α -diimines is less favoured in the case of the Pd derivatives, where it generally leads to equilibrium mixtures. However, both types of MR₂py₂ compounds (M = Ni or Pd) find application for the preparation of derivatives of stronger ligands, such as the 2-imidoylpyridines. The cycloocta-

diene ligand of the metallacycle **4** is readily displaced by α -diimines and 2-imidoyl pyridines, providing a facile method for the preparation of many organometallic complexes of palladium containing these ligands.

4. Experimental

Microanalyses were performed by the Analytical Service of the Instituto de Investigaciones Químicas. The spectroscopic instruments used were Bruker Model Vector 22 for IR spectra, and Bruker DPX-300, DRX-400 and DRX-500 for NMR spectroscopy. The ¹³C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to SiMe₄. The ¹³C{¹H}-NMR assignments were helped in most cases with the use of gated decoupling and two dimensional techniques. ³¹P{¹H}-NMR shifts are referenced to external 85% H₃PO₄. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60 °C. The compounds NiCl₂py₄ [**31a**], PdCl₂py₂ [**31b**] and Pd(CH₂CMe₂-*o*-C₆H₄) (cod) [**3**] were prepared according to literature methods.

Table 4
¹H-NMR data for complexes **1a–d**, **3** and **4**^a

	R			CH _{ar} (py)
	CH ₂	Me	CH _{ar}	
Ni(Me) ₂ py ₂ (1a)		0.20 (bs, 6H)		6.28 (bs, 4H, CH(3)) 6.64 (bs, 2H, CH(4)) 8.56 (bs, 4H, CH(2))
Ni(CH ₂ Ph) ₂ py ₂ (1c)	2.25 (s, 4H)		6.87 (d, 4H, 7.0, <i>o</i> -CH) 6.93 (t, 2H, 7.0, <i>p</i> -CH) 6.99 (t, 4H, 7.0, <i>m</i> -CH)	6.28 (tm, 4H, 6.3, CH(3)) 6.64 (tm, 2H, 7.6, CH(4)) 8.13 (bs, 4H, CH(2))
Ni(CH ₂ CMe ₂ Ph) ₂ py ₂ (1d)	1.17 (bs, 4H)	1.85 (bs, 12H)	6.82 (bs, 4H, <i>m</i> -CH) 6.98 (bs, 2H, <i>p</i> -CH) 7.62 (bs, 4H, <i>o</i> -CH)	6.26 (bs, 4H, CH(3)) 6.69 (bs, 2H, CH(4)) 8.00 (bs, 4H, CH(2))
<i>cis</i> -Ni(2,4,6-C ₆ H ₂ Me ₃) ₂ py ₂ (1e)		2.27 (s, 6H, <i>p</i> -Me) 3.29 (s, 12H, <i>o</i> -Me)	6.73 (s, 4H, <i>m</i> -CH)	6.16 (bs, 4H, CH(3)) 6.63 (bs, 2H, CH(4)) 8.10 (bs, 4H, CH(2))
<i>trans</i> -Ni(2,4,6-C ₆ H ₂ Me ₃) ₂ py ₂ (1e')		2.28 (s, 6H, <i>p</i> -Me) 3.34 (s, 12H, <i>o</i> -Me)	6.82 (s, 4H, <i>m</i> -CH)	6.35 (tm, 2H, CH(4)) 5.89 (tm, 4H, CH(3)) 8.45 (dm, 4H, CH(2))
Ni(2,4,6-C ₆ H ₂ Me ₃)Brpy ₂ (3) ^b		1.99 (s, 3H, <i>p</i> -Me) 3.37 (s, 6H, <i>o</i> -Me)	6.32 (s, 2H, <i>m</i> -CH)	7.00 (t, 4H, 6.8, CH(3)) 7.47 (t, 2H, 7.5, CH(4)) 8.84 (bd, 4H, CH(2))
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)py ₂ (4)	1.76 (s, 2H)	1.91 (s, 6H)	6.42 (d, 1H, 7.2, <i>o</i> -CH) 6.99 (t, 1H, 7.1, <i>m</i> -CH) 7.17–7.27 (m, 2H, <i>o</i> -, <i>m</i> -CH)	6.24 (tm, 2H, 6.4, CH(3)) 6.33 (tm, 2H, 6.3, CH(3)) 6.63 (tm, 1H, 7.6, CH(4)) 6.70 (tm, 1H, 7.6, CH(4)) 8.43 (dm, 2H, 4.8, CH(2)) 8.67 (dm, 2H, 4.7, CH(2))

^a C₆D₆, δ (J, Hz).

^b CD₂Cl₂.

Table 5

 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for complexes **1a–d**, **3** and **4**^{a,b}

	R			C _{ar} H(py)	
	CH ₂	C–Me	C _{ar} H	C _{ar}	
Ni(Me) ₂ py ₂ (1a)		–5.1			123.4 (C _{ar} H(3)) 134.3 (C _{ar} H(4)) 150.1 (C _{ar} H(2))
Ni(CH ₂ Ph) ₂ py ₂ (1c)	23.2		120.6 122.1 128.7	144.0	123.2 (C _{ar} H(3)) 134.4 (C _{ar} H(4)) 149.8 (C _{ar} H(2))
Ni(CH ₂ CMe ₂ Ph)py ₂ (1d)	28.9	34.0 (C–Me) 41.7 (C–Me)	125.4 125.9 127.4		123.8 (C _{ar} H(3)) 133.6 (bs, C _{ar} H(4)) 149.5 (bs, C _{ar} H(2))
<i>cis</i> -Ni(2,4,6-C ₆ H ₂ Me ₃) ₂ py ₂ (1e)		20.6 (<i>p</i> -Me) 27.9 (<i>o</i> -Me)	125.7	130.1 143.4 154.2	123.1 (C _{ar} H(3)) 134.9 (C _{ar} H(4)) 151.2 (C _{ar} H(2))
<i>trans</i> -Ni(2,4,6-C ₆ H ₂ Me ₃) ₂ py ₂ (1e')		20.8 (<i>p</i> -Me) 24.9 (<i>o</i> -Me)	136.3	131.5 142.0 174.6	122.2 (C _{ar} H(3)) 134.0 (C _{ar} H(4)) 154.0 (C _{ar} H(2))
Ni(2,4,6-C ₆ H ₂ Me ₃)Brpy ₂ (3)		20.3 (<i>p</i> -Me) 23.9 (<i>o</i> -Me)	126.6	133.0 140.9 148.0	123.8 (C _{ar} H(3)) 137.0 (C _{ar} H(4)) 153.4 (C _{ar} H(2))
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)py ₂ (4)	44.2	34.7 (C–Me) 48.2 (C–Me)	121.2 (<i>o</i> -C _{ar} H) 122.7 (<i>m</i> -C _{ar} H) 123.2 (<i>m</i> -C _{ar} H) 137.2 (<i>o</i> -C _{ar} H)	161.8 170.5	123.5 (C _{ar} H(3)) 123.6 (C _{ar} H(3)) 134.6 (C _{ar} H(4)) 135.0 (C _{ar} H(4)) 149.9 (C _{ar} H(2)) 150.8 (C _{ar} H(2))

^a C₆D₆, δ (J, Hz).^b Singlets, unless otherwise indicated.

4.1. Synthesis of Ni(Me)₂py₂ (**1a**)

To a cooled (–60 °C) suspension of Ni₂Cl₂py₄ (1.60 g, 3.6 mmol) in 40 ml of Et₂O were added 1 ml of py and 4.5 ml (7.2 mmol) of a 1.60 M solution of MeLi in Et₂O. The mixture was stirred 20 min at this temperature and 10 min at room temperature (r.t.), during which time the colour of the suspension turned dark green. The reaction mixture was taken to dryness and the residue

extracted with 40 ml of toluene and filtered. After addition of 0.5 ml of py, the solvent was partially evaporated and some petroleum ether added. Cooling to –30 °C, provided red crystals of complex **1a** in 50–55% yield.

The compound Pd(Me)₂py₂ (**2a**) was similarly prepared, from PdCl₂py₂ as starting material, and isolated as white crystals in 45–50% yield.

Table 6

 ^1H -NMR data for complexes **2a–c**^a

	R			CH _{ar} (py)
	CH ₂	Me	CH _{ar}	
Pd(Me) ₂ py ₂ (2a)		0.20 (bs, 6H)		6.28 (bs, 4H, CH(3)) 6.64 (bs, 2H, CH(4)) 8.56 (bs, 4H, CH(2))
Pd(CH ₂ SiMe ₃) ₂ py ₂ (2b)	–0.20 (s, 4H)	0.06 (s, 18H)		6.34 (tm, 4H, 7.0, CH(3)) 6.62 (tm, 2H, 7.0, CH(4)) 8.81 (dm, 4H, 6.5, CH(2))
Pd(CH ₂ Ph) ₂ py ₂ (2c)	3.12 (s, 4H)		6.90 (t, 4H, 6.7, <i>m</i> -CH) 7.04 (t, 2H, 6.7, <i>p</i> -CH) 7.16 (d, 4H, 6.5, <i>o</i> -CH)	6.32 (bs, 4H, CH(3)) 6.67 (bs, 2H, CH(4)) 8.06 (dm, 4H, 6.5, CH(2))

^a C₆D₆, δ (J, Hz).

Table 7
 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for complexes **2a–c**^{a,b}

	R			C _{ar} H(py)
	CH ₂	Me	C _{ar} H	
Pd(Me) ₂ py ₂ (2a)		−5.1		123.4 (C _{ar} H(3)) 134.3 (C _{ar} H(4)) 150.1 (C _{ar} H(2))
Ni(CH ₂ SiMe ₃) ₂ py ₂ (2b)	18.6	3.0		123.7 (C _{ar} H(3)) 134.8 (C _{ar} H(4)) 153.5 (C _{ar} H(2))
Ni(CH ₂ Ph) ₂ py ₂ (2c)	23.6		120.5 (C _{ar} H) 127.2 (C _{ar} H) 127.7 (C _{ar} H)	153.5 123.6 (C _{ar} H(3)) 135.4 (C _{ar} H(4)) 150.3 (C _{ar} H(2))

^a C₆D₆, δ (J, Hz).^b Singlets, unless otherwise indicated.Table 8
 ^1H -NMR data for complexes **7a–d**, **8a–c** and **15a**, **b**^a

	R			L		
	CH ₂	Me	CH _{ar}	R ¹	R ²	CH _{ar} (L)
Ni(Me) ₂ L (7a)		1.92 (s, 6H)		2.15 (s, 12H, Me)	8.66 (s, 2H)	7.16 (m, 4H, <i>m</i> -CH) 7.23 (t, 2H, 7.4, <i>p</i> -CH)
Ni(Me) ₂ L (7b)		1.20 (s, 6H)		2.15 (s, 12H, Me)	−0.28 (s, 6H, Me)	7.16 (s, 6H, <i>m,p</i> -CH)
Ni(Me) ₂ L (7c)		1.96 (s, 6H)		0.96 (d, 12H, 6.9, Me) 1.37 (d, 12H, 6.9, Me) 3.28 (h, 4H, 6.8, CH)	9.03 (s, 2H)	7.31 (d, 4H, 7.1, <i>m</i> -CH) 7.40 (t, 2H, 6.1, <i>p</i> -CH)
Ni(Me) ₂ L (7d)		1.09 (s, 6H)		0.99 (d, 12H, 6.9, Me) 1.42 (d, 12H, 6.7, Me) 3.14 (h, 4H, 6.8, CH)	−0.11 (s, 6H, Me)	7.30 (m, 6H, <i>m,p</i> -CH)
Ni(CH ₂ SiMe ₃) ₂ L (8a)	2.06 (bs, 4H)	0.02 (bs, 18H)		2.18 (bs, 12H)	8.56 (bs, 2H)	7.12 (d, 4H, 6.6, <i>m</i> -CH) 7.22 (t, 2H, 6.7, <i>p</i> -CH) 7.13 (bm, 6H, <i>m,p</i> -CH)
Ni(CH ₂ SiMe ₃) ₂ L (8b)	0.95 (bs, 4H)	0.12 (bs, 18H)		2.16 (bs, 12H)	−0.25 (bs, 6H, Me)	7.13 (bm, 6H, <i>m,p</i> -CH)
Ni(CH ₂ SiMe ₃) ₂ L (8c)	2.26 (bs, 4H)	0.03 (bs, 18H)		0.83 (d, 12H, 6.6, Me) 1.47 (d, 12H, 6.5, Me) 3.53 (h, 4H, 5.7, CH)	9.03 (s, 2H)	7.31 (d, 4H, 7.5, <i>m</i> -CH) 7.39 (t, 2H, 7.5, <i>p</i> -CH)
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (15a)	4.29 (s, 2H)	1.18 (s, 6H)	6.63 (dm, 1H, 7.4) 6.84 (tm, 1H, 7.4) 7.01 (tm, 1H, 7.4) 8.15 (dm, 1H, 7.3)	2.14 (s, 6H, Me) 2.15 (s, 6H, Me)	8.19 (s, 1H) 8.30 (s, 1H)	7.05 (d, 2H, 7.5, <i>m</i> -CH) 7.07 (d, 2H, 6.8, <i>m</i> -CH) 7.14 (m, 1H, <i>p</i> -CH) 7.19 (t, 1H, 7.5, <i>p</i> -CH)
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (15b)	4.32 (s, 2H)	1.16 (s, 6H)	6.61 (dm, 1H, 7.1) 6.80 (tm, 1H, 6.9) 6.89 (tm, 1H, 7.1) 8.12 (dm, 1H, 7.7)	0.94 (d, 6H, 6.8, Me) 0.99 (d, 6H, 6.8, Me) 1.14 (d, 6H, 6.8, Me) 1.35 (d, 6H, 6.8, Me) 3.39 (h, 2H, 6.8, CH) 3.49 (h, 2H, 6.8, CH)	8.44 (s, 1H) 8.58 (s, 1H)	7.24 (d, 4H, 7.8, <i>m</i> -CH) 7.30 (t, 1H, 7.6, <i>p</i> -CH) 7.36 (t, 1H, 7.7, <i>p</i> -CH)

^a C₆D₆, δ (J, Hz)

Table 9
 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for complexes **7a–d**, **8a–c** and **15a, b**^{a,b}

	R			L			
	CH ₂	C–Me	C _{ar} H, C _{ar}	R ¹	R ² –C=N	C _{ar} H (L)	C _{ar} (L)
Ni(Me) ₂ L (7a)		–6.9		18.4 (Me)	154.6 (H–C=N)	125.9 (<i>p</i> -C _{ar} H) 127.9 (<i>m</i> -C _{ar} H)	128.2 (<i>o</i> -C _{ar}) 153.6 (C _{ar})
Ni(Me) ₂ L (7b)		–5.3		18.3 (Me)	19.9 (<i>Me</i> –C=N) 164.1 (<i>Me</i> –C=N)	125.6 (<i>p</i> -C _{ar} H) 128.2 (<i>m</i> -C _{ar} H)	129.2 (<i>o</i> -C _{ar}) 149.2 (C _{ar})
Ni(Me) ₂ L (7c)		–6.7		23.1 (Me) 24.1 (Me) 28.5 (CH)	154.3 (H–C=N)	123.3 (<i>m</i> -C _{ar} H) 126.8 (<i>p</i> -C _{ar} H)	139.1 (<i>o</i> -C _{ar}) 150.9 (C _{ar})
Ni(Me) ₂ L (7d)		–4.0		23.1 (Me) 23.4 (Me) 28.5 (CH)	20.9 (<i>Me</i> –C=N) 162.6 (<i>Me</i> –C=N)	123.4 (<i>m</i> -C _{ar} H) 126.4 (<i>p</i> -C _{ar} H)	139.1 (<i>o</i> -C _{ar}) 147.0 (C _{ar})
Ni(CH ₂ SiMe ₃) ₂ L (8a)	–2.0	3.2		19.1 (Me)	154.0 (H–C=N)	126.1 (<i>p</i> -C _{ar} H) 128.2 (<i>m</i> -C _{ar} H)	128.4 (<i>o</i> -C _{ar}) 153.6 (C _{ar})
Ni(CH ₂ SiMe ₃) ₂ L (8b)	–3.2	3.9		19.8 (Me)	18.7 (<i>Me</i> –C=N) 161.8 (<i>Me</i> –C=N)	125.6 (<i>m</i> -C _{ar} H) 128.3 (<i>p</i> -C _{ar} H)	128.7 (<i>o</i> -C _{ar}) 149.7 (C _{ar})
Ni(CH ₂ SiMe ₃) ₂ L (8c)	–3.4	3.1		22.7 (Me) 25.0 (Me) 28.3 (CH)	154.3 (H–C=N)	123.5 (<i>m</i> -C _{ar} H) 126.9 (<i>p</i> -C _{ar} H)	139.5 (<i>o</i> -C _{ar}) 151.0 (C _{ar})
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (15a)	49.4	33.4 (CMe ₂) 47.5 (CMe ₂)	120.8, 122.7, 125.8, 136.6 (C _{ar} H) 150.1, 171.5 (C _{ar})	18.2 (Me) 18.9 (Me)	155.3 (H–C=N) 157.1 (H–C=N)	126.0, 126.1 (<i>p</i> -C _{ar} H) 127.9, 128.3 (<i>m</i> -C _{ar} H)	128.4, 128.8 (<i>o</i> -C _{ar}) 152.9, 153.6 (C _{ar})
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (15b)	49.4	33.2 (CMe ₂) 47.6 (CMe ₂)	120.5, 122.5, 125.4, 137.5 (C _{ar} H) 150.0, 171.3 (C _{ar})	22.2, 22.7, 24.1, 24.6 (Me) 28.4, 28.8 (CH)	156.1 (H–C=N) 156.6 (H–C=N)	123.3, 123.5 (<i>m</i> -C _{ar} H) 127.0, 127.1 (<i>m</i> -C _{ar} H)	139.3, 139.4 (<i>o</i> -C _{ar}) 149.8, 151.1 (C _{ar})

^a C₆D₆, δ (J, Hz).

^b Singlets, unless otherwise indicated.

Table 10
¹H-NMR data for complexes **9a** and **16a–d**^a

	R			L		
	CH ₂	Me	CH _{ar}	R ¹	R ²	CH _{ar} (L)
Pd(Me) ₂ L (9a)		0.76 (s, 6H)		1.07 (d, 12H, 6.9, Me) 1.30 (d, 12H, 6.8, Me) 3.38 (h, 4H, 6.9, CH)	7.40 (s, 2H)	7.12 (m, 6H, <i>p,m</i> -CH)
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16a)	2.44 (s, 2H)	1.48 (s, 6H)	6.55 (dm, 1H, 7.3) 6.87 (tm, 1H, 7.1) 7.00 (m, 2H)	2.09 (s, 6H, Me) 2.15 (s, 6H, Me)	6.96 (s, 2H)	6.94 (m, 6H, <i>p,m</i> -CH)
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16b)	2.17 (s, 2H)	1.52 (s, 6H)	6.24 (dm, 1H, 7.4) 6.87 (tm, 1H, 7.3) 7.03 (m, 2H)	2.08 (s, 6H, Me) 2.14 (s, 6H, Me)	1.08 (s, 3H, Me) 1.13 (s, 3H, Me)	6.90–7.07 (m, 6H, <i>p,m</i> -CH)
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16c)	2.54 (s, 2H)	1.46 (s, 6H)	6.58 (dm, 1H, 7.6) 6.82 (tm, 1H, 7.4) 6.94 (dm, 1H, 7.5) 7.02 (tm, 1H, 7.3)	1.06 (d, 6H, 7.6, Me) 1.08 (d, 6H, 7.1, Me) 1.16 (d, 6H, 6.8, Me) 1.36 (d, 6H, 6.8, Me) 3.43 (h, 2H, 7.1, CH) 3.48 (h, 2H, 6.8, CH)	7.33 (s, 1H) 7.36 (s, 1H)	7.18 (m, 6H, <i>p,m</i> -CH)
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16d)	2.24 (s, 2H)	1.49 (s, 6H)	6.16 (dm, 1H, 7.5) 6.80 (tm, 1H, 7.4) 6.93 (dm, 1H, 7.3) 7.02 (tm, 1H, 7.2)	0.99 (d, 6H, 6.9, Me) 1.05 (d, 6H, 7.0, Me) 1.24 (d, 6H, 6.8, Me) 1.43 (d, 6H, 6.8, Me) 3.21 (h, 2H, 7.3, CH) 3.26 (h, 2H, 6.9, CH)	1.23 (s, 3H, Me) 1.28 (s, 3H, Me)	7.09–7.24 (m, 6H, <i>p,m</i> -CH)

^a C₆D₆, δ (J, Hz).

4.2. Synthesis of Ni(CH₂Ph)₂py₂ (**1c**)

One milliliter of py and 6 ml (4.02 mmol) of a 0.67 M solution of Mg(CH₂Ph)Cl in Et₂O were added to a suspension of NiCl₂py₄ (0.90 g, 2.01 mmol) in 40 ml of Et₂O cooled at –60 °C. The mixture was stirred 10 min at this temperature and 30 min at r.t. The solvent was evaporated under reduced pressure and the residue extracted with a mixture Et₂O–petroleum ether 1:1, to which 0.5 ml of py had been previously added. After filtration, concentration of the solution and cooling to –30 °C, compound **1c** was isolated as red crystals in 55–65% yield.

The complex Pd(CH₂Ph)₂py₂ (**2c**) was identically prepared, from PdCl₂py₂, and obtained as yellow crystals in 50–55% yield.

4.3. Synthesis of Ni(CH₂CMe₂Ph)₂py₂ (**1d**)

A suspension of NiCl₂py₄ (1.34 g, 3.01 mmol) in 40 ml of Et₂O was cooled at –60 °C and treated with 1 ml of py and 7 ml (6.02 mmol) of a 0.86 M solution of Mg(CH₂CMe₂Ph)Cl in Et₂O containing small amounts of iodide. The mixture was stirred 10 min at this temperature and 2 h at r.t. The solvent was evaporated under vacuum and the residue extracted with petroleum

ether (2 × 45 ml). Filtration, partial evaporation of the solvent and cooling to –30 °C furnished dark red crystals of complex **1d** in 30–35% yield.

Mother liquors provided compound **4** in 10–15% yield.

4.4. Reaction of complex **1d** with bipy

A mixture of 0.45 g (0.94 mmol) of **1d** and 0.15 g (0.94 mmol) of bipy was dissolved in 30 ml of Et₂O and cooled at –20 °C and stirred at this temperature for 30 min, then the cold bath was removed and the mixture was stirred at r.t. for 30 min. The solution was filtered and concentrated, upon cooling to –30 °C compound Ni(CH₂CMe₂Ph)bipy [13] was obtained as green crystals in 82% yield. ¹H-NMR (C₆D₆, 20 °C): δ 1.74 (s, 4H, CH₂); 1.88 (s, 12H, CMe₂); 6.51 (t, 2H, *J* = 6.0 Hz, CH(4 or 5) bipy); 6.65 (d, 2H, *J* = 7.0 Hz, CH(3) bipy); 6.80 (t, 2H, *J* = 6.8 Hz, CH(4–5) bipy); 6.93 (t, 4H, *J* = 7.2, *m*-CH_{ar}); 6.97 (t, 2H, *J* = 7.1, *p*-CH_{ar}); 7.71 (d, 4H, *J* = 4H, *o*-CH_{ar}); 8.86 (d, 2H, *J* = 4.9 Hz, CH(6) bipy). ¹³C{¹H} (C₆D₆, 20 °C): δ 33.0 (CMe₂); 34.0 (CH₂); 42.3 (CMe₂); 119.8 (C_{ar}H); 123.7 (C_{ar}H); 125.0 (C_{ar}H); 125.8 (double intensity, C_{ar}H); 126.8 (double intensity, C_{ar}H); 132.2 (C_{ar}H); 147.0 (C_{ar}H); 152.5 (C_{ar}); 154.6 (C_{ar}).

4.5. Reaction of NiCl₂py₄ with Mg(2,4,6-C₆H₂Me₃)Br in the presence of added pyridine

To a suspension of NiCl₂py₄ (0.89 g, 2.04 mmol) in 30 ml of THF cooled at –60 °C, 1 ml of py and 6 ml (4.08 mmol) of a 0.68 M solution of Mg(2,4,6-C₆H₂Me₃)Br in Et₂O were added. The mixture was stirred 10 min at this temperature and 50 min at r.t. and then taken to dryness. The residue was extracted with a mixture Et₂O–petroleum ether 4:1. After filtration, concentration and cooling to –30 °C, compound **1e** was isolated as red crystals in 15–20% yield.

Partial evaporation and cooling to –30 °C of mother liquors provided complex **3** as orange crystals in 8–10% yield.

Subsequent crops were identified as mixtures of compounds **1e'** and **1e**.

4.6. Improved procedure for the synthesis of cis-Ni(2,4,6-C₆H₂Me₃)py₂ (**1e**)

4.65 ml (4 mmol) of a 0.86 M solution of Mg(2,4,6-C₆H₂Me₃)Br in Et₂O were added to a cooled (–60 °C) suspension of NiCl₂py₄ (0.89 g, 2.04 mmol) in 30 ml of THF. The mixture was stirred 10 min at this temperature and 1 h at r.t. The solvent was removed under vacuum and the solid residue extracted with toluene (3 × 50 ml). The brown solution was filtered, and the solvent evaporated. The crude product was recrystallized from a mixture toluene:Et₂O 1:1. Concentration of the deep-orange solution and cooling to –30 °C overnight, furnished orange-brown crystals of complex **1e** in 53% yield. Anal. Calc. for C₂₈H₃₂N₂Ni: C, 73.87; H, 7.08; N, 6.15. Found: C, 73.95; H, 7.16; N, 5.99%.

Table 11
¹³C{¹H}-NMR data for complexes **9a** and **16a–d**^{a,b}

	R			L		
	CH ₂	C–Me	C _{ar} H, C _{ar}	R ¹	R ² –C=	C _{ar} H, C _{ar} (L)
Pd(Me) ₂ L (9a)		–5.4		22.5 (Me) 24.1 (Me) 28.2 (CH)	159.7 (H–C=N)	123.1 (<i>m</i> -C _{ar} H) 126.9 (<i>p</i> -C _{ar} H) 138.6 (<i>o</i> -C _{ar}) 145.4 (C _{ar})
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16a)	46.9	33.9 (CMe ₂) 47.2 (CMe ₂)	121.9, 123.7, 124.1, 134.0 (C _{ar} H) 157.6, 169.4 (C _{ar})	17.7 (Me) 18.1 (Me)	160.5 (H–C=N) 160.6 (H–C=N)	126.2, 126.3 (<i>p</i> -C _{ar} H) 127.5, 128.2 (<i>m</i> -C _{ar} H) 127.6, 128.3 (<i>o</i> -C _{ar}) 148.1, 148.9 (C _{ar})
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16b) ^c	46.4	34.0 (CMe ₂) 47.0 (CMe ₂)	121.6, 123.3, 123.6, 134.0 (C _{ar} H) 158.4, 169.0 (C _{ar})	17.6 (Me) 17.9 (Me)	17.5 (Me–C=N) 168.4 (Me–C=N) 168.8 (Me–C=N)	125.6, 125.7 (<i>p</i> -C _{ar} H) 128.2, 128.4 (<i>m</i> -C _{ar} H) 126.9, 138.8 (<i>o</i> -C _{ar}) 145.9, 146.7 (C _{ar})
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16c)	46.9	33.7 (CMe ₂) 47.5 (CMe ₂)	121.8, 123.5, 124.0, 134.8 (C _{ar} H) 156.8, 169.3 (C _{ar})	22.2, 22.6, 23.8, 24.3 (Me) 28.1, 28.5 (CH)	160.2 (H–C=N) 160.5 (H–C=N)	123.2, 123.4 (<i>p</i> -C _{ar} H) 127.2, 128.0 (<i>m</i> -C _{ar} H) 138.5, 138.8 (<i>o</i> -C _{ar}) 145.9, 146.9 (C _{ar})
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (16d)	46.3	33.8 (CMe ₂) 47.3 (CMe ₂)	121.4, 123.0, 123.4, 134.9 (C _{ar} H) 157.5, 169.4 (C _{ar})	22.8, 23.1, 23.3, 23.4 (Me) 28.4, 28.8 (CH)	19.0 (Me–C=N) 19.5 (Me–C=N) 168.5 (Me–C=N) 169.0 (Me–C=N)	123.4, 123.7 (<i>p</i> -C _{ar} H) 127.0, 128.1 (<i>m</i> -C _{ar} H) 137.7, 137.8 (<i>o</i> -C _{ar}) 143.6, 144.5 (C _{ar})

^a C₆D₆, δ (J, Hz).

^b Singlets unless otherwise indicated.

^c CD₂Cl₂.

Table 12
¹H-NMR data for complexes **10a**, **b**, **11a**, **b** and **12**^a

	R		L	
	CH ₂	Me	R ¹ , H–C=N	CH _{ar} (L)
Ni(Me) ₂ L (10a)		1.08 (s, 3H) 1.23 (s, 3H)	2.13 (s, 6H, Me) 7.99 (s, 1H, H–C=N)	6.58 (d, 1H, 6.8, CH(3)) 6.88 (m, 1H, CH(4 or 5)) 7.05 (m, 3H, <i>m-y p</i> -CH) 7.10 (t, 1H, 7.4, CH(4 or 5)) 9.63 (sa, 1H, CH(6))
Ni(Me) ₂ L (10b)		1.08 (s, 3H) 1.22 (s, 3H)	0.94 (d, 6H, 6.9, Me) 1.32 (d, 6H, 6.8, Me) 3.28 (h, 2H, 6.8, CH) 8.47 (s, 1H, H–C=N)	6.58 (d, 1H, 7.6, CH(3)) 6.88 (t, 1H, 6.0, CH(4 or 5)) 7.12 (t, 1H, 7.9, CH(4 or 5)) 7.23 (m, 3H, <i>m-y p</i> -CH) 9.63 (d, 1H, 5.3, CH(6))
Ni(CH ₂ SiMe ₃) ₂ L (11a)	0.70 (bs, 4H)	0.29 (bs, 18H)	2.20 (s, 6H, Me) 7.86 (s, 1H, H–C=N)	6.50 (d, 1H, 7.6, CH(3)) 6.86 (t, 1H, 6.0, CH(5)) 7.04 (m, 3H, <i>m-y p</i> -CH) 7.07 (t, 1H, 7.9, CH(4)) 9.51 (d, 1H, 5.5, CH(6))
Ni(CH ₂ SiMe ₃) ₂ L (11b)	0.71 (s, 2H) 0.75 (s, 2H)	0.23 (s, 9H) 0.29 (s, 9H)	0.91 (d, 6H, 6.8, Me) 1.40 (d, 6H, 6.8, Me) 3.57 (h, 2H, 6.5, CH) 8.45 (s, 1H, H–C=N)	6.49 (d, 1H, 7.6, CH(3)) 6.87 (t, 1H, 6.6, CH(5)) 7.15 (t, 1H, 8.0, CH(4)) 7.21 (m, 3H, <i>m-y p</i> -CH) 9.46 (d, 1H, 5.5, CH(6))
Pd(Me) ₂ L (12)		0.78 (s, 3H) 1.20 (s, 3H)	1.01 (d, 6H, 6.9, Me) 1.32 (d, 6H, 6.8, Me) 3.44 (h, 2H, 6.8, CH) 7.70 (s, 1H, H–C=N)	6.42 (m, 1H, CH(4 or 5)) 6.46 (d, 1H, 7.6, CH(3)) 6.75 (t, 1H, 7.9, CH(4 or 5)) 7.16 (m, 3H, <i>m-y p</i> -CH) 8.56 (d, 1H, 5.0, CH(6))

^a C₆D₆, δ (J, Hz).

4.7. Synthesis of *trans*-Ni(2,4,6-C₆H₂Me₃)Br(py)₂ (**3**)

A mixture of *cis*-Ni(2,4,6-C₆H₂Me₃)₂(py)₂, **1e**, (0.89 g, 1.96 mmol) and HBr·NEt₃ (0.36 g, 1.96 mmol) was suspended in 40 ml of THF at –60 °C, and stirred for 10 min at this temperature and 2 h at r.t. An orange precipitated was observed. The solvent was removed under reduced pressure, and the residue washed with hexane (2 × 30 ml) and extracted with CH₂Cl₂ (40 ml). After centrifugation, the orange solution was concentrated and cooled to –30 °C, affording complex **3** in 91% yield. Anal. Calc. for C₁₉H₂₁BrN₂Ni: C, 54.86; H, 5.05; N, 6.74. Found: C, 54.84; H, 5.24; N, 6.71%.

4.8. Synthesis of Pd(CH₂SiMe₃)₂py₂ (**2b**)

One milliliter of py and 4.5 ml (4.8 mmol) of a 1.06 M solution of Mg(CH₂SiMe₃)Cl in Et₂O were added to a cooled (–60 °C) suspension of PdCl₂py₂ (0.80 g, 2.4 mmol) in 30 ml of Et₂O. The mixture was stirred 5 min at this temperature and 1 h at r.t. The solvent was stripped off and the residue extracted with 40 ml of petroleum ether and filtered. After partial evaporation of the solution, cooling to –30 °C furnished yellow crystals of complex **2b** in 50–55% yield. Anal. Calc. for C₁₈H₃₂N₂PdSi₂: C, 49.24; H, 7.35; N, 6.38. Found: C, 49.16; H, 7.50; N, 6.58%.

4.9. Synthesis of Ni(CH₂CMe₂-*o*-C₆H₄)py₂ (**4**)

4.9.1. Method A

A solution of complex **1d** (0.48 g, 1 mmol) in 95 ml of petroleum ether was treated with 0.5 ml (0.07 mmol) of a 0.14 M solution of PMe₃ in Et₂O. The mixture was stirred at r.t. for 1 h and a yellow–orange solid precipitated. After filtration, the solid, identified as metallacycle **4**, was washed with some petroleum ether and isolated in 93% yield. Anal. Calc. for C₂₀H₂₂N₂Ni: C, 68.81; H, 6.35; N, 8.02. Found: C, 68.06; H, 6.31; N, 8.02%.

4.9.2. Method B

To a cooled (–60 °C) suspension of NiCl₂py₄ (1.34 g, 3.01 mmol) in 40 ml of Et₂O, were added 1 ml of py and 7 ml (6.02 mmol) of a 0.86 M solution of Mg(CH₂CMe₂Ph)Cl in Et₂O which contained some iodide. The reaction mixture was stirred 15 min at this temperature and 30 min at r.t., then 0.5 ml (0.07 mmol) of a 0.14 M solution of PMe₃ in Et₂O were added, and stirring was continued for 1 h. The solvent was evaporated under reduced pressure and the residue extracted with 50 ml of Et₂O. After filtration, concentration and cooling to –30 °C, compound **4** was isolated as orange crystals in 30–35% yield.

Table 13

 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for complexes **10a**, **b**, **11a**, **b** and **12**^{a,b}

	R		L		
	CH ₂	Me	R ¹ , H–C=N	C _{ar} H(L)	C _{ar} (L)
Ni(Me) ₂ L (10a)		–3.4 –5.0	18.2 (Me) 157.3 (H–C=N)	124.1 (C(3)H), 125.7 (C(4 or 5)H) 126.2 (C(4 or 5)H), 127.8 (<i>m</i> -C _{ar} H) 133.6 (<i>p</i> -C _{ar} H), 148.2 (C(6)H)	129.2 (<i>o</i> -C _{ar}) 149.9 (C _{ar}) 154.5 (C _{ar} (2))
Ni(Me) ₂ L (10b)		–3.4 –4.0	22.8 (Me) 24.4 (Me) 28.0 (CH) 157.4 (H–C=N)	123.1 (<i>m</i> -C _{ar} H), 124.2 (C(3)H) 126.3 (C(4 or 5)H), 126.6 (<i>p</i> -C _{ar} H) 133.8 (C(4 or 5)H), 148.4 (C(6)H)	140.5 (<i>o</i> -C _{ar}) 147.1 (C _{ar}) 154.1 (C _{ar} (2))
Ni(CH ₂ SiMe ₃) ₂ L (11a)	–1.1 2.6	3.0 3.9	18.8 (Me) 156.8 (H–C=N)	124.2 (C(3)H), 125.7 (C(4 or 5)H) 125.9 (C(4 or 5)H), 128.0 (<i>m</i> -C _{ar} H) 133.7 (<i>p</i> -C _{ar} H), 148.2 (C(6)H)	129.9 (<i>o</i> -C _{ar}) 149.8 (C _{ar}) 153.5 (C _{ar} (2))
Ni(CH ₂ SiMe ₃) ₂ L (11b)	–1.8 1.4	2.7 4.0	22.6 (Me) 25.2 (Me) 28.0 (CH) 157.0 (H–C=N)	123.3 (<i>m</i> -C _{ar} H), 124.2 (C(3)H) 125.8 (C(4 or 5)H), 126.9 (<i>p</i> -C _{ar} H) 133.9 (C(4 or 5)H), 148.3 (C(6)H)	140.7 (<i>o</i> -C _{ar}) 147.1 (C _{ar}) 153.1 (C _{ar} (2))
Pd(Me) ₂ L (12)		–6.6 –5.8	22.7 (Me) 24.3 (Me) 27.9 (CH) 162.8 (H–C=N)	123.1 (<i>m</i> -CH), 125.6 (C(3)H) 126.6 (C(4 or 5)H), 127.3 (<i>p</i> -CH) 136.2 (C(4 or 5)H), 148.2 (C(6)H)	139.2 (<i>o</i> -C _{ar}) 145.2 (C _{ar}) 152.9 (C _{ar} (2))

^a C₆D₆, δ (J, Hz).^b Singlets unless otherwise indicated.

4.10. Synthesis of $M(\text{Me})_2\text{L}$ ($M = \text{Ni}$, $L = \mathbf{5a-d}$, $\mathbf{7a-d}$; $M = \text{Pd}$, $L = \mathbf{5c}$, $\mathbf{9a}$; $M = \text{Ni}$, $L = \mathbf{6a, b}$, $\mathbf{10a, b}$; $M = \text{Pd}$, $L = \mathbf{6b}$, $\mathbf{12}$)

These complexes have been prepared by reacting compounds **1a** or **2a** with the corresponding nitrogen ligands **5a–d** or **6a, b**, following the procedure described below for complex **7d**:

A solution of 0.26 g (0.65 mmol) of **5d** in 10 ml of toluene was added to 0.16 g (0.65 mmol) of compound **1a** dissolved in 20 ml of toluene, at -20°C . The mixture was stirred 10 min at this temperature and 1 h at r.t., changing the colour of the solution to deep blue. The solvent was partially evaporated and some petroleum ether added. Upon cooling to -30°C , compound **7d** was obtained as deep blue crystals in 93% yield. Anal. Calc. for C₃₀H₄₆N₂Ni: C, 73.03; H, 9.40; N, 5.68. Found: C, 73.03; H, 9.10; N, 5.68%.

Compound **7a**: Deep blue. 90% yield. Anal. Calc. for C₂₀H₂₆N₂Ni: C, 68.03; H, 7.42; N, 7.93. Found: C, 67.20; H, 7.22; N, 7.98%.

Compound **7b**: Deep blue. 93% yield. Anal. Calc. for C₂₂H₃₀N₂Ni: C, 69.32; H, 7.93; N, 7.35. Found: C, 69.08; H, 7.77; N, 7.43%.

Compound **7c**: Deep blue. 90% yield. Anal. Calc. for C₂₈H₄₂N₂Ni: C, 72.27; H, 9.10; N, 6.02. Found: C, 71.66; H, 9.34; N, 6.19%.

Compound **9a**: Red. 65% yield. Anal. Calc. for C₂₈H₄₂N₂Pd: C, 65.55; H, 8.25; N, 5.46. Found: C, 65.78; H, 8.09; N, 5.66%.

Compound **10a**: Green. 96% yield. Anal. Calc. for C₁₆H₂₀N₂Ni: C, 64.26; H, 6.74; N, 9.37. Found: C, 64.21; H, 6.64; N, 9.48%.

Compound **10b**: Green. 94% yield. Anal. Calc. for C₂₀H₂₈N₂Ni: C, 67.64; H, 7.95; N, 7.89. Found: C, 67.19; H, 7.88; N, 7.90%.

Compound **12**: Red. 92% yield. Anal. Calc. for C₂₀H₂₈N₂Pd: C, 59.63; H, 7.01; N, 6.95. Found: C, 59.42; H, 6.70; N, 7.02%.

4.11. Synthesis of $M(\text{CH}_2\text{SiMe}_3)_2\text{L}$ ($M = \text{Ni}$, $L = \mathbf{5a-c}$, $\mathbf{8a-c}$; $M = \text{Ni}$, $L = \mathbf{6a, b}$, $\mathbf{11a, b}$)

The preparation of these compounds involves the reaction of Ni(CH₂SiMe₃)₂py₂, **1b**, with the appropriate nitrogen ligands **5a–c** or **6a, b**. A representative example of the experimental procedure to synthesize **8c** is as follows:

A solution of 0.5 g (1.30 mmol) of Ni(CH₂SiMe₃)₂py₂ in 20 ml of Et₂O was cooled at -30°C and treated with 0.49 g (1.30 mmol) of **5c** dissolved in 15 ml of Et₂O. The mixture was stirred 15 min at this temperature and 2 h at r.t. and then taken to dryness. The residue was extracted with 40 ml of petroleum ether. Concentration and cooling at -30°C provided complex **8c** as deep green crystals in 96% yield. Anal. Calc. for C₃₄H₅₈N₂NiSi: C, 66.98; H, 9.59; N, 4.59. Found: C, 66.84; H, 8.67; N, 4.68%.

Compound **8a**: Green. 90% yield. Anal. Calc. for C₂₆H₄₂N₂NiSi: C, 62.77; H, 8.51; N, 5.63. Found: C, 62.91; H, 8.44; N, 5.83%.

Table 14

¹H-NMR Data for complexes **17** and **18a, b**^a

	R			L	
	CH ₂	Me	CH _{ar}	R ¹ , H–C=N	CH _{ar} (L)
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (17)	2.57 (s, 2H)	1.67 (s, 6H)	6.80–7.20 (m, 2H) 7.02 (d, 1H, 6.8) 7.20 (m, 1H)	0.99 (d, 6H, 6.9, Me) 1.11 (d, 6H, 6.9, Me) 3.64 (h, 2H, 6.8, CH) 8.09 (s, 1H, H–C=N)	6.47 (d, 1H, 7.7), 6.60 (tm, 1H, 7.0) 7.15 (m, 3H, <i>p,m</i> -CH) 8.98 (d, 1H, 5.3)
Ni(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (17')	3.04 (s, 2H)	1.60 (s, 6H)	6.80–7.20 (m, 2H) 7.31 (tm, 1H, 7.3) 8.04 (d, 1H, 7.2)	0.90 (d, 6H, 6.7, Me) 1.31 (d, 6H, 6.7, Me) 3.47 (h, 2H, 6.8, CH) 8.16 (s, 1H, H–C=N)	6.54 (d, 1H, 7.6), 6.67 (tm, 1H, 7.0) 7.00 (tm, 1H, 7.6) 7.15 (m, 3H, <i>p,m</i> -CH) 9.59 (d, 1H, 5.3)
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (18a)	2.57 (s, 2H)	1.30 (s, 6H)	5.96 (dm, 1H, 7.5) 6.31 (tm, 1H, 7.3) 6.63 (dm, 1H, 7.5) 6.71 (tm, 1H, 7.2)	2.27 (s, 6H, Me) 8.46 (s, 1H, H–C=N)	7.13–7.17 (m, 3H, <i>p,m</i> -CH), 7.69 (m, 1H, CH(5)) 7.80 (dm, 1H, 6.9, CH(3)), 8.02 (tm, 1H, 7.7, CH(4)) 8.88 (dm, 1H, 4.5, CH(6))
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (18a')	1.67 (s, 2H)	1.18 (s, 6H)	6.73 (m, 1H) 6.91 (m, 2H) 7.53 (m, 1H)	2.29 (s, 6H, Me) 8.42 (s, 1H, H–C=N)	7.13–7.17 (m, 3H, <i>p,m</i> -CH), 7.75 (m, 1H, CH(5)) 7.80 (d, 1H, 6.9, CH(3)), 8.10 (tm, 1H, 7.0, CH(4)) 9.22 (dm, 1H, 5.0, CH(6))
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (18b)	3.02 (s, 2H)	1.81 (s, 6H)	6.58 (dm, 1H, 6.9) 6.87 (tm, 1H, 5.7) 7.10 (m, 2H)	1.02 (d, 6H, 6.9, Me) 1.19 (d, 6H, 6.8, Me) 3.46 (h, 2H, 6.9, CH) 7.71 (s, 1H, H–C=N)	7.05–7.25 (m, 3H, <i>p,m</i> -CH) 6.43 (tm, 1H, 7.7, CH(5)), 6.50 (dm, 1H, 7.7, CH(3)) 6.77 (tm, 1H, 7.7, CH(4)), 8.44 (dm, 1H, 5.0, CH(6))
Pd(CH ₂ CMe ₂ - <i>o</i> -C ₆ H ₄)L (18b')	2.40 (s, 2H)	1.68 (s, 6H)	7.20 (m, 1H) 7.31 (m, 2H) 7.91 (d, 1H, 6.6)	0.97 (d, 6H, 6.9, Me) 1.34 (d, 6H, 6.8, Me) 3.45 (ph, 2H, 6.9, CH) 7.70 (s, 1H, H–C=N)	7.05–7.25 (m, 3H, <i>p,m</i> -CH), 6.43 (tm, 1H, 7.7, CH(5)) 6.47 (dm, 1H, 7.7, CH(3)), 6.80 (tm, 1H, 7.7, CH(4)) 9.01 (dm, 1H, 4.5, CH(6))

^a C₆D₆, δ (J, Hz).

Compound **8b**: Green. 95% yield. Anal. Calc. for C₂₈H₄₆N₂NiSi: C, 63.99; H, 8.82; N, 5.33. Found: C, 63.72; H, 8.78; N, 5.47%.

Compound **11a**: Green. 83% yield. Anal. Calc. for C₂₂H₃₆N₂NiSi: C, 59.59; H, 8.18; N, 6.32. Found: C, 60.33; H, 8.21; N, 5.85%.

Compound **11b**: Green. 85% yield. Anal. Calc. for C₂₆H₄₄N₂NiSi: C, 62.52; H, 8.88; N, 5.61. Found: C, 61.81; H, 8.14; N, 5.87%.

4.12. Synthesis of Ni(CH₂Ph)₂(TMED) (**13**)

To a solution of complex **1c** (0.40 g, 2 mmol) in 35 ml of Et₂O, an excess of TMED (1 ml) was added. The mixture was stirred at r.t. for 2 h. The solvent was evaporated under vacuum and the residue extracted with a mixture Et₂O–petroleum ether 1:3 and filtered. After concentration and cooling to –30 °C, compound **13** was isolated as red crystals in 52% yield. ¹H-NMR

Table 15

 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for complexes **17** and **18a, b**^{a,b}

	R			L		
	CH ₂	Me	CH _{ar}	R ¹ , H–C=N	CH _{ar} (L)	C _{ar} (L)
$\text{Ni}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)\text{L}$ (17)	47.9	34.0 (CMe ₂) 47.7 (CMe ₂)	120.9, 121.5, 123.5, 134.2 (C _{ar} H) 156.4, 170.3 (C _{ar})	22.3 (Me) 24.6 (Me) 28.0 (CH) 159.4 (H–C=N)	123.2 (<i>m</i> -C _{ar} H), 126.9 (C(3)H), 137.0 (C(4)H), 149.6 (C(6)H)	140.0 (<i>o</i> -C _{ar}) 147.9 (C _{ar}) 153.7 (C _{ar} (2))
$\text{Ni}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)\text{L}$ (17)	47.3	34.2 (CMe ₂) 48.7 (CMe ₂)	121.2, 123.8, 124.3, 134.3 (C _{ar} H) 160.7, 170.8 (C _{ar})	22.7 (Me) 24.8 (Me) 28.5 (CH) 158.7 (H–C=N)	123.2 (<i>m</i> -C _{ar} H), 126.7 (C(3)H), 126.9 (C(5)H), 137.7 (C(4)H), 151.5 (C(6)H)	140.5 (<i>o</i> -C _{ar}) 146.6 (C _{ar}) 153.4 (C _{ar} (2))
$\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)\text{L}$ (18a)	46.0	33.9 (CMe ₂) 47.1 (CMe ₂)	121.7, 123.3, 123.4, 133.8 (C _{ar} H) 157.3, 169.6 (C _{ar})	18.7 (Me) 165.5 (H–C=N)	126.5 (<i>p</i> -C _{ar} H), 127.7 (C(3)H), 128.5 (<i>m</i> -C _{ar} H), 128.6 (C(5)H), 138.6 (C(4)H), 150.2 (C(6)H)	129.2 (<i>o</i> -C _{ar}) 149.2 (C _{ar}) 153.6 (C _{ar} (2))
$\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)\text{L}$ (18a')	44.3	33.6 (CMe ₂) 47.5 (CMe ₂)	122.1, 123.4, 124.1, 134.9 (C _{ar} H) 160.3, 169.3 (C _{ar})	18.4 (Me) 165.7 (H–C=N)	126.2 (<i>p</i> -C _{ar} H), 127.6 (C(3)H), 128.3 (<i>m</i> -C _{ar} H), 128.7 (C(5)H), 138.5 (C(4)H), 151.0 (C(6)H)	129.2 (<i>o</i> -C _{ar}) 149.0 (C _{ar}) 157.3 (C _{ar} (2))
$\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)\text{L}$ (18b)	46.4	34.3 (CMe ₂) 47.3 (CMe ₂)	121.8, 123.1, 123.3, 134.6 (C _{ar} H) 157.0, 165.1 (C _{ar})	22.5 (Me) 24.1 (Me) 28.1 (CH) 162.8 (H–C=N)	123.4 (<i>m</i> -C _{ar} H), 126.5 (C(3)H), 126.9 (C(5)H), 127.2 (<i>p</i> -C _{ar} H), 136.7 (C(4)H), 151.9 (C(6)H)	139.3 (<i>o</i> -C _{ar}) 146.7 (C _{ar}) 152.5 (C _{ar} (2))
$\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)\text{L}$ (18b')	45.2	33.9 (CMe ₂) 48.1 (CMe ₂)	122.3, 123.6, 124.0, 135.0 C _{ar} H 160.1, 168.9 (C _{ar})	24.3 (Me) 24.7 (Me) 27.9 (CH) 164.6 (H–C=N)	123.4 (<i>m</i> -C _{ar} H), 126.8 (C(5)H), 126.9 (C(3)H), 136.8 (C(4)H), 150.9 (C(6)H)	138.9 (<i>o</i> -C _{ar}) 145.7 (C _{ar}) 152.5 (C _{ar} (2))

^a C₆D₆, δ (J, Hz).^b Singlets unless otherwise indicated.

(C₆D₆, 20 °C): δ 1.17 (s, 4H, CH₂ tmed); 1.42 (s, 4H, CH₂–Ni); 1.79 (s, 12H, Me tmed); 7.12 (t, 2H, *J* = 6.9 Hz, *p*-CH); 7.26 (t, 4H, *J* = 7.4 Hz, *m*-CH); 7.73 (d, 4H, *o*-CH). $^{13}\text{C}\{^1\text{H}\}$ (C₆D₆, 20 °C): δ 12.4 (CH₂–Ni); 47.2 (Me tmed); 58.2 (CH₂ tmed); 121.0 (CH); 127.6 (CH); 129.0 (CH); 155.2 (C_{ar}).

4.13. Synthesis of $\text{Ni}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)(\text{L})(\text{L} = \mathbf{5a}, \mathbf{c}, \mathbf{15a}, \mathbf{b})$

A solution of 0.10 g (0.29 mmol) of complex **4** in 30 ml of Et₂O was treated with a solution of **5a** (0.08 g, 0.31 mmol) in 10 ml of Et₂O, at r.t. The mixture was stirred 1

h at this temperature and filtered. After partial evaporation of the solvent and cooling to $-30\text{ }^{\circ}\text{C}$, compound **15a** was isolated as green crystals in 87% yield. This complex crystallizes with 0.5 molecules of Et_2O . Anal. Calc. for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{Ni}$: C, 73.87; H, 7.08; N, 6.15. Found: C, 73.66; H, 6.78; N, 6.34%.

Compound **15b** was similarly prepared and obtained as deep blue crystals in 90% yield (respect to the ligand). It crystallizes with 0.5 molecules of the ligand **5c**. Anal. Calc. for $\text{C}_{36}\text{H}_{48}\text{N}_2\text{Ni}$: C, 77.77; H, 8.92; N, 5.55. Found: C, 77.57; H, 8.91; N, 5.69%.

4.14. Synthesis of $\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)_2(\text{L})$ ($\text{L} = \mathbf{5a-d}$, **16a-d**; $\text{L} = \mathbf{6a, b, 18a, b}$)

These complexes were prepared by the reaction of $\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)_2(\text{cod})$ with the nitrogen ligands **5a-d** or **6a, b** following the synthesis described for compound **16d**.

A solution of $\text{Pd}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)_2(\text{cod})$ (0.34 g, 1 mmol) and **5d** (0.40 g, 1 mmol) in 40 ml of Et_2O was cooled at $-30\text{ }^{\circ}\text{C}$ and stirred at this temperature for 30 min, then the cold bath was removed and the mixture stirred at r.t. for 4 h. The solvent was evaporated under reduced pressure and the residue extracted with a mixture Et_2O –petroleum ether 2:1 and filtered. After partial evaporation of the solvent and cooling to $-30\text{ }^{\circ}\text{C}$, complex **16d** was isolated as red crystals in quantitative yield. Anal. Calc. for $\text{C}_{38}\text{H}_{52}\text{N}_2\text{Pd}$: C, 70.78; H, 8.30; N, 4.23. Found: C, 70.53; H, 8.49; N, 4.21%.

Compound **16a**: Red. Quantitative yield. Anal. Calc. for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{Pd}$: C, 66.86; H, 6.41; N, 5.57. Found: C, 66.88; H, 6.48; N, 5.62%.

Compound **16b**: Yellow. Quantitative yield. Anal. Calc. for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{Pd}$: C, 67.75; H, 7.06; N, 5.10. Found: C, 68.06; H, 6.99; N, 5.29.

Compound **16c**: Red. Quantitative yield. Anal. Calc. for $\text{C}_{36}\text{H}_{48}\text{N}_2\text{Pd}$: C, 70.12; H, 8.03; N, 4.42. Found: C, 70.09; H, 8.27; N, 4.68%.

Compound **18a**: Red. 83% yield. Anal. Calc. for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{Pd}$: C, 64.22; H, 5.84; N, 6.24. Found: C, 64.30; H, 5.58; N, 6.30%.

Compound **18b**: Red. 93% yield. Anal. Calc. for $\text{C}_{28}\text{H}_{34}\text{N}_2\text{Pd}$: C, 66.61; H, 6.74; N, 5.55. Found: C, 66.40; H, 6.77; N, 5.42%.

4.15. Synthesis of $\text{Ni}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)_2(\text{L})$ ($\text{L} = \mathbf{6b, 17}$)

To a cooled ($-30\text{ }^{\circ}\text{C}$) solution of complex **4** (0.29 g, 0.83 mmol) in 20 ml of Et_2O was added a solution of **6b** (0.22 g, 0.83 mmol) in 10 ml of Et_2O . The mixture was stirred 10 min at this temperature and 1.5 h at r.t. The

solvent was evaporated under vacuum and the residue extracted with 40 ml of petroleum ether and filtered. Concentration and cooling at $-30\text{ }^{\circ}\text{C}$ provided green crystals of compound **17** in 68% yield. Anal. Calc. for $\text{C}_{28}\text{H}_{34}\text{N}_2\text{Ni}$: C, 73.55; H, 7.49; N, 6.13. Found: C, 73.18; H, 7.11; N, 6.17%.

4.16. X-ray structure determination of **1c**

A crystal showing well defined faces was mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo- K_α radiation, $\lambda = 0.71067\text{ \AA}$) operating 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of three sets exposures. Each exposure of 10 s covered 0.3° in ω . The crystal to detector distance was 6.05 cm. Coverage of the unique set was over 92% complete to at least 23° in θ . Unit cell dimensions were determined by a least squares refinement using reflections with $I > 20\sigma(I)$ and $6^\circ < 2\theta < 46^\circ$. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentz and polarization effects. Full matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. H atoms were included in their calculated positions. Refinement on F^2 for all reflections, weighted R factors (R_w) and all goodness-of-fit S are based on F^2 , while conventional R factors (R) are based on F . A summary of the fundamental crystal and refinement data are given in Table 1. Complete structural data have been deposited as CCDC 206445 [32]. Calculations were carried out with SMART software for data collection [33] for data reduction and SHELXTL [33] for structure solution and refinements.

4.17. X-ray structure determination of **1e** as toluene–petroleum ether solvate **1e·solv**

A brown plate was mounted on a Siemens/Bruker Smart CCD diffractometer equipped with a sealed tube X-ray source (Mo- K_α radiation, $\lambda = 0.71067\text{ \AA}$, graphite monochromator) and a LT2 crystal cooling unit. Data were collected over a complete sphere of the reciprocal space by a combination of four sets each 606 exposures. Each exposure of 15 s covered 0.3° in ω . The crystal to detector distance was 4.45 cm. Coverage of the unique set was over 99.7% complete to 27° in θ . Unit cell dimensions were determined by a least squares refinement using 7653 reflections with $5^\circ < 2\theta < 54^\circ$. The data were corrected for absorption. The structure was solved with direct methods and refined on F^2 with anisotropic displacement parameters for non-hydrogen atoms. Aromatic H atoms were included in their calculated positions, CH_3 groups were geometrically idealized but refined in orientations. The structure contains two independent Ni complexes. Disordered

solvent molecules (toluene/petroleum ether) were found to be present in channels extending parallel to **a** (two per unit cell, each with a net volume of 294 \AA^{-3}) and produced very diffuse electron densities with maximum values of $1.97 e \text{ \AA}^{-3}$. They were taken into account with procedure SQUEEZE of program PLATON [34] giving an electron count to 139 electrons per unit cell, equivalent to about three toluene molecules per eight Ni complexes of one unit cell. Crystal and refinement data are given in Table 1. Complete structural data have been deposited as CCDC 206446 [32]. Other programs used were those given above [35].

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References

- [1] B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 1, VCH, Weinheim, 1996.
- [2] (a) L.K. Johnson, C.M. Killian, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 4414; (b) C.M. Killian, L.K. Johnson, M. Brookhart, *Organometallics* 16 (1997) 2005; (c) S.A. Svejda, L.K. Johnson, *J. Am. Chem. Soc.* 121 (1999) 10634; (d) D.P. Gates, S.A. Svejda, E. Oñate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, *Macromolecules* 33 (2000) 2320.
- [3] (a) S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (2000) 1169; (b) L.K. Johnson, C.M. Killian, in: J. Scheirs, W. Kaminsky (Eds.), *Metallocene-based Polyolefins*, vol. 1, J. Wiley & Sons, Chichester, 1999; (c) S. Mecking, *Coord. Chem. Rev.* 203 (2000) 325; (d) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283.
- [4] (a) R.J. Maldanis, J.S. Wood, A. Chandrasekaran, M.D. Rausch, J.C.W. Chien, *J. Organomet. Chem.* 645 (2000) 158; (b) L.C. Simon, R.S. Mauler, R.F. De Souza, *J. Polym. Chem.* 37 (1999) 4656.
- [5] (a) D. Pappalardo, M. Mazzeo, C. Pellechia, *Macromol. Rapid Commun.* 18 (1997) 1017; (b) S. Tsuji, D.C. Swenson, R.F. Jordan, *Organometallics* 18 (1999) 4758; (c) T. Schleis, J. Heinemann, T.S. Spaniol, R. Mulhaupt, R. Mülhaupt, J. Okuda, *Inorg. Chem. Commun.* 1 (1998) 431.
- [6] L.K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* 118 (1999) 267.
- [7] (a) A.K. Smith, in: G. Wilkinson, F.G.A. Stone, E. Abel (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 9, Pergamon, Oxford, 1995; (b) A.J. Canty, in: G. Wilkinson, F.G.A. Stone, E. Abel (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 9, Pergamon, Oxford, 1995.
- [8] (a) R.H. Crabtree, *The Chemistry of the Transition Metals*, 3rd ed., J. Wiley & Sons, New York, 2001, p. 91; (b) P. Fantucci, *Comments Inorg. Chem.* 13 (1992) 241.
- [9] T. Schleis, T.P. Spaniol, J. Okuda, J. Heinemann, R. Mulhaupt, *J. Organomet. Chem.* 569 (1998) 159.
- [10] W. Kaschube, K.R. Pörschke, G. Wilke, *J. Organomet. Chem.* 355 (1988) 525.
- [11] (a) J. de Graaf, J. Boersma, W.J.J. Smeets, A.-L. Spek, G. van Koten, *Recl. Trav. Chim. Pays-Bas* 107 (1988) 299; (b) J. de Graaf, J. Boersma, W.J.J. Smeets, A.-L. Spek, G. van Koten, *Organometallics* 8 (1989) 2907.
- [12] P.K. Byers, A. Canty, *Organometallics* 9 (1990) 210.
- [13] E. Carmona, F. González, M.L. Poveda, J.L. Atwood, R.D. Rodgers, *J. Chem. Soc., Dalton Trans.* (1981) 777.
- [14] J. Cámpora, J.A. López, P. Palma, D. del Río, E. Carmona, P. Valerga, C. Graiff, A. Tiripicchio, *Inorg. Chem.* 40 (2001) 4116.
- [15] E. Carmona, J.M. Marín, M. Paneque, M.L. Poveda, *Organometallics* 6 (1987) 1757.
- [16] (a) E. Carmona, P. Palma, M. Paneque, M.L. Poveda, E. Gutiérrez-Puebla, A. Monge, *J. Am. Chem. Soc.* 108 (1986) 6424; (b) E. Carmona, E. Gutiérrez-Puebla, M. Marín, M. Paneque, M.L. Poveda, C. Ruiz, *J. Am. Chem. Soc.* 111 (1989) 2883.
- [17] I. Black, G.B. Young, *Polyhedron* 8 (1989) 585.
- [18] (a) J. Cámpora, E. Gutiérrez, M.L. Poveda, C. Ruiz, E. Carmona, *J. Chem. Soc., Dalton Trans.* (1992) 1769; (b) B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, *J. Am. Chem. Soc.* 123 (2001) 5352.
- [19] A. Klein, *Z. Anorg. Allg. Chem.* 627 (2001) 645.
- [20] A. Klein, M. Niemayer, *Z. Anorg. Allg. Chem.* 626 (2000) 1191.
- [21] R. Hay-Motherwell, G. Wilkinson, T.K.N. Sweet, M.B. Hursthouse, *Polyhedron* 15 (1996) 3163.
- [22] D. Walther, T. Döhler, K. Heubach, B. Schweder, H. Górls, *Z. Anorg. Allg. Chem.* 625 (1999) 923.
- [23] (a) A. Klein, T. Scheiring, W. Kaim, *Anorg. Allg. Chem.* 625 (1999) 1177; (b) A. Klein, H.-D. Hausen, W. Kaim, *J. Organomet. Chem.* 440 (1992) 207; (c) A. Klein, W. Kaim, E. Waldhor, H.-D. Hausen, *J. Chem. Soc., Perkin Trans. 2* (1995) 2121; (d) A. Klein, E.J.L. McInnes, W. Kaim, *J. Chem. Soc., Dalton Trans.* (2002) 2371.
- [24] M. Brookhart, M.L.H. Green, L.L. Wong, *Prog. Inorg. Chem.* 36 (1988) 1.
- [25] J. Cámpora, P. Palma, E. Carmona, *Coord. Chem. Rev.* 193-195 (1999) 207.
- [26] Attempts to carry out the PMe_3 exchange with the α -diimines **4a** and **4c** (see Scheme 4) met limited success, and led to the corresponding metallacycles **12a** and **12b** in ca. 20% yield. These results were substantially improved by addition of $\text{Pd}(\eta^5\text{-Cp})(\eta^3\text{-C}_3\text{H}_5)$, a phosphine sponge.
- [27] E. Carmona, M. Paneque, M.L. Poveda, E. Gutiérrez-Puebla, A. Monge, *Polyhedron* 8 (1989) 1069.
- [28] D.C. Griffiths, G.B. Young, *Organometallics* 8 (1986) 875.
- [29] E. Uhlig, W. Poppitz, *Z. Anorg. Allg. Chem.* 477 (1981) 167.
- [30] (a) T.V. Laine, M. Klinga, M. Leskelä, *Eur. J. Inorg. Chem.* (1999) 959; (b) T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, *J. Organomet. Chem.* 606 (2000) 112.

- [31] (a) L.M. Vallarino, W.R. Hill, J.V. Quagliano, *Inorg. Chem.* 4 (1965) 1508;
(b) P. Gupte, R.V. Chaudhari, *J. Mol. Catal.* 24 (1984) 197.
- [32] CCDC nos. 206445–206446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via: <http://www.ccdc.cam.ac.uk/conts/retrieving/html> (or from the CCDC, 12 Union Road, Cambridge CB121EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
- [33] SMART and SELXTL; Siemens Energy and Automation, Inc., Analytical Instrumentation, Madison, WI, 1996.
- [34] A.L. Spek. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2003.
- [35] Programs SMART, SAINT, SADABS, and SELXTL; Siemens Energy and Automation, Inc., Analytical Instrumentation, Madison, WI, 1998.