

# Nickelacycles with anionic C–N–N' terdentate ligands containing (5,5), (5,6), (5,7) and (6,5) membered fused rings. Reaction with ethylene†

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A series of nickelacycle complexes with di-Schiff bases acting as terdentate CNN<sup>−</sup> anionic ligands has been prepared. Oxidative addition of one C–X bond in mono- or di-*ortho*-halogenoaryl substituted ligands, *N,N'*-dibenzylidene-alkane-1,2-diamines (ethane, propane and butanediamines) and *N,N'*-bis(1,2-diphenylethylidene)ethane-1,2-diamine, to [Ni(cod)<sub>2</sub>] gives neutral complexes [NiX(CNN)] containing (5,5), (5,6), (5,7) and (6,5)-membered fused chelate rings (NiCN and NiNN respectively). Complexes from monohalogenoaryl substituted ligands are obtained as mixtures of two non-interchanging configurational isomers (*E* or *Z* stereochemistry about the non-metallated imine group). Cationic complexes [NiL(CNN)]BF<sub>4</sub> are generated by halide abstraction from these neutral complexes by using TIBF<sub>4</sub> and 2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N or CH<sub>3</sub>CN as stabilizing ligand. In ionic compounds from monohalogenoaryl substituted ligands the formation of isomers by restricted rotation around the C<sub>phenyl</sub>–C<sub>methinic</sub> bond is also observed. The <sup>1</sup>H NMR spectra of complexes with (5,5), (5,6), (6,5) fused rings show fluxional behavior, the data being consistent with interconversion of two chelate ring conformations that are associated with the relative position of the non-metallated methinic moiety in the lower or the upper side of the coordination plane. Molecular structures of three ionic complexes [Ni(2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N)(CNN)]BF<sub>4</sub>, were determined by X-ray single-crystal diffraction, revealing the effects of chelate sizes on the distortion of the coordination sphere around nickel. Ionic complexes [Ni(CH<sub>3</sub>CN)(CNN)]BF<sub>4</sub> were tested as precursors of active species in the reaction with ethylene under pressure. The influence of the nickelacycle ring size on the insertion reaction is discussed, with moderate activities being observed only when the Ni–C bond is involved in a six-membered ring.

## Introduction

Metal complexes of nitrogen donor ligands as precursors in different homogeneous catalytic reactions have received increasing attention in recent years.<sup>1</sup> Those with ligands containing sp<sup>2</sup>-hybridized nitrogen atoms, particularly when acting as bi- or poly-dentate ligands, give very stable coordination compounds. Of them, diimine ligands containing the 1,4-diaza-1,3-butadiene skeleton (N=CC=N) with two conjugated C=N iminic bonds, have attracted most interest. Brookhart and co-workers have reported the development of highly active cationic Ni<sup>II</sup>- and Pd<sup>II</sup>-based catalysts of general type [M(NN)(Me)(L)]<sup>+</sup> that polymerize ethylene and  $\alpha$ -olefins.<sup>2</sup> The palladium complexes also catalyse co-polymerization of ethylene and  $\alpha$ -olefins with functionalized olefins such as acrylates and methyl vinyl ketone.<sup>3</sup> These complexes contain bidentate diimine ligands, a weak coordinating ligand as well as a Ni–C bond which after the insertion of olefin and  $\beta$ -elimination produce the nickel-hydride active catalyst species. The different steps in these catalytic processes have been subject to various theoretical studies.<sup>4</sup> Closely related to these are the di-Schiff-base ligands

containing two N sp<sup>2</sup> donor atoms as part of a non-conjugated (=NCCN=) system. Those derived from salicylaldehyde and diamines (*N,N'*-bis(salicylidene)ethylenediamine) are recognized chelating agents, giving complexes of almost all metal ions, in which complex formation is determined by metal–nitrogen and metal–oxygen bonds (O,N,N,O-tetradentate).<sup>5</sup> Although some coordination compounds of Ni<sup>II</sup>, [NiX<sub>2</sub>(NN)], are known,<sup>6</sup> the synthesis of related organometallic complexes containing di-Schiff bases acting as neutral bidentate ligands [NiX(R)(NN)] has not been reported.

Furthermore, nitrogen donors are frequently used to form part of chelating systems, together with phosphorus or carbon donors. In most cases cyclometallation reactions permit complexes of Pd<sup>II</sup> and Pt<sup>II</sup> to be obtained. However, few organonickel complexes of this kind were reported. In most cases they are obtained by oxidative addition of Ni<sup>0</sup> to C–X bonds. Four- and five-membered phosphonickelacycles were prepared in this way.<sup>8</sup> Also, van Koten and co-workers reported the synthesis and reactivity of nickel(II) complexes containing the mono-anionic *trans* terdentate ligand (NCN) [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup> with two sp<sup>3</sup> N atoms, and in a previous study we reported the synthesis of related metallacycle complexes<sup>10</sup> based on the monoanionic *cis*-terdentate ligands C<sub>6</sub>X<sub>n</sub>H<sub>5−n</sub>–CH=NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> and C<sub>6</sub>X<sub>n</sub>H<sub>5−n</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> with sp<sup>2</sup>/sp<sup>3</sup>, and sp<sup>3</sup>/sp<sup>3</sup> hybridized N atoms. We now extend our studies to dibenzylideneamines [C<sub>6</sub>X<sub>n</sub>H<sub>5−n</sub>CH=N(CH<sub>2</sub>)<sub>m</sub>–N=CH(C<sub>6</sub>X<sub>n</sub>H<sub>5−n</sub>)], also potentially terdentate, from which

† Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

Electronic supplementary information (ESI) available: ligand synthesis; ORTEP plots of **2c**, **2e** and **2f**; a schematic of the proposed dynamic behaviour making the upper and lower sides of the iminic moiety equivalent. See <http://www.rsc.org/suppdata/doi/10.1039/b008520k/>

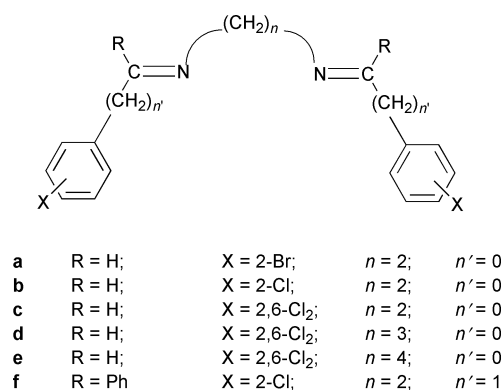
few organometallic compounds have been prepared. To the best of our knowledge from such ligands only a seven-coordinate tungsten(II) complex obtained by the oxidative addition of  $[\text{W}(\text{CO})_6]$  to a C-Cl bond<sup>11</sup> and  $[\text{PtMe}\{1-(\text{N}=\text{CHC}_6\text{H}_4)-2-(\text{N}=\text{CHC}_6\text{H}_5)\text{C}_6\text{H}_{10}\}]$ , obtained by metallation of one of the phenyl substituents of the diimine ligand in the reaction with  $[\text{Pt}_2\text{Me}_4(\mu-\text{SMe}_2)]$ , have been described.<sup>12</sup>

Following our studies on C–N nickelacycles, we describe here the reaction of  $[\text{Ni}(\text{cod})_2]$  and different *ortho*-halogeno-substituted di-Schiff bases that allow the synthesis of a new series of metallacyclic nickel(II) complexes possessing (5,5), (5,6), (5,7) and (6,5) cumulated ring systems. We also present a full characterization of the complexes both in solution and in the solid state. The use of these complexes as precursors in the oligomerization of ethylene has also been tested in order to analyse the effect of chelate ring size on the activation step of the process.

## Results and discussion

## Ligands

The dibenzylidene alkane diamines (**a–e**) and 1,2-diphenylethylidene ethane diamine (**f**) (see Scheme 1) were prepared by con-



### Scheme 1

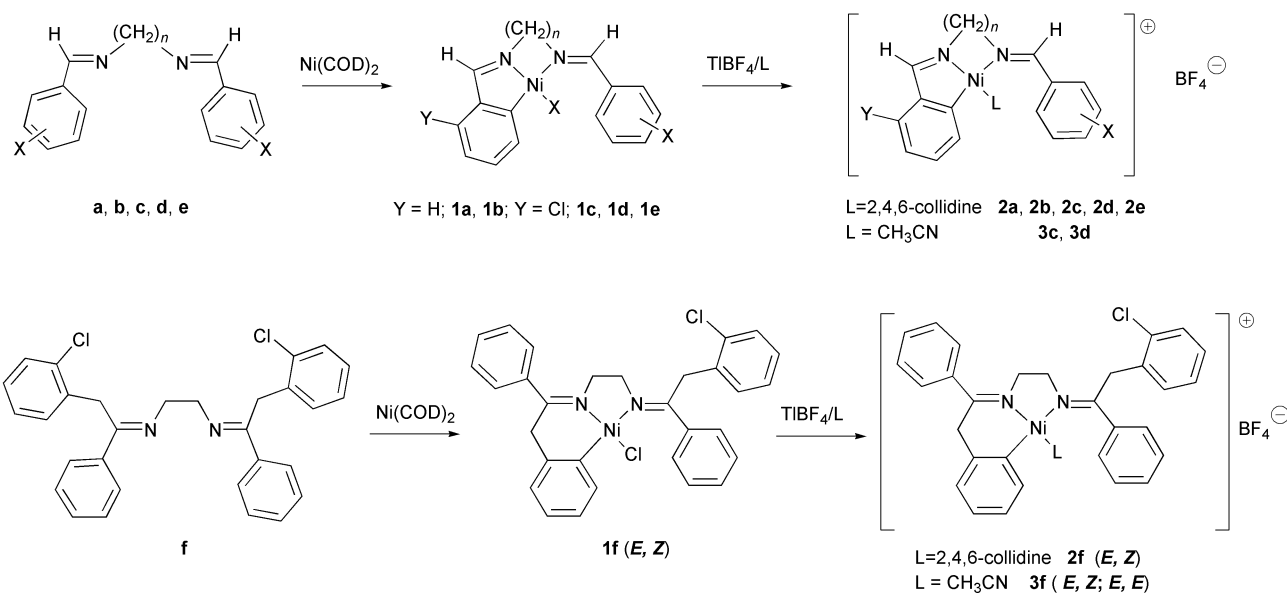
denation reactions between the corresponding diamine and a stoichiometric amount of the appropriate carbonylic compound. In general, N-substituted aldimines and ketimines exist in the solid state and in solution only in the more stable *anti* (*E*) form, but in some cases a significant concentration of the less stable *syn* (*Z*) form has been found in equilibrium.<sup>13</sup> The room temperature <sup>1</sup>H NMR spectra of these ligands, in CDCl<sub>3</sub> solu-

tions, showed only one set of signals in all cases. Owing to the strong NOE interaction observed between the HC=N protons and the methylenic protons, ligands **a–e** could be assigned to the *E* form. The two-dimensional <sup>1</sup>H–<sup>1</sup>H NOESY spectra of ligand **f** showed a NOE contact between the methylenic protons of the bridge and the benzylic protons, which is also consistent with the *E* configuration around each iminic HC=N bond.

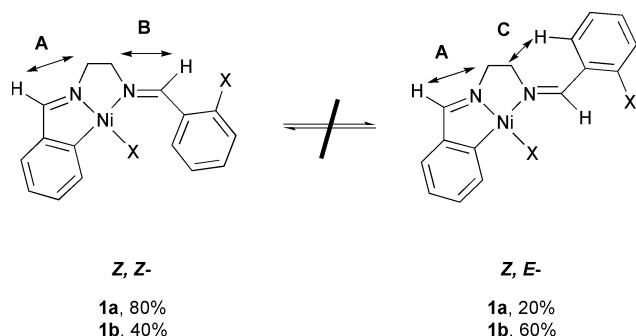
### Neutral complexes [NiX(CNN')]

Complexes **1a–1f** were prepared by reaction of  $[\text{Ni}(\text{cod})_2]$  with the potentially terdentate N-donor ligands (**a–f**) in THF or toluene (see Scheme 2). The new compounds obtained were slightly air-sensitive, bright orange solids (**1a–1e**) which can be stored under nitrogen for several months. In contrast, **1f** was yellow and moderately unstable under nitrogen. The compounds were only slightly soluble in common solvents. All were characterized by elemental analyses, infrared spectra and  $^1\text{H}$  NMR. The IR spectra showed two bands due to the  $\nu(\text{C}=\text{N})$  stretching at lower ( $\Delta\nu = 2\text{--}10\text{ cm}^{-1}$ ) and higher ( $\Delta\nu = 20\text{--}40\text{ cm}^{-1}$ ) wavenumbers than the corresponding band of the free imine, which is consistent with the presence of two different methinic groups.

<sup>1</sup>H NMR spectra were recorded in CD<sub>3</sub>COCD<sub>3</sub> solutions at room temperature. For complexes **1a** and **1b** two sets of well resolved signals with unequal intensities, owing to the presence of two isomers in solution, were observed. The spectra of **1a** and **1b** were similar. The results obtained from the bromo complex, **1a**, with a 4 : 1 composition of the isomers serves to illustrate the isomer identification. The methinic region displayed four broad singlets at  $\delta$  9.06, 8.87, 8.36 and 8.32 in a 1 : 4 : 4 : 1 intensity ratio, as a consequence of unresolved coupling with the methylene protons of the ethylene backbone of the ligand. The methylenic region displayed two pairs of sharp triplets, at  $\delta$  4.33, 3.86, 3.97 and 3.75, due to the major and minor isomers respectively. The aromatic region was complex. Particularly interesting was the presence of a downfield doublet at  $\delta$  9.19, corresponding to the major isomer. We presume that isomers referred to as *Z,Z* and *Z,E*, according to the *Z* or *E* configuration adopted by each CH=N bond of the dibenzylidene diamine, were present in solution (see Scheme 3). So the very large downfield shift ( $\Delta\delta = 2$  ppm) undergone by one aromatic proton in the major isomer could be explained if this proton was held above the coordination plane close to the metal, a situation only possible if the coordinated ligand adopts a *Z,Z* configuration.



### Scheme 2



Scheme 3

According to the literature,<sup>14</sup> the two signals of the methine protons high-field shifted with respect to the free imine can be assigned to the protons of the imine groups included in the metallacycle. The other methine proton in the minor isomer is downfield shifted up to *ca.* 0.4 ppm relative to that of the free imine as expected in the *Z,E* isomers. This effect is caused by the proximity between the methine proton and the nickel atom. In the major isomer, assumed to be *Z,Z*, the corresponding methine proton appears only slightly downfield (up to *ca.* 0.10 ppm) relative to that of the free imine.

The composition of the mixture of the two isomers obtained from complex **1b** was reversed, where *Z,E* was the major isomer (*Z,Z* : *Z,E* = 4 : 6). In this case the *Z,E* isomer was isolated separately by crystallization in hot toluene. The <sup>1</sup>H NMR spectrum at ambient temperature, recorded at different times, showed that no isomerization occurred.

Two dimensional <sup>1</sup>H-<sup>1</sup>H COSY and NOESY spectroscopy experiments conducted on complex **1a** were also entirely consistent with this assignment. The key features of the assignments (see Scheme 3) were a strong NOE interaction between the two pairs of imine and methylene protons (**A**, δ 8.43–3.91, and **B**, 4.37–8.91) from the major *Z,Z* isomer. Correlations between one methine and one methylene group (**A**, δ 8.37–3.79) and the other methylene group with the *ortho* hydrogen of the aromatic non-metallated group (**C**, 4.01–7.64) were observed for the minor *Z,E* isomer.

It is noteworthy that the formation of isomers of this type in complexes **1a** and **1b** implies that the *E-Z* isomerization of one of the C=N double bonds of the dibenzylidene ethane diamines takes place upon coordination to the Ni<sup>0</sup>. This isomerization process has not been observed in analogous nickel coordination complexes.<sup>6</sup> However, formation of exocyclic cyclopalladated compounds of benzylidenebenzylamines is also accompanied by the *E-Z* isomerization of the ligand.<sup>14</sup> A rotational mechanism, which would proceed through heterolytic cleavage of the π bond of the nitrogen-carbon double bond, could be favoured by the π back bonding properties of d<sup>10</sup> metal centers and has been proposed to explain this kind of isomerization in d<sup>8</sup> complexes.<sup>15</sup>

From the reaction of the nickel(0) compound with the *N,N'*-bis(2,6-dichlorobenzylidene)ethane-1,2-diamine, **c**, only one isomer was obtained. Based on the chemical shifts of the <sup>1</sup>H NMR spectrum, this could be assigned to the *Z,Z* isomer.

In this study we have also explored the influence of the length of the N,N-chelating chain on the preparation of mono- or poly-nuclear complexes with diimine-bridged structure, similar in nature to those isolated in earlier studies in our laboratory.<sup>10</sup> Under these conditions only mononuclear species with two fused 5(CNiN) and 6- or 7-(NNiN) membered rings were obtained. To simplify the characterization of the complexes, ligands derived from 2,6-dichlorobenzaldehyde and propane- or butane-diamine, **d** and **e**, were used. Compounds **1d** and **1e** appeared as a single isomer, which in accordance with their chemical shifts could also be assigned to the *Z,Z* isomer.

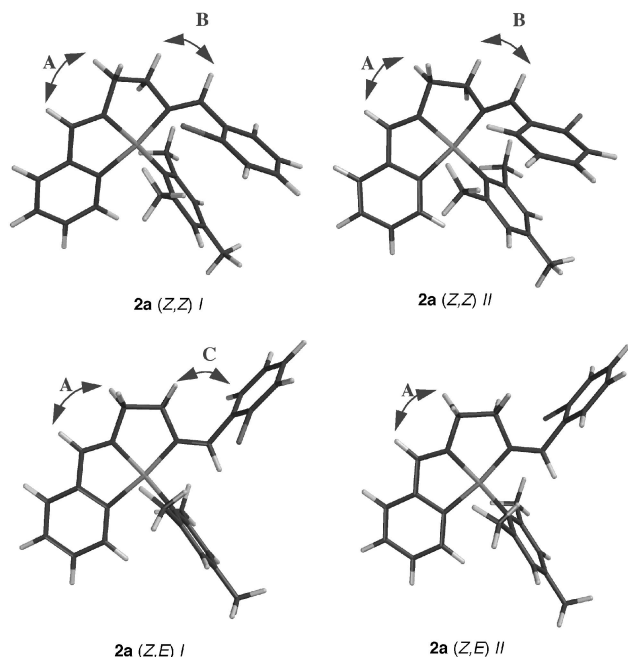
In order to study the Ni-C activation towards insertion reaction we prepared ligand **f** to obtain complexes with six-

membered NiCN rings. There is only one nickel(II) complex with a six-membered C,N-nickelacycle reported in the literature.<sup>16</sup> Compound **1f** containing fused 6- and 5-membered rings (see Scheme 2) was obtained by the same general procedure. According to the <sup>1</sup>H NMR spectra, only one isomer is present (see Scheme 2). The most relevant information about the configuration is the appearance of a deshielded multiplet signal at δ 8.7. This could be attributed to the two *ortho* aromatic protons of the non-metallated phenyl ring that in the *E,Z* isomer are held above the coordination plane close to the nickel. The methylene protons of the NCH<sub>2</sub>CH<sub>2</sub>N bridge occur as two triplets at δ 4.3 and 3.7, and those from the CH<sub>2</sub> group contained in the nickelacycle and from the benzylic CH<sub>2</sub>Ph group as two singlets at δ 4.4 and 4.2. It should be noted that isomerization of the imine group is necessary to produce the nickelacycle. So the longer times needed for oxidative addition could be associated with the isomerization in the nickel(0) complex.

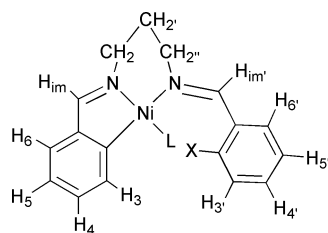
### Ionic complexes [Ni(CNN')(2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N)]BF<sub>4</sub>

The addition of TlBF<sub>4</sub> and the Lewis base 2,4,6-trimethylpyridine in acetone or THF to compounds **1a–1f** afforded the ionic derivatives **2a–2f** (see Scheme 2), which were characterized by elemental analyses, infrared spectra, <sup>1</sup>H NMR spectroscopy and crystal structure determination of **2c**, **2e** and **2f** (see below). The complexes were yellow solids highly soluble in THF, CHCl<sub>3</sub> and acetone. In their IR spectra the characteristic pattern of the BF<sub>4</sub><sup>-</sup> ion between 1030 and 1050 cm<sup>-1</sup> was clearly observed. The ν(C=N) overlapped with some bands of the collidine ligand.

In the <sup>1</sup>H NMR spectra of complex **2a** three isomers were observed, one of them *ca.* 85%. In the case of **2b** as many as four isomers were present, in relative amounts of 1 : 2 : 3 : 4. In the <sup>1</sup>H NMR spectra of the ionic compounds **2c**, **2d**, **2e** only one isomer was observed. It is to be noted that ionic compounds were obtained from the corresponding neutral ones, **1a**, **1b**, which were isomeric mixtures of the *Z,Z* and *Z,E* compounds, and from **1c**, **1d**, **1e**, which were constituted only by the *Z,Z* isomer. The formation of new isomers comes from restricted rotation around the C<sub>phenyl</sub>-C<sub>methine</sub> bond. In complexes **2a**, **2b** containing mono-*ortho*-halogenosubstituted non-metallated phenyl rings, each *Z,Z* and *Z,E* configurational isomer gives two different conformations, with the *ortho*-halogeno substituent of the phenyl ring in an adjacent (**I**) or opposite (**II**) direction to the imine hydrogen (Fig. 1). The existence of rotational isomers has been proposed in the literature to explain the <sup>1</sup>H NMR of an analogous cyclometallated compound.<sup>17</sup> To identify these isomers, we center our attention on the chemical shift of H<sup>3</sup> *ortho* to the Ni-C bond. So, in the <sup>1</sup>H NMR spectrum of complex **2b** four doublets (*J* = 7.5 Hz) of different intensity 3 : 4 : 2 : 1 were observed at δ 5.57, 5.51, 5.22 and 5.14. These doublets were assigned to the aromatic proton *ortho* to the Ni-C bonds which as well as those from the collidine ligand are shifted to high fields, showing the *cis* arrangement of both ligands. The greatest effect was observed in the *Z,Z* isomers where the collidine was forced to be closer to the aromatic metallated ring, due to the proximity of the non-metallated aromatic ring. Their assignment to type **I** or **II** isomers can tentatively be proposed according to the isomer shifts (δ 5.22 (**I**) and 5.14 (**II**)) shown by this signal. Depending on the relative position of the *ortho*-halogen substituent, the collidine ligand is pushed in varying degrees towards the H<sup>3</sup> atom (see Scheme 4 for numbering of the atoms). The isomeric composition of compound **2b** could be described as a mixture of 10% *Z,Z*(**I**), 20% *Z,Z*(**II**), 30% *Z,E*(**I**) and 40% *Z,E*(**II**). Also significant differences in the position of the imine proton from the non-metallated moiety between the *Z,Z* and the *Z,E* compounds were observed. Those from the *Z,Z* compounds appeared at δ 9.15 and 9.07 and those from the *Z,E* compounds



**Fig. 1** Lowest-energy configurations of the *Z,Z* and *Z,E* isomers of complex **2a** as calculated with the PM3(tm) model.



**Scheme 4**

are included in the aromatic region because of the ring current effect from the heterocycle. Also the four signals of the iminic protons corresponding to the metallated moiety are clearly seen at  $\delta$  8.73, 8.48, 8.46 and 8.34 with the relative intensities 1 : 3 : 2 : 4.

The same trend in the chemical shift displacements was observed in the spectrum of complex **2a**. The isomers can be assigned analogously, the major one to *Z,Z* (I) and the two minor isomers to the *Z,E* (I) and *Z,E* (II) configurations.

NOESY experiments were carried out to confirm the proposed geometry of the isomers present in solution for complexes **2a** and **2b**. This enabled us to identify the long range contacts between the methylenic groups and the iminic protons (A, B, Fig. 1) in two of the isomers assigned to the *Z,Z* configuration, but only one (A) in the other two isomers assigned to the *Z,E* configuration. In the *Z,Z* isomers there was no evidence of any correlation that permitted their assignment to one of the rotational isomers, but the correlation between the aromatic *ortho* H from the non-metallated ring and one of the CH<sub>2</sub> of the bridge (C) in only one of the isomers *Z,E* suggests that it is probably the *Z,E* (I) isomer. In *Z,E* (II) no such correlation was observed. The transformation of the neutral to the ionic complexes does not alter the configuration adopted by the ligands. Thus, **2b** was mainly in the *Z,E* form, and **2a** mainly in the *Z,Z* form.

Compounds **2c**, **2d** and **2e** are *Z,Z*, as were the neutral compounds. Evidence that rotation around the C<sub>phenyl</sub>–C<sub>methinic</sub> bond is also restricted in ionic complexes from 2,6-dichloro substituted ligands is provided by their <sup>1</sup>H NMR spectra in the aromatic region. In **1e** the three aromatic protons of the non-metallated aromatic ring appeared as a broad singlet centered at  $\delta$  7.49, but for **2e** the signals split in two doublets at  $\delta$  7.25 and 7.74 and one triplet at  $\delta$  7.6.

The energy gap for rotation of the non-metallated ring in the *Z,Z* and *Z,E* isomers of complexes **1b** and **2b** has been calculated at the PM3(tm) level. The energy barrier for free rotation of 5–8 kcal mol<sup>–1</sup> calculated in the ionic complexes is higher than that calculated for the neutral ones, 2–3 kcal mol<sup>–1</sup>, according to the trend experimentally observed and an evidently lower impediment to rotation for the neutral complexes.

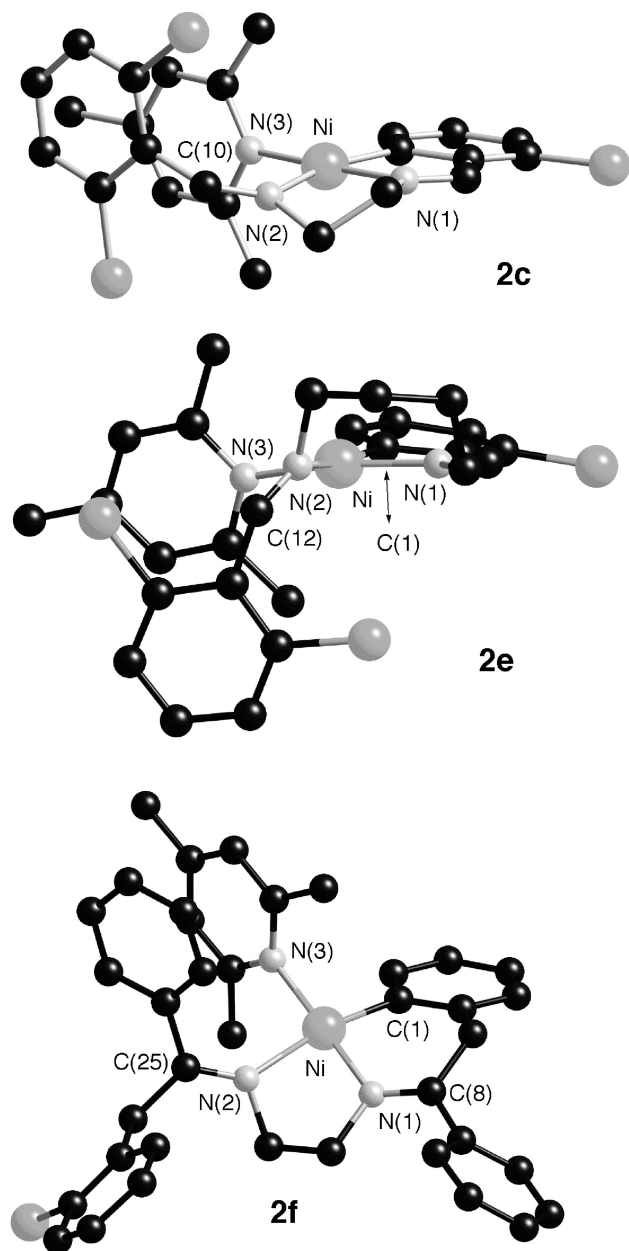
The aliphatic protons of the (CH<sub>2</sub>)<sub>n</sub> bridge appeared as sharp signals for all ionic complexes except in **2e** where broad signals were observed for each proton. Two sets of triplets for **2a–2c** and two triplets and one quintuplet for **2d** were observed.

The methyl resonance of collidine offers information about the number of isomers and also the dynamic processes. In the spectra of compounds **2a–2d** the two *ortho*-methyl groups and the two aromatic hydrogen atoms of the collidine in each isomer appear at the same chemical shift. It is noteworthy that the same behaviour is observed for compounds with di-*ortho*- and mono-*ortho*-halogen substituted non-metallated rings. However, for **2e**, the two *ortho*-methyl groups appeared at a different chemical shift. These findings can be explained if we bear in mind that the increase in bond angle N–Ni–N' upon increasing ring size (from five to seven membered) is countered by puckering of the ring, which would also increase the dihedral angle between the coordination plane and the non-metallated iminic moiety, as can be observed in the molecular structures of **2c** and **2e** (see below). The fast mutual interconversion of the two chelate ring conformations that are associated with the relative position of the non-metallated methinic moiety in the lower or upper side of the coordination plane involves an energy barrier that seems to increase with the number of atoms in the chain. This is broadly confirmed by semiempirical calculations of the energy barrier for movement of the non-metallated ring bridge system as it goes from one side of the coordination plane to the other. The results showed an energy gap rising progressively from the five- (5 kcal mol<sup>–1</sup>) to the six- (13 kcal mol<sup>–1</sup>) and to the seven- (17 kcal mol<sup>–1</sup>) membered ring (figure 4S Supporting material). The <sup>1</sup>H NMR spectrum of compound **2f** revealed the presence of only one isomer in the *E,Z* configuration. The chemical shifts of the bridge CH<sub>2</sub> groups are similar to those observed for the former neutral compound. This shows that they are not under the influence of the ring currents from the collidine ring, a situation that would only be possible in the *E,Z* configuration. The two *ortho*-methyl groups of the collidine appear at the same chemical shift, analogously to that observed for all complexes containing the ethylene bridge.

The crystal structures of compounds **2c**, **2e** and **2f** were determined in order to compare the effects of ring size. Fig. 2 shows the molecular structures with the numbering scheme. Selected bond distances, angles and crystallographic data are shown in Table 1. The determination of the molecular structure confirms the presence of the anionic terdentate ligand (CNN) and the collidine in the coordination sphere of the nickel atom, and also the proposed configurations, *Z,Z* in the case of complexes **2c** and **2e**, and *E,Z* in the case of **2f**. In **2c** the coordination sphere is nearly planar (the distances of Ni, C(1), N(1), N(2) and N(3) from the least-squares plane defined by these atoms are small, less than 0.06 Å). However, **2e** and **2f** show tetrahedral distortion from the ideal square-planar situation. Deviations from the mean plane defined as the coordination plane are larger, and the largest are those observed in compound **2f** (maximum deviations, 0.14 and 0.19 Å for **2e** and **2f** respectively). In all complexes the coordination plane and the collidine molecule are almost perpendicular (angles: 87.72 (**2c**), 76.8 (**2e**), 74.2° (**2f**)) and the *ortho* methyl groups of the aromatic amine occupy the apical sites in the coordination sphere (the estimated distances between the Ni and the C of the methyl groups being between 2.97 and 3.1 Å). Two rings, CNiN and NNiN, are present in these complexes. The angles C(1)–Ni–N(1) in the five-membered rings of **2c** (5,5) and **2e** (5,7) are 82.5

**Table 1** Selected structural data (bond lengths in Å, angles in °) for complexes **2c**, **2e** and **2f**

	<b>2c</b>		<b>2e</b>		<b>2f</b>
NiC(1)	1.94(3)	NiC(1)	1.906(3)	NiC(1)	1.910(4)
NiN(1)	1.90(2)	NiN(1)	1.912(2)	NiN(1)	1.892(3)
NiN(2)	2.01(2)	NiN(2)	1.978(2)	NiN(2)	2.006(3)
NiN(3)	1.92(2)	NiN(3)	1.918(2)	NiN(3)	1.902(3)
C(7)N(1)	1.28(3)	C(7)N(1)	1.287(4)	C(8)N(1)	1.284(5)
C(10)N(2)	1.28(2)	C(12)N(2)	1.265(3)	C(25)N(2)	1.265(3)
C(1)NiN(1)	82.5(12)	C(1)NiN(1)	84.30(11)	C(1)NiN(1)	92.36(15)
N(1)NiN(2)	83.8(10)	N(1)NiN(2)	93.07(9)	N(1)NiN(2)	84.03(13)
C(1)NiN(2)	165.3(11)	C(1)NiN(2)	171.72(10)	C(1)NiN(2)	163.51(15)
Dihedral angles					
N(1)NiN(2)C(10)	25.9(86)	N(1)NiN(2)C(12)	60.33(4)	N(1)NiN(2)C(10)	25.19(4)

**Fig. 2** Representation of the cationic fragment of complexes **2c**, **2e** and **2f** with the numbering scheme emphasizing the geometry of the coordination sphere.

and 84.30° in the range found for similar nickelacyclic compounds.<sup>10,18</sup> All these five-membered metallacycles are nearly planar, as are those described as containing the methinic group with deviations of C(7) from the plane in the range of 0.011(16)

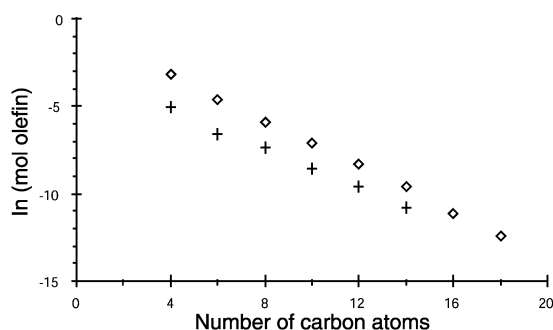
(**2c**) and −0.019(2) Å (**2e**). The bite angle C(1)–Ni–N(1) in the six-membered compound **2f** (6,5) is 92.36°, which is noticeably larger than the angle of 88.2° observed in a binuclear cyclic complex containing a bridging 2-imidoyl ligand (the only six-membered nickelacyclic compound found in the Cambridge Data Base).<sup>16</sup> The six-membered metallacycle is in a boat conformation with the Ni and the C(7) at the apex of the boat.

In compounds **2c**, **2f** and **2e** the angles N(1)–Ni–N(2) are 83.8(10), 84.03(13) and 93.07(9)° close to those observed in square-planar nickel complexes in which the Schiff bases are coordinated through both N atoms giving five- or seven-membered rings.<sup>19,20</sup> The NCH<sub>2</sub>CH<sub>2</sub>N chain in **2c** and **2f** shows the characteristic staggered conformation. The seven-membered metallacycle **2e** adopts a twist-chair conformation. It is also interesting, by way of confirming the experimental evidence from the NMR spectra and the results obtained by PM3 calculations, that in none of the structurally characterized compounds is the methinic group from the non-metallated moiety contained in the coordination plane. The dihedral angles defined by N(1), Ni, N(2) and the carbon of the non-metallated iminic group are as follows: 25.079 for **2c**, 60.334 for **2e**, and 25.194° for **2f**. Also the dichlorophenyl ring in **2c** and **2e** and the phenyl ring in **2f** are twisted out of the iminic plane and are nearly orthogonal to each other. The planes between the collidine group and the 2,6-dichlorophenyl or the phenyl group are roughly parallel. The angles between the normals to the planes are 3.6, 9.9 and 13.7° in compounds **2c**, **2e** and **2f** respectively. The Ni–C(1) distances, ranging from 1.906 to 1.943 Å are comparable to those in arylnickel(II) complexes. The Ni–N(1) and Ni–N(2) distances are also in their normal range, when *trans* influences of anionic carbon donors and amine ligands are taken into account.<sup>21</sup>

Note that the lengths of the carbon–nitrogen double bonds in the metallacycles are essentially the same as those from the non-metallated arm and also compare well with organic C=N bonds, in accord with the non-back-bonding character of the N–Ni bond.

#### Ionic complexes [Ni(CNN')(CH<sub>3</sub>CN)]BF<sub>4</sub>

To test these ionic complexes as precursors of active catalytic species in the olefin oligomerization reaction it is convenient to have at least one labile position in the coordination sphere. Therefore we prepared analogous compounds using CH<sub>3</sub>CN instead of 2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N as stabilizing ligand. Such complexes with a labile position and a Ni–C bond might give, after insertion of olefin in the Ni–C bond and subsequent β elimination, an active nickel hydride intermediate. The yellow compounds, **3c**, **3d** and **3f**, were obtained by reaction of the neutral compounds, **1c**, **1d** and **1f**, in THF or acetone, with a small quantity in excess of CH<sub>3</sub>CN and a stoichiometric amount of TIBF<sub>4</sub>. Unfortunately, satisfactory microanalyses were only obtained for **3c**. The MS/FAB of **3d** and MS/ESI of **3f** clearly



**Fig. 3** (◇) Schulz–Flory distribution of olefins at 25 °C and 20 bars of ethylene ( $\alpha = 0.27$ ,  $\beta = 2.73$  where  $\alpha$  is the molar growth factor and  $\beta$  is the chain length distribution). Each point represents the whole mixture of linear and branched olefins of  $C_n$ . (+) The same experiment performed in the presence of 1-hexene ( $\alpha = 0.32$ ,  $\beta = 2.15$ ).

show a signal corresponding to  $[M - BF_4 - CH_3CN]^+$ . For **3f** the fragment corresponding to  $[M - BF_4]^+$  was also observed. The IR spectra revealed the presence of tetrafluoroborate as an anion not coordinated to nickel. In common with almost all N-bonded nitrile complexes, our products show a very weak band  $\nu(CN)$  at higher frequencies ( $2252\text{ cm}^{-1}$ ) than those of the free nitrile.<sup>22</sup> Two bands, at  $1650$  and  $1608\text{ cm}^{-1}$ , assigned to the  $\nu(C=N)$  of the diimine ligand were observed.

The  $^1\text{H}$  NMR spectra of complexes **3c** and **3d** at low temperature (240 K) were consistent with the presence of a single isomer in solution, which according to the shift experienced by the iminic protons is the *Z,Z*. All the signals were slightly broad, except those assigned to the proton *ortho* to the metal center, at  $\delta$  6.5, which was very broad. The spectra of both compounds also showed the nitrile methyl protons as a singlet downfield from free acetonitrile. The methylene protons were observed as separate broad singlets. In the aromatic region two multiplets, the result of a pair and a single proton of the metallated ring, and a broad singlet for the protons of the non-metallated ring were observed. This was similar to the signal pattern found for the neutral complexes where there was free rotation of this ring. However the  $^1\text{H}$  NMR spectrum of **3f** in acetone was complex revealing the existence of two isomers in nearly the same relative amounts.

### Ethylene oligomerization

When  $\text{CH}_2\text{Cl}_2$  solutions of the ionic compounds **3c** and **3d** were treated with ethylene at moderate temperature and pressure the starting compounds were recovered unchanged. On increasing the pressure and temperature up to 70 bars and 70 °C only decomposition of the complex was observed. However, when **3f** was used the oligomerization of ethylene to a Schulz–Flory type distribution (see Fig. 3) of linear and branched olefins in the range  $C_4$ – $C_{18}$  was observed (detected in the crude catalytic mixture by GC analysis). A turnover frequency of  $1100\text{ h}^{-1}$  was obtained in experiments carried out in 3 hours at 25 °C under 20 bar of initial ethylene pressure. The molar growth factor  $\alpha$  of the reaction gave values around 0.3, according to a maximum weight fraction at  $C_4$ . Characterization by  $^1\text{H}$  NMR spectroscopy of the oligomer fraction insoluble in MeOH (mainly  $C_{18}$ – $C_{22}$ ) reveals the presence of terminal and internal olefins in a ratio of 1 : 3. The corresponding resonances were observed at  $\delta$  2.0, attributed to allylic methylene groups of the type  $\text{CH}_2\text{--CH=CH}_2$ , a broad resonance centered at  $\delta$  5.5 attributed to *cis*- and *trans*- $\text{CH=CH}$  and at  $\delta$  5.8 and 4.9 attributed to vinyl end groups  $\text{CH=CH}_2$  and  $\text{CH=CH}_2$  respectively. Aliphatic proton resonances were observed at  $\delta$  1.27 for the  $\text{CH}_2$  group and at  $\delta$  0.9 for the  $\text{CH}_3$  group in a ratio close to 3 : 1.

The different behavior shown by complexes **3c**–**3d** and **3f** as precursors in the oligomerization reaction may be related to the starting step for the generation of the active hydride species, ethylene insertion in the Ni–C bond and subsequent  $\beta$  elimin-

ation. This process occurs in the six- but not in five-membered nickelacycles, showing the extreme inertness to insertion reactions of this five-membered metallacycle, probably due to an unfavorable transition-state geometry, according to our previous results.<sup>10</sup>

Cationic nickel(II) catalysts based on unhindered  $\alpha$ -diimine ligands used by Brookhart and co-workers exhibit high activities and selectivities for the preparation of linear  $\alpha$ -olefins ranging from  $C_4$  to  $C_{26}$ .<sup>2</sup> Comparatively low activity is obtained using **3f** as precursor. This may be related to the different structural properties of the diimine ligands in our complex. The terdentate ligand CNN' present in the precursor complex leads, after the activation step, to the presence of a styrenyl group dangling close to the metal center that could stabilize the active species and compete with the incoming ethylene.

The formation of branched olefins might be related to the competition between ethylene and  $\alpha$ -olefins in the chain propagation reaction. A test experiment was carried out by adding 1-hexene to an oligomerization reaction in a 200 : 1 excess with respect to the nickel precursor. A decrease in the turnover frequency to  $170\text{ h}^{-1}$  and changes either in the molecular weight distribution ( $\alpha$  increases) (see Fig. 3) or in the relative amounts of isomers in each of the  $C_{6+n}$  fractions were observed. So, the competition between ethylene and 1-hexene for the hydride and the alkyl olefin intermediate species decreased the reaction rate and allowed the incorporation of both olefins into the oligomeric mixture giving the branched olefin.

### Experimental

$^1\text{H}$  NMR spectra were obtained using Bruker DRX 250, Varian XL-500 and Varian Gemini-200 spectrometers. Chemical shifts (in ppm) were measured relative to  $\text{SiMe}_4$ . Coupling constants in Hz, numbering is as shown in Scheme 4. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses were performed by the Serveis Científics-Tècnics de la Universitat de Barcelona using an Eager 1108 microanalyzer. Mass spectra (FAB or ES) were recorded on a Fisons VG-Quattro spectrometer. The oligomer products were analysed on a Hewlett-Packard 5890 gas chromatograph equipped with a 50 m ultra-2 cross-linked 5% phenyl methyl silicone capillary column and a flame ionization detector. The molecular mechanics calculations were performed using the Mac Spartan Plus 1.1.7 program.<sup>23</sup>

### Materials and synthesis

All manipulations of organonickel compounds were carried out under a purified nitrogen atmosphere using standard Schlenk and high-vacuum techniques. The solvents were dried and degassed by standard procedures. All reagents are commercially available except 2-chlorobenzyl phenyl ketone<sup>24</sup> and  $[\text{Ni}(\text{cod})_2]$ <sup>25</sup> which were prepared following published methods. Ethylene (99.95% quality) was used as received.

### Synthesis of the ligands

**a–e.** These ligands were prepared by standard procedures.<sup>26,27</sup> Stoichiometric amounts of the halogenoaryl carbonyl compound and the primary diamines were dissolved in ethanol and the resulting solution was refluxed for 30 minutes. The solvent was then evaporated and the crude product obtained as a white solid. The ligands can be recrystallized in hot ethanol, if necessary (yields = 75–90%).

**f.** This was obtained by refluxing for three days a mixture of 8 mmol of 2-chlorobenzyl phenyl ketone, 4 mmol of 1,2-diaminoethane and a catalytic amount of  $\text{H}_2\text{SO}_4$  in toluene in a Dean–Stark apparatus. After cooling the solvent was removed in vacuum and ethanol added. After standing for several days in a refrigerator white-yellow crystals were obtained (yield = 66%).

Analytical, IR and  $^1\text{H}$  NMR data of the new ligands are deposited as Electronic Supplementary Information (ESI).

### Synthesis of the neutral complexes

**1a.** Over a suspension of 3.42 mmol of  $[\text{Ni}(\text{cod})_2]$  in 10 ml of THF at  $-78^\circ\text{C}$ , 3.59 mmol (5% excess) of ligand **a** were added. Then the mixture was stirred for 16 h at room temperature. The formation of an orange solid was observed. The solid was filtered off, washed several times with diethyl ether and water, and finally dried in vacuum (yield = 77%) (Found: C, 42.6; H, 3.3; N, 6.3. Calc. for  $\text{C}_{16}\text{H}_{14}\text{Br}_2\text{N}_2\text{Ni}$ : C, 42.44; H, 3.12; N, 6.19%). IR:  $\nu(\text{C}=\text{N})$  1638 and  $1608\text{ cm}^{-1}$ .  $^1\text{H}$  NMR [500 MHz, acetone- $d_6$ ; mixture of two isomers A (Z,Z), B (Z,E)]:  $\delta$  3.75 (t,  $^3J = 6$ ,  $\text{CH}'_2$  B), 3.86 (t,  $^3J = 6$ ,  $\text{CH}'_2$  A), 3.97 (t,  $^3J = 6.5$ ,  $\text{CH}_2$  B), 4.33 (t,  $^3J = 6.1$ ,  $\text{CH}_2$  A), 6.9–7.8 (m), 8.32 (s,  $\text{H}_{\text{im}}$  B), 8.36 (s,  $\text{H}_{\text{im}}$  A), 8.87 (s,  $\text{H}'_{\text{im}}$  A), 9.06 (s,  $\text{H}'_{\text{im}}$  B) and 9.19 (d,  $^3J = 7.2$ ,  $\text{H}^6$  A).

**1b.** The complex was prepared following the above procedure, but using ligand **b** (yield = 93%) (Found: C, 51.6; H, 3.4; N, 7.4. Calc. for  $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Ni}$ : C, 52.81; H, 3.88; N, 7.70%). IR:  $\nu(\text{C}=\text{N})$  1637 and  $1612\text{ cm}^{-1}$ .  $^1\text{H}$  NMR [500 MHz, acetone- $d_6$ , isolated isomer Z,E]:  $\delta$  3.76 (td,  $^3J = 6.8$ ,  $^4J = 1.3$ ,  $\text{CH}'_2$ ), 4.01 (td,  $^3J = 6.8$ ,  $^4J = 2.0$ ,  $\text{CH}_2$ ), 6.9–7.6 (m), 8.29 (t,  $^4J = 1.8$ ,  $\text{H}_{\text{im}}$ ) and 8.91 (t,  $^4J = 2.0$  Hz,  $\text{H}'_{\text{im}}$ ).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ , isomer Z,Z from the mixture of both isomers):  $\delta$  3.8 (td,  $^3J = 6.3$ ,  $^4J = 1.7$ ,  $\text{CH}'_2$ ), 4.3 (td,  $^3J = 6.3$ ,  $^4J = 1.2$ ,  $\text{CH}_2$ ), 6.9–7.7 (m), 8.31 (t,  $^4J = 1.8$ ,  $\text{H}_{\text{im}}$ ), 8.9 (broad singlet,  $\text{H}'_{\text{im}}$ ) and 9.15 (dd,  $^3J = 8.5$ ,  $^4J = 1.5$ ,  $\text{H}^6$ ).

**1c.** The complex was prepared following the general procedure described for **1a**, by using ligand **c** (yield = 86%) (Found: C, 43.9; H, 2.8; N, 6.3. Calc. for  $\text{C}_{16}\text{H}_{12}\text{Cl}_4\text{N}_2\text{Ni}$ : C, 44.40; H, 2.79; N, 6.47%). IR:  $\nu(\text{C}=\text{N})$  1651 and  $1604\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  3.93 (td,  $^3J = 6.4$ ,  $^4J = 2.1$ , 2H,  $\text{CH}'_2$ ), 4.39 (td,  $^3J = 7.0$ ,  $^4J = 1.3$ , 2H,  $\text{CH}_2$ ), 6.9–7.5 (m, 6H), 8.57 (t,  $^4J = 1.7$ , 1H,  $\text{H}_{\text{im}}$ ) and 8.80 (broad singlet, 1H,  $\text{H}'_{\text{im}}$ ).

**1d.** The complex was prepared following the general procedure described for **1a**, by using ligand **d** and toluene as the solvent (yield = 87%) (Found: C, 44.8; H, 3.3; N, 6.1. Calc. for  $\text{C}_{17}\text{H}_{14}\text{Cl}_4\text{N}_2\text{Ni}$ : C, 45.70; H, 3.16; N, 6.27%). IR:  $\nu(\text{C}=\text{N})$  1647 and  $1601\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  2.41 (q,  $^3J = 6.1$ , 2H,  $\text{CH}'_2$ ), 3.69 (td,  $^3J = 6.1$ ,  $^4J = 1.3$ , 2H,  $\text{CH}'_2$ ), 4.43 (td,  $^3J = 6.9$ ,  $^4J = 1.2$ , 2H,  $\text{CH}_2$ ), 6.8–7.6 (m, 6H), 8.42 (t,  $^4J = 1.3$ ,  $\text{H}_{\text{im}}$ ) and 8.65 (t,  $^4J = 1.8$ ,  $\text{H}'_{\text{im}}$ ).

**1e.** The complex was prepared following the procedure described for **1d**, by using ligand **e** (yield = 85%) (Found: C, 47.8; H, 3.7; N, 6.0. Calc. for  $\text{C}_{18}\text{H}_{16}\text{Cl}_4\text{N}_2\text{Ni}$ : C, 46.91; H, 3.50; N, 6.08%). IR:  $\nu(\text{C}=\text{N})$  1629 and  $1604\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ): very broad signals in the aliphatic zone, corresponding to the  $(\text{CH}_2)_4$  bridge,  $\delta$  6.6–7.6 (m, 6H), 8.35 (broad singlet,  $\text{H}_{\text{im}}$ ) and 8.67 (broad singlet,  $\text{H}'_{\text{im}}$ ).

**1f.** The complex was prepared following the procedure described for **1d**, by using ligand **f** (yield = 85%) (Found: C, 64.4; H, 5.1; N, 4.4. Calc. for  $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{N}_2\text{Ni}$ : C, 66.22; H, 5.15; N, 4.82%).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  3.68 (t,  $^3J = 6.6$ , 2H,  $\text{CH}'_2$ ), 4.29 (t,  $^3J = 6.5$ , 2H,  $\text{CH}_2$ ), 4.24 (s, 2H,  $\text{CH}_{2\text{bz}}$ ), 4.43 (s, 2H,  $\text{CH}_{2\text{bz}}$ ), 6.6–7.6 (m, 16H) and 8.63 (m, 2H).

### Synthesis of ionic complexes with 2,4,6- $\text{Me}_3\text{C}_5\text{H}_2\text{N}$

**2a.** In 20 ml of THF, 9.1 mmol of 2,4,6- $\text{Me}_3\text{C}_5\text{H}_2\text{N}$  were added over 8.8 mmol of the neutral complex **1a**, and, while stirring, 9.1 mmol of  $\text{TlBF}_4$ . A suspension of the insoluble thallium halide was formed instantaneously, and after 30 minutes was separated by filtering over zeolite. The solvent was then evaporated to dryness and the remaining resin stirred with ether until a suspension of yellow solid was obtained. The

product was filtered off, and washed several times with water and ether (yield = 64%) (Found: C, 49.8; H, 4.3; N, 7.2. Calc. for  $\text{C}_{24}\text{H}_{25}\text{BBrF}_4\text{N}_3\text{Ni}$ : C, 49.62; H, 4.34; N, 7.23%).  $^1\text{H}$  NMR [500 MHz, acetone- $d_6$ , mixture of three isomers, (Z,Z)-A, and two rotational isomers of (Z,E)-B]:  $\delta$  2.31 (s,  $\text{Me}_p$ , A), 2.44 (s,  $\text{Me}_p$ , B), 2.47 (s,  $\text{Me}_p$ , B), 3.32 (s,  $\text{Me}_o$ , A), 3.50 (s,  $\text{Me}_o$ , b), 3.55 (s,  $\text{Me}_o$ , b), 3.83 (t,  $\text{CH}_2$ , B), 3.97 (t,  $^3J = 5.6$ ,  $\text{CH}'_2$ , A), 3.97 (t,  $^3J = 6.5$ ,  $\text{CH}_2$ , B), 4.33 (t,  $^3J = 6.1$ ,  $\text{CH}_2$ , A), 5.23 (d,  $^3J = 7.5$ ,  $\text{H}^3$ , A), 5.51 (d,  $\text{H}^3$ , B), 5.57 (d,  $\text{H}^3$ , B), 6.8–7.8 (m), 8.47 (s,  $\text{H}_{\text{im}}$ , A), 8.48 (s,  $\text{H}_{\text{im}}$ , B) and 9.06 (s,  $\text{H}'_{\text{im}}$ , A).

**2b.** The complex was prepared following the procedure described for **2a**, by using **1b** (yield = 65%) (Found: C, 53.4; H, 4.8; N, 7.9. Calc. for  $\text{C}_{24}\text{H}_{25}\text{BClF}_4\text{N}_3\text{Ni}$ : C, 53.74; H, 4.70; N, 7.83%).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ , mixture of four isomers, in order of decreasing abundance: A, B, C, D):  $\delta$  2.31 (s,  $\text{Me}_p$ , C), 2.37 (s,  $\text{Me}_p$ , D), 2.44 (s,  $\text{Me}_p$ , A), 2.47 (s,  $\text{Me}_p$ , B), 3.28 (t,  $\text{CH}'_2$ , A), 3.31 (s,  $\text{Me}_o$ , C), 3.33 (s,  $\text{Me}_o$ , D), 3.51 (s,  $\text{Me}_o$ , A), 3.55 (s,  $\text{Me}_o$ , B), 3.84 (t,  $^3J = 6.3$ ,  $\text{CH}_2$ , A), 3.98 (t,  $^3J = 6.0$ ,  $\text{CH}_2$ , B and C), 4.08 (t,  $\text{CH}_2$ , D), 4.31 (t,  $^3J = 6.8$ ,  $\text{CH}'_2$ , B), 4.54 (t,  $^3J = 5.8$ ,  $\text{CH}'_2$ , C), 4.70 (t,  $\text{CH}'_2$ , D), 5.14 (d,  $^3J = 7.0$ ,  $\text{H}^3$ , D), 5.22 (d,  $^3J = 7.5$ ,  $\text{H}^3$ , C), 5.51 (d,  $^3J = 7.5$ ,  $\text{H}^3$ , A), 5.57 (d,  $^3J = 7.5$ ,  $\text{H}^3$ , B), 6.65–7.70 (m), 8.34 (s,  $\text{H}_{\text{im}}$ , A), 8.46 (s,  $\text{H}_{\text{im}}$ , C), 8.48 (s,  $\text{H}_{\text{im}}$ , B), 8.73 (s,  $\text{H}_{\text{im}}$ , D), 9.07 (s,  $\text{H}'_{\text{im}}$ , D) and 9.15 (s,  $\text{H}'_{\text{im}}$ , C).

**2c.** The complex was prepared following the procedure described for **2a**, by using **1c** and acetone as the solvent (yield = 91%) (Found: C, 47.0; H, 4.1; N, 6.9. Calc. for  $\text{C}_{24}\text{H}_{23}\text{BCl}_3\text{F}_4\text{N}_3\text{Ni}$ : C, 47.62; H, 3.83; N, 6.94%).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ):  $\delta$  2.32 (s,  $\text{Me}_p$ ), 3.27 (s,  $\text{Me}_o$ ), 4.03 (t,  $^3J = 6.2$ ,  $\text{CH}'_2$ ), 4.66 (t,  $^3J = 6.2$ ,  $\text{CH}_2$ ), 5.14 (d,  $^3J = 7.4$ ,  $\text{H}^3$ ), 6.86 (t,  $^3J = 7.8$ ), 7.02 (d,  $^3J = 8.0$  Hz), 7.3–7.5 (m), 8.70 (s,  $\text{H}_{\text{im}}$ ) and 9.04 (s,  $\text{H}'_{\text{im}}$ ).

**2d.** The complex was prepared following the procedure described for **2a**, by using **1d** (yield = 78%) (Found: C, 48.0; H, 4.1; N, 6.8. Calc. for  $\text{C}_{25}\text{H}_{25}\text{BCl}_3\text{F}_4\text{N}_3\text{Ni}$ : C, 48.48; H, 4.07; N, 6.78%).  $^1\text{H}$  NMR:  $\delta$  2.31 (s, 3H,  $\text{Me}_p$ ), 2.43 (m, 2H,  $\text{CH}'_2$ ), 3.17 (s, 6H,  $\text{Me}_o$ ), 3.75 (t,  $^3J = 6.8$ , 2H,  $\text{CH}'_2$ ), 4.88 (t,  $^3J = 6.5$ , 2H,  $\text{CH}_2$ ), 4.90 (d,  $^3J = 7.5$  Hz,  $\text{H}^3$ ), 6.6–7.5 (m, 7H), 8.33 (s, br,  $\text{H}_{\text{im}}$ ) and 8.67 (s, br,  $\text{H}'_{\text{im}}$ ).

**2e.** The complex was prepared following the procedure described for **2a**, by using **1e** (yield = 77%) (Found: C, 49.7; H, 4.5; N, 6.6. Calc. for  $\text{C}_{26}\text{H}_{27}\text{BCl}_3\text{F}_4\text{N}_3\text{Ni}$ : C, 49.30; H, 4.30; N, 6.63%).  $^1\text{H}$  NMR (250 MHz, acetone- $d_6$ ): between  $\delta$  1.5 and 3 (broad signals,  $\text{CH}'_2$  and  $\text{CH}_2$ ), 2.32 (s, 3H,  $\text{Me}_p$ ), 2.88 (s, 3H,  $\text{Me}_o$ ), 3.35 (s, 3H,  $\text{Me}_o$ ), 3.56 (dm,  $^2J = 210$ , 2H,  $\text{CH}'_2$ ), 4.58 (dm,  $^2J = 340$ , 2H,  $\text{CH}_2$ ), 4.78 (d,  $^3J = 7.5$ , 1H,  $\text{H}^3$ ), 6.57 (s,  $\text{H}_m$ ), 6.6–7.6 (m), 8.29 (s,  $\text{H}_{\text{im}}$ ) and 8.67 (s,  $\text{H}'_{\text{im}}$ ).

**2f.** The complex was prepared following the procedure described for **2a**, by using **1f** (yield = 71%) (Found: C, 62.5; H, 5.2; N, 5.6. Calc. for  $\text{C}_{38}\text{H}_{37}\text{BClF}_4\text{N}_3\text{Ni}$ : C, 63.68; H, 5.20; N, 5.86%).  $^1\text{H}$  NMR (250 MHz, acetone- $d_6$ ):  $\delta$  2.17 (s, 3H,  $\text{Me}_p$ ), 3.24 (s, 6H,  $\text{Me}_o$ ), 3.86 (t,  $^3J = 6.5$ , 2H,  $\text{CH}'_2$ ), 4.37 (s, 2H,  $\text{CH}_{2\text{bz}}$ ), 4.60 (s, 2H,  $\text{CH}_{2\text{bz}}$ ), 4.86 (t,  $^3J = 6.5$ , 2H,  $\text{CH}_2$ ), 6.02 (d,  $^3J = 7.6$ , 1H,  $\text{H}^3$ ), 6.54 (t,  $^3J = 6.8$ , 1H), 6.76 (s, 2H,  $\text{H}_m$ ), 6.79 (t,  $^3J = 6.9$ , 1H) and 6.9–7.7 (m, 15H).

### Synthesis of ionic complexes with acetonitrile

**3c.** The complex was prepared following the procedure described for **2a**, by using a 300% excess of acetonitrile instead of 2,4,6- $\text{Me}_3\text{C}_5\text{H}_2\text{N}$  (yield = 68%) (Found: C, 40.4; H, 3.0; N, 7.9. Calc. for  $\text{C}_{18}\text{H}_{15}\text{BCl}_3\text{F}_4\text{N}_3\text{Ni}$ : C, 41.17; H, 2.88; N, 8.00%).  $^1\text{H}$  NMR (240 K, 250 MHz, acetone- $d_6$ ):  $\delta$  2.18 (s, 3H,  $\text{Me}_{\text{nit}}$ ), 3.92 (broad triplet, 2H,  $\text{CH}'_2$ ), 4.52 (broad triplet, 2H,  $\text{CH}_2$ ), 6.66 (broad singlet, 1H,  $\text{H}^3$ ), 7.0–7.7 (m, 5H), 8.58 (s, 1H,  $\text{H}_{\text{im}}$ ) and 9.02 (s, 1H,  $\text{H}'_{\text{im}}$ ).

**Table 2** Crystal data and structure refinement for compounds **2c**, **2e** and **2f**

	<b>2c</b>	<b>2e</b>	<b>2f</b>
Empirical formula	C <sub>24</sub> H <sub>23</sub> BCl <sub>3</sub> F <sub>4</sub> N <sub>3</sub> Ni	C <sub>26</sub> H <sub>27</sub> BCl <sub>3</sub> F <sub>4</sub> N <sub>3</sub> Ni	C <sub>38</sub> H <sub>37</sub> BClF <sub>4</sub> N <sub>3</sub> Ni·C <sub>3</sub> H <sub>7</sub>
Formula weight	605.32	633.38	759.76
<i>T</i> /K	293(2)	298(2)	298(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	13.745(8)	8.310(2)	11.9227(4)
<i>b</i> /Å	13.387(7)	11.8520(15)	12.9488(5)
<i>c</i> /Å	14.802(5)	14.316(4)	23.6540(9)
<i>a</i> <sup>o</sup>		98.571(15)	
<i>β</i> <sup>o</sup>	98.22(5)	98.98(2)	97.5220(10)
<i>γ</i> <sup>o</sup>		93.02(2)	
<i>V</i> /Å <sup>3</sup>	2696(2)	1373.0(5)	3620.4(2)
<i>Z</i>	4	2	4
<i>μ</i> /mm <sup>−1</sup>	1.063	1.048	0.665
Reflections collected	2924	12380	15010
Independent reflections	2808	6742	6383
	[ <i>R</i> (int) = 0.0101]	[ <i>R</i> (int) = 0.0182]	[ <i>R</i> (int) = 0.0284]
Final <i>R</i> 1, <i>wR</i> 2 indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0677, 0.1684	0.0481, 0.1317	0.0537, 0.1366
(all data)	0.2045, 0.2675	0.0597, 0.1408	0.0723, 0.1509

**3d.** The complex was prepared following the procedure described for **3c**, by using **1d** (yield = 86%) (Found: C, 40.3; H, 3.6; N, 6.2. Calc. for C<sub>19</sub>H<sub>17</sub>BCl<sub>3</sub>F<sub>4</sub>N<sub>3</sub>Ni: C, 42.32; H, 3.18; N, 7.79%). MS/FAB(+): M<sup>+</sup> − CH<sub>3</sub>CN, *m/z* 411 <sup>1</sup>H NMR [250 MHz, CDCl<sub>3</sub> (broad signals, no couplings detected)]: δ 2.20 (br, 3H, Me<sub>nit</sub>), 2.39 (br s, 2H, CH'<sub>2</sub>), 3.52 (br s, 2H, CH''<sub>2</sub>), 4.38 (br s, 2H, CH<sub>2</sub>), 6.46 (br s, 1H, H<sup>3</sup>), 6.96 (br s, 2H), 7.57 (br s, 3H), 8.18 (br s, H<sub>im</sub>) and 8.67 (br s, H'<sub>im</sub>).

**3f.** The complex was prepared following the procedure described for **3c**, by using **1f** (yield = 81%). MS/ESP(+): M<sup>+</sup> − CH<sub>3</sub>CN, *m/z* 507. <sup>1</sup>H NMR (250 MHz, acetone-*d*<sub>6</sub>, two isomers present in solution): δ 1.97 (s, Me<sub>nit</sub>), 3.75–3.82 (two overlapped t, CH'<sub>2</sub>), 3.40–4.90 (m, CH'<sub>2bz</sub> + CH<sub>2</sub>), 4.62 (br s, CH<sub>2bz</sub>), 6.39 (d, <sup>3</sup>*J* = 7.2, H<sup>3</sup>), 6.7–7.6 (m, 15H) and 8.42 (m, 2H).

### Structure determinations

**Complex 2c.** A prismatic crystal of complex **2c** was mounted on an Enraf-Nonius CAD4 four circle diffractometer. Crystal data are summarized in Table 2. Graphite monochromatized Mo-*K*α radiation with λ = 0.71069 Å was used. Data were corrected for Lorentz and polarization effects. The structure was solved by Patterson synthesis, using the SHELXS 86 computer program<sup>28</sup> for crystal structure determination and refined by full-matrix least squares with SHELXL 93,<sup>29</sup> using 2758 reflections (very negative intensities were not included). All hydrogen atoms were computed and refined with an overall isotropic thermal parameter using a riding model.

**Complex 2e.** A block-like, translucent, intense orange crystal of complex **2e** was mounted on a Siemens SMART CCD area detector single crystal diffractometer with graphite monochromatized Mo-*K*α radiation (λ = 0.71073 Å) operating at room temperature. Absorption corrections were applied using SADABS.<sup>30</sup> The structure was solved by direct methods using SHELXS 86 for crystal structure determination and refined by full-matrix least squares on *F*<sup>2</sup>, with SHELXL 93,<sup>29</sup> 6742 Reflections were included in the refinement and no restraints were applied to the 343 parameters. Hydrogen atoms were included in calculated positions and refined in riding mode.

**Complex 2f.** A yellow block crystal of complex **2f** was used and treated as for **2c**. 6383 Reflections were included in the refinement and 73 restraints applied to the 479 parameters. Hydrogen atoms were included in calculated positions and refined in riding mode. The intensity data of the three struc-

tures were collected with different equipment, **2e** and **2f** with a CCD detector and **2c** with a standard detector. The different exposure time produced a ratio between the number of independent reflections and refined parameters of about 20 and 15 : 1 with the CCD detector and 9 : 1 with the standard detector. This fact explains the lower accuracy of the structure determination of **2c**.

CCDC reference numbers 153646, 153647 and 153658.

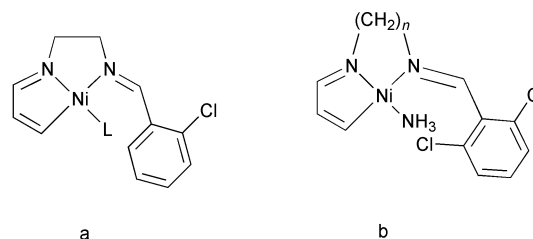
See <http://www.rsc.org/suppdata/dt/b0/b008520k/> for crystallographic data for **2e** (153646) and **2f** (153647) in CIF or other electronic format.

### General procedure for the reactions with ethylene

Ethylene reactions were performed on a Berghof type reactor of 100 ml capacity equipped with a magnetic stirring bar, two gas valves, a manometer, and a thermocouple or a stainless-steel autoclave fitted with an external jacket connected to a thermostatted bath. 4 × 10<sup>−5</sup> mol of the catalyst precursor were dissolved in 15 ml of CH<sub>2</sub>Cl<sub>2</sub>, and transferred under argon *via* syringe to the reactor, which had previously been purged. Ethylene was then admitted until the desired pressure was reached. Gas samples were analysed by GC. The quantitative distribution of the oligomers obtained was determined by GC analysis, using undecane as internal standard.

### Calculations on the restricted rotation of aromatic rings (complexes **1a** and **1b**) and on the restricted movement of the (CH<sub>2</sub>)<sub>*n*</sub> bridges (**1c**, **1d**, **1e**)

The calculations were made using the software pack MacSpartan Plus. The molecules were simplified in order to reduce the calculation time (see Scheme 5(a, b)). Isomers *Z,Z* and *Z,E*

**Scheme 5**

of complexes **1a** and **1b** (Scheme 5a) were minimized employing the semiempirical level of calculation PM3(tm). The dihedral angle ω was forced to rotate 360° in 10° intervals. For every angle minimization of the structure was realized, at the same

level of calculation. Complexes with  $n = 2, 3$  or  $4$  (Scheme 5b) were minimized, and then the dihedral angle  $\omega$  turned from  $60$  to  $-60^\circ$ ; at every step a new minimization with the fixed angle was realized. Each single point energy was then calculated by using the *ab initio* method 3-21G(\*), included in the same calculation software pack, in order to estimate the energy barrier for this fluxional process for each value of  $n$ .

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