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Nickelacycles with anionic C–N–N′ terdentate α-diimine based ligands. Reaction with ethylene †

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A series of chloro-substituted 1,4-diaza-1,3-butadiene (**a**–**e**) and pyridine-imine (**f**, **g**) ligands have been prepared. The oxidative addition of five of the bidentate ligands to $[Ni(cod)_2]$ gave a group of neutral complexes containing an anionic terdentate ligand [NiCl(CNN′)] with five-and six-membered nickelacycles (**1a**, **1b**, **1e**, **1f**, **1g**). Two isomers were obtained with the 1,4-diaza-1,3-butadiene ligands **a** and **b** due to a 1,3-prototropic rearrangement. The reaction of the neutral complexes (**1**) with $TlBF_4$ in the presence of 2,4,6-trimethylpyridine yields well-defined cationic complexes $[NiL(CNN')]BF_4$ (**2**). The low solubility of the neutral compounds (**1**) complicates their characterisation which could be completed only after preparation of the ionic complexes (**2**). The molecular structure of compound **2a** $[NiL[(2\text{-}Ph)CH_2\text{–}N{=}C(CH_3)C(CH_3){=}N\text{–}CH_2\text{–}(2\text{-}ClC_6H_4)]]BF_4$ has been determined by X-ray diffraction methods. Four ionic complexes $[Ni(NCCH_3)(CNN')]BF_4$ (**3**) have been obtained and tested as precursors of catalytic species in the reaction of ethylene oligomerisation. The catalytic results are limited, as expected, due to the structural type of the nitrogenated ligands. However it is possible to use these relatively stable nickelacycles as one-component precursors for the oligomerisation reaction. Similar palladacycles are not suitable for this purpose.

Introduction

In recent years nitrogen ligands containing the 1,4-disubstituted-1,4-diaza-1,3-butadiene skeleton (R-DAB) have been extensively studied due to their application in a wide variety of catalytic reactions (Chart 1).[1,2] After the initial simple open chain molecules other families of compounds with increased steric strain have been developed.[3] In particular, the group of Ar-BIAN (bis-(aryl)acenaphthenequinonediimine) ligands investigated by Elsevier and co-workers have been used in the formation of nickel, palladium and ruthenium complexes employed as catalysts in several processes.[4] Probably one of the most promising recent applications was reported by Brookhart and others in the field of the oligomerisation/polymerisation of ethylene and α-olefins in a series of publications using Fe,[5] Ni[6] and Pd[7] complexes containing DAB ligands. The potential of this new system has attracted sufficient interest to justify studies related to the immobilisation of the system,[8] biphasic methods, the use of ionic liquids,[9] the importance of the activator[10] and the extension to other metals such as copper.[11] The use of pyridine-diimines with Fe and Co systems gave also interesting results.[12] Furthermore, a number of publications have appeared concerning theoretical discussions of the nature of the system, the effect of the diimine moiety in the elementary steps of the polymerisation process,[13] the electronic and steric effects of the substituents in the diimine ligand[14] and the comparison between nitrogen and phosphorus atom donors.[15]

Ionic nickel and palladium compounds containing a metal–methyl bond, the origin of the hydride active catalyst, are the one-component precursors of the catalytic species. In contrast to the highly air-sensitive nickel analogues, the well-defined cationic palladium–alkyl species are more easily synthesised and handled. Recently, simple ionic palladium complexes, lacking a metal–carbon bond, have been proposed as catalytic precursors. The resulting species showed lower activities than those obtained with the Brookhart type precursors.[16]

The formation of palladacycles has been observed by Brookhart and co-workers when some cationic ether adducts undergo decomposition by activation of the C–H bond of the *ortho*-aryl substituent of the DAB ligands with the parallel elimination of methane.[7a] These compounds remain inert in the presence of ethylene.

We have observed similar resistance to the ethylene insertion reaction in nickelacycles obtained from *N*,*N*′-dibenzylidene-alkane-1,2-diimine ligands (Chart 2).[17] The rigid planar disposition of the metallacycles fixed by a sequence of four sp^2 atoms and the difficult access to the labile *cis* coordination position could be an impediment for the insertion of ethylene. The effect observed after changing the ring size of the cycles NiCN or NiNN′ points in this direction. The general use of the nickel system with DAB ligands could be facilitated if stable easy-to-handle precursors were available, even though some loss of activity might occur. Thus, the present paper describes the preparation of some nickel–DAB and pyridine-imine complexes containing a NiCNN′ bicyclic skeleton and their reaction with ethylene. In this direction, zwitterionic allyl–nickel complexes have been successfully tested as single-component precursors in ethylene polymerisation.[18]

Results and discussion

Synthesis and characterisation of the ligands

The α-diimine ligands, 1,4-diaza-1,3-butadienes **a**, **b**, **c**, **d** and **e** and the analogous pyridine-imines **f**, **g** were synthesized by condensation reactions between carbonyl and amine compounds (See Scheme 1). Distinct conditions were required in the synthesis of each particular ligand. In general, the synthesis of diimines starting from α-ketoaldehyes or α,β-diketones usually requires severe reaction conditions and prolonged reaction times compared to the condensation with glyoxal due to the recognised higher reactivity of the aldehyde group toward amines than the keto group.[19] Moreover the condensation of

† Electronic supplementary information (ESI) available: Synthesis and characterisation of ligands; Fig. S1; Shulz–Flory distribution. See http://www.rsc.org/suppdata/dt/b3/b302375c/

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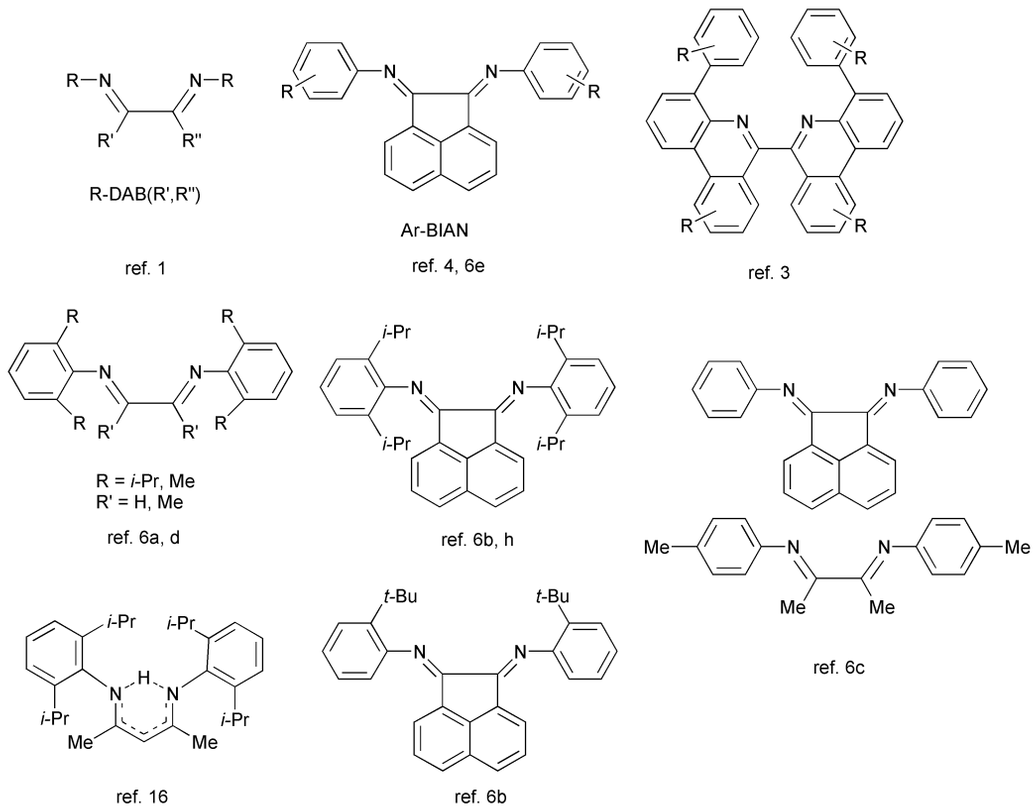


Chart 1

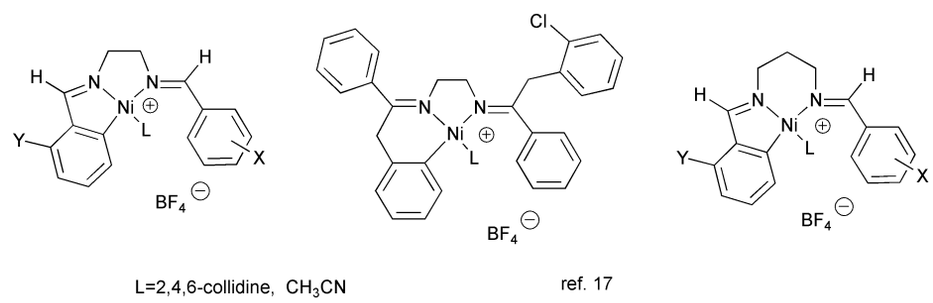
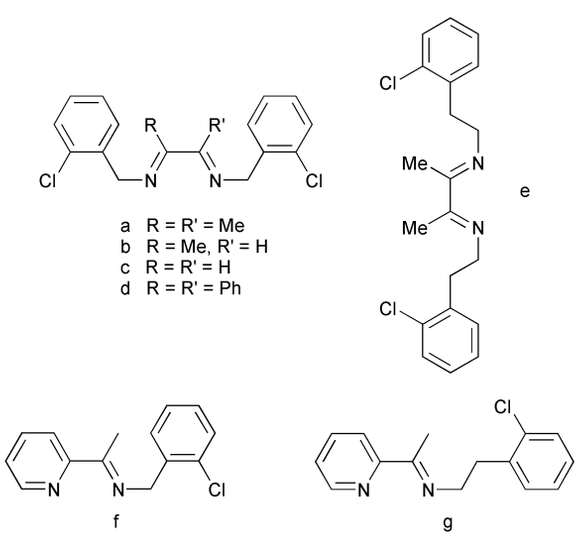


Chart 2

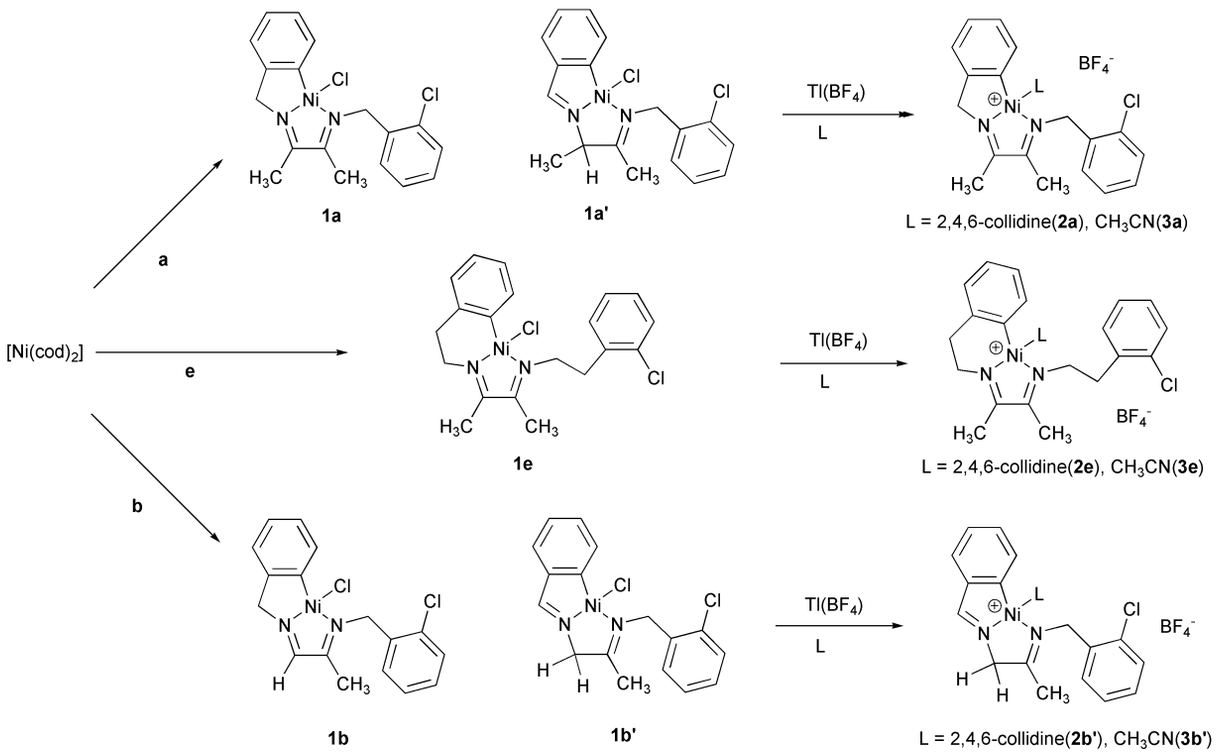


Scheme 1 Synthesized α-diimine ligands **a**–**g**.

dicarbonylic compounds with aliphatic amines with secondary or tertiary α-carbons often gives unwanted products.[20] Thus, in order to obtain **a** and **e**, the condensation reaction of 2,3-butanedione with 2-chlorobenzylamine or 2-(2-chlorophenyl)-ethylamine was performed in the presence of a catalytic amount of formic acid and molecular sieves. In analogous conditions the reaction between methylglyoxal and 2-chlorobenzylamine gives the unsymmetrical 1,4-diazabutadiene **b**. The successive formation of the imine-oxo and the α-diimine compounds were followed by ^{1}H NMR spectroscopy as previously described for similar compounds.[21] Neither the addition of catalyst nor the elimination of water was necessary for the formation of **c** from glyoxal (as hydrate) and 2-chlorobenzylamine. Diimine **d** was obtained in low yield by the reaction of 1,2-diphenylethanedione with benzylamine in refluxing toluene and in the presence of $TiCl_4$ in a similar method already described.[22] The pyridine-imines **f** and **g** were obtained by condensation between 2-acetylpyridine with an equimolar amount of the benzyl- or phenethyl-amine derivatives in anhydrous ethanol, in a slight modification of the literature method.[23] The new compounds were characterized by ^{1}H NMR spectroscopy and mass spectrometry. Only one isomer was observed in solution, the *E*-s-*trans*-*E* conformation, according to the literature

Synthesis and characterisation of the diazabutadiene complexes

Neutral complexes [NiCl(CNN′)] 1a, 1b, 1e. The results and structures of the complexes obtained from the reaction between $[Ni(cod)_2]$ and the 1,4-diaza-1,3-butadiene ligands **a, b, c, d, e** require detailed comment. In all cases, equimolar amounts of $[Ni(cod)_2]$ and the ligand were mixed in tetrahydrofuran at



Scheme 2 Preparation of the diazabutadiene complexes.

−78 °C, the temperature was raised until room temperature, and the stirring was continued for variable periods of time. When ligands **a, b** and **e** were used neutral complexes of general formulae [NiCl(CNN′)], **1a**, **1a′**, **1b**, **1b′** and **1e** were obtained (see Scheme 2). In similar conditions the ligands **c** and **d** did not give the analogous compounds. The reaction probably consists in the substitution of one cyclooctadiene (cod) by the diimine ligand[24] followed by the oxidative addition of the C–Cl bond to Ni(0). Although in all cases the colour of the reaction mixture changes from yellow to red when room temperature is reached, probably due to the new Ni(0) species formed, only when the basicity of the ligand is enhanced by the presence of electron donor substituents at the iminic carbons (CH_3 relative to Ph, H), affording a more basic metal center,[25] is the oxidative addition favoured. In the literature the lack of reactivity of the C–Cl bond of 1,4-bis(2-chlorobenzyl)-2,3-dimethyl-1,4-diaza-2,3-butadiene (molecular skeleton, R–N=C(R′)–C(R′)=N–R) compared with that of the related ligand, di-2-chlorobenzyl-ideneethanediamine (molecular skeleton, R=N–CH_2–CH_2–N=R) to W(0) complexes was attributed to structural differences between both ligands.[26] But in our case this seems not to be the reason because the necessary isomerisation of the diimine ligand from the *E*,*E*-*trans* to the *E*,*E*-*cis* conformation, or the fact that the phenyl groups can move easily away from the metal atom, do not preclude the reaction.

Of note is the structure of the neutral complexes **1a**, **1a′**, **1b**, **1b′** and **1e** obtained. When the reaction between [Ni(cod)$_2$] and **a** was stopped after 2 h at room temperature, a magenta solid was obtained, soluble only in coordinating solvents such as DMSO. The ^{1}H NMR spectrum in DMSO-d_6, shows the presence of a mixture of two compounds, **1a** and **1a′**, in an approximate ratio of 3 : 2. Four singlets, at 1.96 and 2.00 ppm from two methyl protons and at 4.84 and 4.93 ppm from two methylene protons can be assigned to the major isomer according to the expected structure of the oxidative addition product **1a**. The minor isomer **1a′** seems the result of a 1,3-prototropic rearrangement[27] of the diimine ligand **a**. A singlet at 8.38 ppm showed the presence of an iminic proton, a broad quartet at 4.86 ppm and a doublet at about 1.60 ppm are compatible with the presence of a Ph–C*H*=N–C*H*(CH_3)–C fragment. After 24 h of stirring at room temperature only compound **1a** was present.

It seems that after coordination of the DAB ligand to the Ni(0) moiety the prototropic rearrangement became possible. In this way the oxidative addition gives a mixture of both isomers **1a** and **1a′** that finally evolves to the thermodynamically stable **1a**. In this case the conjugation of the two C=N double bonds is preferred (Scheme 2). In the isomer **1a′** the ligand acts also as anionic CNN′ containing the C=N double bond in the five-membered nickelacycle.

From the reaction between [Ni(cod)$_2$] and the asymmetric 1,4-diaza-1,3-butadiene **b** a mixture of two compounds was also obtained. Two groups of similar signals in an approximate initial ratio of 3 : 2 were observed in the ^{1}H NMR spectrum recorded in DMSO-d_6. It is possible to observe a group of four singlets at 1.86, 4.64, 4.82 and 8.17 ppm from the major isomer and another group at 1.94, 4.87, 4.97 and 8.36 ppm corresponding to the minor isomer. The signals could be assigned to one methyl, two non-equivalent methylene fragments and an iminic hydrogen, respectively. However, in this case, the same pattern is possible for three different isomers. Two of these could be expected from the oxidative addition reaction depending on the aryl substituent involved in the process since the DAB **b** ligand is not symmetric. Furthermore another isomer arising from a 1,3-prototropic rearrangement must also be considered.

The composition of the mixture was followed by ^{1}H NMR spectroscopy. In 6 h evolution to a single isomer, the major species in the initial mixture, was observed. These results point towards a pair of isomers associated by the 1,3-prototropic rearrangement. However, at this point its structure was uncertain because the high insolubility of these compounds precludes the realisation of 2D NMR spectroscopy. The information obtained from the NOESY spectra of the ionic complexes discussed in the next section (see Scheme 2) allows assignment of the structures to the minor (**1b**) and major (**1b′**) isomers. Thus it seems that the oxidative addition takes place in *trans* position to the more basic nitrogen atom and that in this case the conjugation between the C=N double bond and the aromatic ring is more efficient.

From the reaction between [Ni(cod)$_2$] and **e**, only complex **1e**, containing a six-membered nickelacycle was obtained. The ^{1}H NMR spectrum in $CDCl_3$ showed two signals for the CH_3

fragments, whereas three of the methylene protons appear as multiplets between 3.20 and 3.50 ppm and the fourth CH_2 appears as a triplet at 4.09 ppm. This ligand did not show the 1,3-prototropic rearrangement because the stabilisation by conjugation is achieved only between the two C=N bonds.

The rearrangements of diimine ligands are relatively common[16,27,28] but the mechanism of the proton displacements is unclear. The imine isomerisation observed in hydrogen transfer conditions with ruthenium catalysts probably proceeds through a ruthenium–amine intermediate.[29] In the case of the imines **a** and **b**, the isomerisation seems to be possible in the Ni(0) and Ni(II) complexes and probably the same kind of allyl intermediate could be present.

Ionic complexes [Ni(CNN′)L)]BF_4, 2. The general procedure for obtaining ionic compounds **2** was by direct abstraction of halide ligand of complexes **1** with $TlBF_4$ in the presence of a neutral ligand (Scheme 2). The excess of 2,4,6-trimethylpyridine (collidine) must be limited to avoid partial substitution of the DAB ligand.[25] The collidine-containing complexes were suficiently soluble and inert to allow their characterisation in solution.

The ionic complex **2a** was obtained from a sample that contains nearly pure **1a**. The ^{1}H NMR spectrum confirms the proposed structure. The upfield shift of the doublet at 5.18 ppm assigned to the aromatic proton *ortho* to the Ni–C bond, arises from anisotropic shielding by the 2,4,6-trimethylpyridine ring, nearly in perpendicular position with respect to the coordination plane. The *ortho*-methyl protons of the 2,4,6-trimethylpyridine appear as one singlet, showing that these protons are equivalent because of the existence of a symmetry plane defined by the coordination sphere in these molecules. This observation is common in all the ^{1}H NMR spectra of similar ionic complexes.[17,30] From CH_2Cl_2–pentane solutions suitable single crystals were obtained and the crystal structure determined (see below).

The ^{1}H NMR spectrum of **2e**, was recorded at 298 and at 240 K in acetone-d_6, the differences showing the lack of rigidity of the six-membered nickelacycle. At both temperatures, the characteristic upfield shift of the aromatic proton *ortho* to the Ni–C bond is observed. However, if we compare with the value observed for the same proton in the five-membered nickelacycle, **2a**, a minor influence of the collidine ring current is apparent. The other aromatic signals show the same pattern at both temperatures, but several different chemical shifts are evident for the methylenic and methylic protons, showing the lack of rigidity of the six-membered nickelacycle. At 298 K, signals at 2.42, 2.46 and 3.46, with intensities 1 : 2 : 2, could be assigned to the *para*-CH_3 group of the collidine, the two methyl groups of the DAB ligand, and the two *ortho*-methyl groups of the collidine. Also, the four methylene protons appear as broad singlets at 2.73, 3.07, 3.7 and 3.40 ppm. At 240 K the two CH_3 groups of the DAB ligand show different chemical shifts at 2.51 and 2.47, but the *ortho*-methyl protons of the collidine and the methylene fragments appear as broad multiplets between 2.6 and 3.7 ppm.

The mixture of compounds **1b** and **1b′** was reacted with $TlBF_4$ and 2,4,6-collidine. After the conventional workup of the reaction mixture only a single product was obtained. The 500 MHz ^{1}H NMR spectrum in acetone-d_6 shows five singlets, at 2.34 and 2.38 corresponding to two methyl groups, at 3.13 ppm of the two *ortho* methyl substituents of the collidine and at 4.27 and 5.18 of the remaining two methylene groups. The aromatic hydrogen atom *ortho* to the Ni–C bond appears as a doublet at 5.37 and the hydrogen iminic atom as a singlet at 8.32 ppm. 2D-NMR has proved to be useful in determining the structure of the ionic complex. The combination of the COSY and NOESY experiments permits the unambiguous assignation of all the signals. The complete set of contacts observed in the NOESY experiment are indicated in Fig. 1. The sequence of

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

Ni–N(1)	1.849(6)	N(2)–C(10)	1.279(9)
Ni–N(3)	1.879(7)	N(2)–C(12)	1.451(9)
Ni–C(1)	1.917(7)	C(1)–C(6)	1.382(10)
Ni–N(2)	1.980(6)	C(6)–C(7)	1.531(9)
N(1)–C(8)	1.308(8)	C(8)–C(10)	1.485(10)
N(1)–C(7)	1.493(8)		
N(1)–Ni–N(3)	177.1(3)	N(1)–Ni–N(2)	81.4(3)
N(1)–Ni–C(1)	84.6(3)	N(3)–Ni–N(2)	97.3(3)
N(3)–Ni–C(1)	96.9(3)	C(1)–Ni–N(2)	165.7(3)

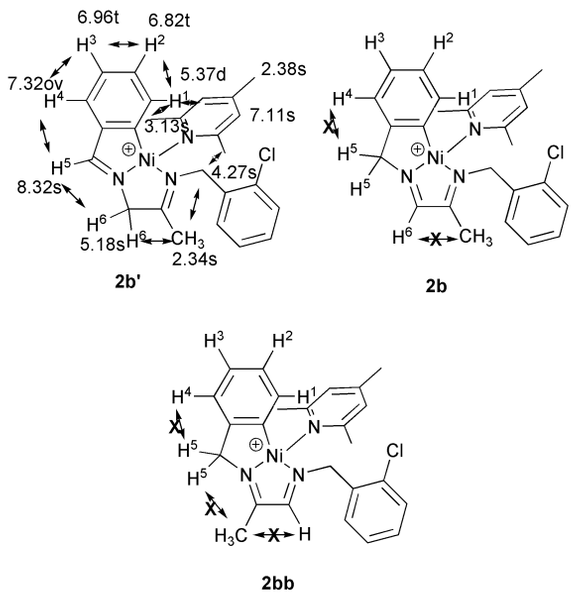


Fig. 1 NOE contacts observed showing compatibility with structure **2b′**.

contacts around the iminic proton is compatible only with structure **2b′**, with the ligand containing the C=N bond conjugated with the aromatic system, and isomer **2b** or **2bb** can be discarded.

Molecular structure of 2a. The crystal structure of **2a** has been determined (Fig. 2). Selected bond lengths and angles are listed in Table 1.

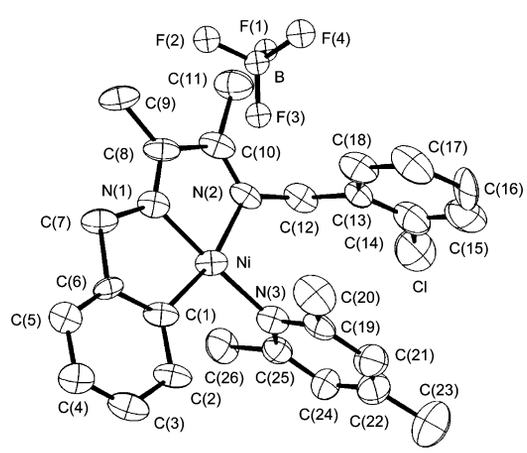


Fig. 2 ORTEP view and labelling scheme of **2a**. Hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability.

The crystal structure consists of discrete molecules separated by van der Waals distances. The nickel atom is located in a slightly distorted square-planar environment, coordinated to carbon, pyridinic nitrogen and two iminic nitrogen atoms, the deviations from the mean plane (plane a) being: Ni, −0.002(1)

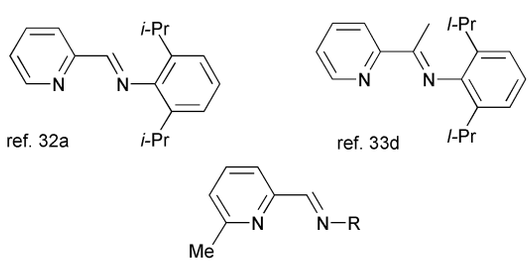
Å; N(1) 0.044(5) Å; N(2), −0.038(5) Å; N(3), 0.034(5) Å; C(1) −0.038(7) Å. The bite angle of the metallacycle C(1)–Ni–N(1) of 84.4(3)° is slightly larger than the N(2)–Ni–N(1) angle of 81.4(3)° of the chelate ring. The same trend is observed in the nickel compound derived from a 1,4-diaza-1,3-butadiene reported in the literature,[31] and is the reverse to the trend reported for five-membered nickelacycles where the C=N bond is contained in the nickelacycle and not in the NNiN five-membered chelate ring.[17,30]

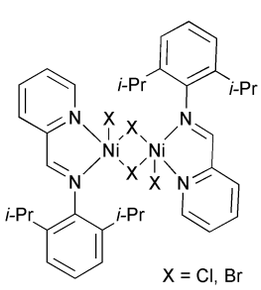
The distances between the nickel and the coordinated atoms are similar to those reported for other analogous compounds. The Ni–N(2) distance is slightly greater than Ni–N(1) as a result of the stronger *trans* influence of the anionic carbon donor relative to the pyridinic nitrogen. The two C=N bond distances are different, N(1)–C(8) 1.313(8) and N(2)–C(10) 1.278(9) Å, both in the range of a double bond. The aromatic and the two fused five-membered rings are nearly coplanar. The metallated phenyl ring C(1)–C(6) (plane b), the ring containing the two iminic moieties NiN(1)C(8)C(10)N(2) (plane c), and the nickelacycle NiC(1)C(6)C(7)N(1) (plane d) are nearly coplanar, with normals between b–d and c–d of 2.21(3) and 3.01(3)°, respectively.

The collidine is nearly orthogonal to the coordination sphere, the angle between normals being 82.46(3)°. The *ortho* methyl fragments 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 are the same, 3.03(1) Å. The carbon atom of the methylenic group C(12) is nearly contained in the mean plane defined by the coordination sphere, the dihedral angle, C(12)–N(2)–Ni–N(3), being 2.45°, and the *ortho*-chlorophenyl group is completely located on one side of the coordination plane. The planes between the collidine group and the non-metallated *o*-chlorophenyl group are roughly parallel; the angles between normals to the planes are 12.6(4)°.

Synthesis and characterisation of the pyridine-imine complexes

A number of pyridine-imine ligands have been reported and their coordination behaviour studied (Chart 3).[32] The most interesting structural pattern is their ability to stabilise pentacoordinate complexes.[23] They have also been tested as precursors in the ethylene polymerisation reaction.[33]

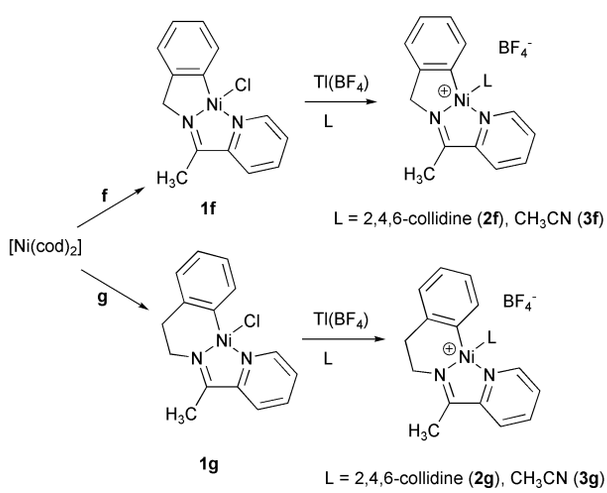




ref. 23

Chart 3

Neutral complexes [NiCl(CNN′)] 1f, 1g. The reaction between [Ni(cod)$_2$] and the pyridine-imine ligands **f** or **g** in THF gives, by coordination of the two nitrogen atoms and the oxidative addition of the C–Cl bond to the Ni(0), the expected neutral compounds [NiCl(CNN′)] **1f** and **1g** (see Scheme 3). The new complexes were air-stable red solids characterized by elemental analyses, infrared spectra and ^{1}H NMR. Both complexes are rather insoluble in common solvents. The ^{1}H NMR spectrum of **1f** was recorded in DMSO-d$_6$, and that of **1g**, slightly more soluble, was recorded in a $CDCl_3$ and DMSO-d$_6$ solution. In both complexes, the signals of the methyl group experience an upfield shift whilst those of the methylene group a downfield shift upon coordination compared to the free ligands. Narrow and separate signals were observed for all the aromatic protons in the spectra in DMSO. Of note was the downfield shift of the characteristic doublet of the hydrogen atom *ortho* to the pyridinic nitrogen due to the relatively strong deshielding effect of the chloride ligand in *cis* position.[34] This downfield shift is greater ($\Delta\delta$ 0.8 ppm) in $CDCl_3$ solution than in DMSO-d$_6$ solution ($\Delta\delta$ 0.4 ppm). Although separate signals were observed for all the aromatic protons in DMSO solution, their poor solubility precludes their assignation by 2D ^{1}H NMR spectroscopy. The formation of pentacoordinate species have not been observed probably due to the steric requirements of the CNN′ ligands.



Scheme 3 Preparation of the pyridine-imine complexes.

Ionic complexes [Ni(CNN)(2,4,6-Me$_3$C$_5$H$_2$N)]BF$_4$, 2f, 2g. The addition of $TlBF_4$ and the Lewis base 2,4,6-trimethylpyridine in acetone to compounds **1f** and **1g**, afforded the ionic derivatives **2f** and **2g** (see Scheme 3), which were characterized by elemental analyses, and ^{1}H NMR spectroscopy in acetone-d$_6$. These complexes were air-stable orange solids that were highly soluble in most common solvents. The most relevant aspect of the ^{1}H NMR spectrum of both complexes was the upfield shift of the two aromatic protons *ortho* to the N(py)–Ni and C–Ni bonds. Both protons are under the influence of the ring current of 2,4,6-trimethylpyridine. Comparing the values, a smaller influence of the collidine current ring is apparent for the six- than for the five-membered ring complexes (**2g** *vs.* **2f**). In complex **2f** the two *ortho*-methyl protons of the 2,4,6-collidine appear at 3.38 ppm, indicating that in solution at room temperature the coordination plane acts as a symmetry plane. Complex **2g**, containing a six-membered ring, shows in acetone-d$_6$ solution at room temperature, a broad signal centered at 3.30 ppm due to the two *ortho*-methyl protons of the 2,4,6-trimethylpyridine.

Ethylene oligomerisation

Ionic complexes of the general formula, [Ni(CH_3CN)(CNN′)]-BF_4 (**3**), were synthesised for testing as precursors in the

Table 2 Results of the ethylene oligomerisation reaction using precursors **3a**, **3e**, **3f** and **3g**

	TOF/h^{-1}	Products	α
3a	1630	C_4–C_{18}	0.37
3e	390	C_4–C_{20}	0.43
3f	50	C_4–C_{16}	0.42
3g	165	C_4–C_{18}	0.40

Reaction conditions: CH_2Cl_2, [Ni] = 4.10^{-5} M, t = 3 h, P_i = 20 bar, T = 25 °C.

oligomerisation of ethylene. It is well known that the insertion reaction of ethylene is favoured in ionic complexes, particularly complexes containing a weakly coordinating stabilising ligand, which may be a solvent molecule or the olefin monomer, if the cationic complex is generated in the presence of such a ligand.[35]

A stoichiometric amount of $TlBF_4$ was added to an acetone suspension of the neutral complexes **1a**, **1e**, **1f** and **1g**, containing acetonitrile in excess. After careful separation of the slowly formed thallium chloride, the solvent was removed under vacuum. The syrupy orange residue gives, in most cases, after several washes with diethyl ether, yellow–orange solids, which were characterized by ^{1}H NMR, IR and elemental analyses. Correct analytical data for complexes could not always be obtained probably due to the presence of small amounts of thallium salts, water as ligand, or the limited stability of the complexes themselves. The ^{1}H NMR spectra in acetone of **3a**, **3e**, **3f**, **3g** shows in all cases that no rearrangements of the ligands had occurred (see Schemes 2 and 3).

In the five-membered nickelacycles **3a** and **3f** besides the methyl resonances due to the diimine ligand, singlets at 2.33 and 2.28 ppm are observed. These could be assigned to the coordinated acetonitrile. Also the upfield shifted doublets of the *ortho* hydrogens to the Ni–C bond were observed at 6.40 and 6.60 ppm. Compared with the shifts produced by the 2,4,6-trimethylpyridine rings, the anisotropic effects of the acetonitrile triple bond are weaker. Other features of the spectrum remained similar to those described for complexes **2a** and **2f**.

The ^{1}H NMR spectra of the six-membered nickelacycles **3e** and **3g**, in acetone-d_6 do not show a clear signal for the acetonitrile ligand. Moreover, the chemical shifts of all the aromatic protons are in the region between 6.8 and 8.6 ppm. Compared with the five-membered nickelacycles, the upfield shift of the *ortho* proton to the Ni–C is not observed. Both facts may be related either to a more labile behaviour of the acetonitrile or with a not so close disposition between the aromatic *ortho* protons and the acetonitrile.

The acetonitrile-stabilized ionic complexes (**3a**, **3e**, **3f**, **3g**) were tested for the ethylene oligomerisation. The catalytic results and the conditions for the reactions are summarized in Table 2. Some differences in activities but not in the nature of the oligomeric products were observed for the different complexes. In all cases a Schulz–Flory type distribution of oligomers with α values ranging from 0.37 to 0.43 was obtained (see ESI †). For each C_{2n} fraction, the linear terminal olefin is the major product. The ^{1}H NMR spectrum of the insoluble fraction in MeOH, C_{16}–C_{28}, was used in determining product linearity. Besides the main-chain CH_2 and CH_3 resonances at 1.28 and 0.90 ppm, respectively, the two characteristic broad multiplets of vinyl terminal groups CH_2=CH–, at 5.81 and 4.96 ppm, were observed. Much weaker resonances of *cis* and *trans* internal olefins –CH=CH– at 5.41 ppm, adjacent methylene protons CH_2–CH=CH, at 1.98 ppm, and a sharp doublet at 1.61 ppm attributed to the CH_3 group in CH_3CH=CH were observed. From intensity measurements the percentage of terminal olefins obtained is about 70%. Notably, compounds containing similar di-Schiff base type anionic CNN ligands[17] direct the reaction towards branched oligomeric products. This different behaviour coud be related to the almost planar rigid environement around the nickel atom in the hydride active species generated from compounds **3**, that obstructs the coordination of linear olefins more efficiently than the analogous di-Schiff system, avoiding the formation of branched products. The activity of the catalyst precursors derived from 1,4-diaza-1,3-butadiene ligands (**3a**, **3e**) are higher than those observed for complexes with pyridineimine ligands (**3f**, **3g**). The insolubility of these latter complexes in CH_2Cl_2 can be invoked in order to explain this behaviour. Compound **3a**, which contains a five-membered metallacycle derived from the diazabutadiene ligand, showed higher reactivity by a factor of four than **3e**, which contains a six-membered ring. This behaviour also contrasts with the previously observed analogous compounds containing di-Schiff base complexes,[17] where no ethylene insertion into the Ni–C(phenyl) bond of the rigid five-membered nickelacycle takes place.

The activity observed in this kind of ligand is very limited compared with those reported by Brookhart *et al*. The inherently low stability of the complexes, containing poorer coordinating ligands,[36] and the fundamental structural differences could be the reason for the much reduced activity. The BIAN type diimine ligands of the active systems are more rigid and have substituents in *ortho* position in the phenyl group directly bonded to the nitrogen donor, thus avoiding fast β-elimination in the oligomerisation process.

However, the relatively stable compounds of type **3** can be used as one-component precursors of the catalytic species without further addition of MAO derivatives. Thus it should be possible to prepare a nickel precursor containing a five- or six-membered metallacycle based on a BIAN type diimine ligand since the activation of the Ni–carbon bond of the cycle seems possible. This kind of activation was not observed with the palladium metallocycles.[7a]

Experimental

General

All manipulations of the 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 methods. Diethyl ether, tetrahydrofuran and toluene were distilled over sodium–benzophenone, under nitrogen, before use, dichloromethane was distilled over $CaCl_2$ under nitrogen before use. All reagents are commercially available except [Ni(cod)$_2$] which was prepared following published methods.[37]

^{1}H NMR spectra were obtained using a Bruker DRX 250 and Varian VXR-500 spectrometers. Solvents used were $CDCl_3$, acetone-d_6 or DMSO-d_6. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^{1}H; coupling constants in Hz. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona using an Eager 1108 microanalyzer. Mass spectra were recorded on a Fisons VG-Quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzyl alcohol for FAB analysis and then subjected to bombardment with caesium atoms. The oligomer products were analysed on a Hewlett-Packard 5890 gas chromatograph equipped with a 50 m ultra-2 cross-linked 5% phenyl methyl silicon capillary column and a flame ionisation detector.

Synthesis of the ligands

The α-diimine ligands were prepared with slight modifications of literature procedures.[20–23] Experimental details concerning the preparation and characterisation of the ligands are deposited as ESI. †

General procedure for the synthesis of neutral complexes [NiCl(CNN)] (1a/1a′, 1b/1b′, 1e, 1f, 1g)

To a suspension of $[Ni(cod)_2]$ (1.42 g, 5.20 mmol) in THF (30 cm^3) at −78 °C was added the corresponding diimine (6.2 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 24 h under these conditions. The formation of a deep red to purple solid was observed (**1a**, brown, **1b/1b′**, deep red, **1e**, purple, **1f**, brick red, **1g**, deep red). After cooling at −10 °C for several hours, the solid was filtered off, washed several times with diethyl ether and water, and finally dried in vacuum. Compounds **1** were obtained in 70–90% yields. If the reaction between $[Ni(cod)_2]$ and diimine **a** was stopped after 4 h, a mixture of **1a** and **1a′** was obtained. Data for **1a** and **1a′**: Anal. Found: C, 54.8; H, 4.6; N, 7.2. Calc. for $C_{18}H_{18}Cl_2N_2Ni$: C, 55.16; H, 4.63; N, 7.15%. ^{1}H NMR for **1a** (DMSO-d_6): δ 7.60 (m, 2H), 7.40–7.30 (m, 2H), 7.01 [d, ^3J(HH) = 7.5, 1H)], 6.94 [t, ^3J(HH) = 7.0, 1H], 6.80 [(d, ^3J(HH) = 6.4, 1H], 6.70 [t, ^3J(HH) = 7.5, 1H], 4.93 (s, 2H, CH_2), 4.84 (s, 2H, CH_2), 2.00 (s, 3H, CH_3), 1.96 (s, 3H, CH_3). ^{1}H NMR for **1a′** (DMSO-d_6): δ 8.38 (s, 1H, H_{im}), 7.50–6.90 (m, 8H), 4.86 (q, 1H, CH), 4.72 (s, 2H, CH_2), 1.92 (s, 3H, CH_3), 1.60 (d, 3H, CH_3). Data for **1b** and **1b′**: Anal. Found: C, 52.8; H, 4.4; N, 7.0. Calc. for $C_{17}H_{16}Cl_2N_2Ni$: C, 54.03; H, 4.27; N, 7.41%. ^{1}H NMR (DMSO-d_6): Minor isomer **1b**: δ 8.36 (s, H_{im}), 6.6–7.5 (m, aromatic), 4.97 (s, 2H, CH_2), 4.87 (s, 2H, CH_2), 1.94 (s, 3H, CH_3). Major isomer **1b′**: δ 8.17 (s, H_{im}), 6.6–7.5 (m, aromatic), 4.82 (s, 2H, CH_2), 4.64 (s, 2H, CH_2), 1.86 (s, 3H, CH_3). Data for **1e**: Anal. Found: C, 57.3; H, 5.4; N, 6.4. Calc. for $C_{20}H_{22}Cl_2N_2Ni$: C, 57.19; H, 5.28; N, 6.67%. ^{1}H NMR ($CDCl_3$): δ 7.62 (br s, 1H), 7.40–7.10 (m, 4H), 6.90–6.80 (m, 3H), 4.09 (t, 2H), 3.50–3.20 (m, 6H), 1.88 (s, 3H, CH_3), 1.82 (s, 3H, CH_3). Data for **1f**: Anal. Found: C, 55.1; H, 4.4; N, 9.5. Calc. for $C_{14}H_{13}ClN_2Ni$: C, 55.42; H, 4.32; N, 9.23%. ^{1}H NMR (DMSO-d_6): δ 8.80 [d, ^3J(HH) = 5.0, 1H], 8.21 [td, 1H, ^3J(HH) = 7.8, ^4J(HH) = 1.6, 1H], 8.00 [d, ^3J(HH) = 7.8, 1H], 7.81 [t, 1H, ^3J(HH) = 6.3], 7.21 [d, ^3J(HH) = 7.4, 1H], 6.94 [td, 1H, ^3J(HH) = 7.3, 4J(HH) = 1.2, 1H], 6.80 [d, 1H, ^3J(HH) = 6.9], 6.73 [td, 1H, ^3J(HH) = 7.4, ^4J(HH) = 1.1, 1H], 4.93 (s, 2H, CH_2), 2.31 (s, 3H, CH_3). Data for **1g**: Anal. Found: C, 56.4; H, 4.9; N, 8.6. Calc. for $C_{15}H_{15}ClN_2Ni$: C, 56.75; H, 4.76; N, 8.82%. ^{1}H NMR ($CDCl_3$): δ 9.35 [d, ^3J(HH) = 4.5, 1H], 7.95 [t, ^3J(HH) = 7.6, 1H], 7.65–7.50 (m, 3H), 6.80–6.90 (m, 3H), 3.31 (br s, 4H, CH_2), 2.25 (s, 3H, CH_3).

General procedure for the synthesis of the ionic complexes [Ni(CNN)(2,4,6-trimethylpyridine)]BF_4 (2a, 2b′, 2e, 2f, 2g). To a suspension of 1.1 mmol of **1a**, **1b/1b′**, **1e**, **1f**, **1g**, in acetone (50 cm^3) at room temperature $TlBF_4$ (0.38 g, 1.3 mmol) and 2,4,6-trimethylpyridine (0.17 g, 1.32 mmol) were added. A suspension of the insoluble thallium halide was formed instantaneously, and after 4 h of stirring was separated by filtering over Celite. The solvent was partialy removed under vacuum and diethyl ether was added. Compounds **2a**, **2b′**, **2e**, **2f**, **2g** were precipitated as orange solids. Data for **2a**: Anal. Found: C, 55.5; H, 5.2; N, 7.6. Calc. for $C_{26}H_{29}BClF_4N_3Ni$: C, 55.32; H, 5.18; N, 7.44%. ^{1}H NMR (acetone-d_6): δ 7.37–7.33 (m, 4H), 7.12 (s, 2H), 6.96–7.00 (m, 2H), 6.60 [t, ^3J(HH) = 7.2, 1H], 5.18 [d, ^3J(HH) = 7.6, 1H], 5.01 (s, 2H, CH_2), 4.42 (s, 2H, CH_2), 3.00 (s, 6H, CH_3), 2.49 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.38 (s, 3H, CH_3). Data for **2b′**: Anal. Found: C, 53.3; H, 4.9; N, 7.1. Calc. for $C_{25}H_{27}BF_4N_3NiCl$: C, 54.55; H, 4.94; N, 7.63%. ^{1}H NMR (acetone-d_6, 298 K): δ 8.32 (s, H_{im}, 1H), 7.20–7.40 (m, 5H), 7.11 (s, 2H), 6.96 [t, ^3J(HH) = 7.1, 1H], 6.82 [t, ^3J(HH) = 6.5, 1H], 5.37 [d, ^3J(HH) = 7.3, 1H], 5.18 (s, 2H, CH_2), 4.27 (s, 2H, CH_2), 3.13 (s, 6H, CH_3), 2.38 (s, 3H, CH_3), 2.34 (s, 3H, CH_3). Data for **2e**: Anal. Found: C, 55.5; H, 5.9; N, 7.4. Calc. for $C_{28}H_{33}BClF_4N_3Ni$: C, 56.76; H, 5.61; N, 7.09%. ^{1}H NMR (acetone-d_6, 240 K): δ 7.39–7.22 (m, 5H), 6.98–6.84 (m, 3H), 6.56 [t, ^3J(HH) = 7.2, 1H], 5.74 [d, ^3J(HH) = 7.7, 1H], 3.7–2.6 (several m, 14H), 2.51 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). Data for **2f**: Anal. Found: C, 55.0; H, 5.2; N, 9.0. Calc. for $C_{22}H_{24}BF_4N_3Ni$: C, 55.52; H, 5.08; N, 8.83%. ^{1}H NMR (acetone-d_6) 8.34 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.6, 1H], 8.22 [d, ^3J(HH) = 7.8, 1H], 7.74 (m, 1H), 7.44 (s, 2H), 7.28 [d, ^3J(HH) = 5.2, 1H], 7.01–7.06 (m, 2H), 6.68 (m, 1H), 5.40 [d, ^3J(HH) = 7.6, 1H], 5.14 (s, 2H, CH_2), 3.38 (s, 6H, CH_3), 2.63 (s, 3H, CH_3), 2.48 (s, 3H, CH_3). Data for **2g**: Anal. Found: C, 56.3; H, 5.5; N, 8.3. Calc. for $C_{23}H_{26}BF_4N_3Ni$: C, 56.38; H, 5.35; N, 8.58%. ^{1}H NMR (acetone-d_6, 240 K): δ 8.39–8.41 (m, 2H), 7.68–7.74 (m, 1H), 7.4 (br s, 2H), 6.98–7.01 (m, 2H), 6.88 [td, ^3J(HH) = 7.2, 1H], 6.59 [td, ^3J(HH) = 7.7, ^4J(HH) = 1.5, 1H], 5.90 [d, ^3J(HH) = 7.6, 1H], 3.43 (br s, 4H, $2CH_2$), 3.30 (br s, 6H, $2CH_3$), 2.72 (s, 3H, CH_3), 2.44 (s, 3H, CH_3).

General procedure for the synthesis of the ionic complexes [Ni(CNN)(CH_3CN)]BF_4 3a, 3e, 3f, 3g. Over a stirred solution of 0.88 mmol of the neutral complex **1a**, **1e**, **1f**, **1g** in 30 cm^3 of tetrahydrofuran–acetone (2 : 1), 2.64 mmol of CH_3CN (0.14 cm^3) and 0.91 mmol of $TlBF_4$ were added. The insoluble thallium halide was formed instantaneously, and after 1 hour it was separated by filtering over Celite. The solvent was then evaporated to dryness and the remaining resin stirred with diethyl ether until a suspension of orange–brown solid was obtained. The product was filtered off, and washed several times with ether (Yield = 70–75%). Data for **3a**: Anal. Found: C, 50.1; H, 4.5; N, 8.7. Calc. for $C_{20}H_{21}BClF_4N_3Ni$: C, 49.60; H, 4.37; N, 8.68%. ^{1}H NMR (acetone-d_6, 240 K): δ 7.45–7.60 (m, 4H), 7.07 [t, ^3J(HH) = 7.9, 1H], 6.94 [d, ^3J(HH) = 7.6, 1H], 6.77 [t, ^3J(HH) = 7.0, 1H], 6.40 [d, ^3J(HH) = 7.2, 1H], 4.96 (s, 2H, CH_2), 4.90 (s, 2H, CH_2), 2.48 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.33 (s, 3H, CH_3). Data for **3e**: Anal. Found: C, 50.1; H, 4.9; N, 8.0. Calc. for $C_{22}H_{25}BClF_4N_3Ni$: C, 51.57; H, 4.92; N, 8.20%. MS/FAB(+): m/z 348 ($M^+ - CH_3CN - Cl$). ^{1}H NMR (acetone-d_6, 298 K): δ 7.62–7.36 (m, 4H), 6.91–6.78 (m, 4H), 3.85 (m, 2H), 3.27–3.16 (m, 6H), 2.38 (s, 3H), 2.22 (s, 3H). (CD_3CN, 298 K): δ 7.55–7.53 (m, 2H), 7.45–7.40 (m, 2H), 7.1–6.89 (m, 4H), 3.87 (t, 2H, CH_2), 3.24 (t, 2H, CH_2), 3.16 (s, 4H, $2CH_2$) 2.21 (s, 3H, CH_3). Data for **3f**: Anal. Found: C, 48.5; H, 4.0; N, 10.3. Calc. for $C_{16}H_{16}BF_4N_3Ni$: C, 48.55; H, 4.07; N, 10.62%. ^{1}H NMR (acetone-d_6, 298 K): δ 8.40 [t, ^3J(HH) = 7.2, 1H], 8.18 [d, ^3J(HH) = 8, 1H], 7.90 (br s, 2H), 7.08 [t, ^3J(HH) = 7.5, 1H], 6.93 [d, ^3J(HH) = 7.7, 1H], 6.84 [t, ^3J(HH) = 7.2, 1H], 6.61 (br s, 1H), 5.03 (s, 2H), 2.58 (s, 3H, CH_3), 2.28 (s, 3H, CH_3). Data for **3g**: Anal. Found: C, 47.3; H, 4.3; N, 9.2. Calc. for $C_{17}H_{18}BF_4N_3Ni$: C, 49.82; H, 4.43; N, 10.25%. MS/FAB(+): m/z 323 (M^+), 282 ($M^+ - CH_3CN$). ^{1}H NMR (acetone-d_6, 298 K): δ 8.55 (br s, 1H), 8.36–8.43 (m, 2H), 7.94 (br s, 1H), 7.08 [d, ^3J(HH) = 6.3, 1H], 7.00 (br s, 2H), 6.86 (br s, 1H), 3.41 (s, 2H, CH_2), 3.26 (s, 2H, CH_2), 2.71 (s, 3H, CH_3); ^{1}H NMR (CD_3CN, 298 K): δ 8.57 (br s, 1H), 8.30 (m, 1H), 8.09 (m, 1H), 7.84 (m, 1H), 7.29 (br s, 1H), 7.01–6.92 (m, 3H), 3.32 (br s, 2H, CH_2), 3.25 (br s, 2H, CH_2) 2.54 (br s, 3H, CH_3).

X-Ray crystallographic structure determination of [Ni{2-[CH_2N=C(Me)C(Me)=NCH_2(2-ClC_6H_4]C_6H_4}(2,4,6-Me_3-C_5H_2N)]BF_4, 2a. Single crystals of **2a** were recrystallised from acetone–diethyl ether and mounted on an Enraf-Nonius CAD4 four-circle diffractometer.

Crystal data. $C_{26}H_{29}BClF_4N_3Ni$, M = 564.49, monoclinic, space group $P2_1/n$, a = 9.959(2), b = 7.832(6), c = 34.913(6) Å, β = 96.743(15)°, U = 2704(2) Å^3, T = 293(2), Z = 4, μ(Mo-Kα) = 0.863 mm^{-1}, Reflections collected: 3031, unique: 2981 (R_{int} = 0.032), which were used in all calculations. The final $R(F)$ was 0.0444 (observed data) and $wR(F^2)$ was 0.1002 (all data).

CCDC reference number 204459.

See http://www.rsc.org/suppdata/dt/b3/b302375c/ for crystallographic data 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 thermostated bath.

4×10^{-5} mol of the catalyst precursor were dissolved in 15 ml of CH_2Cl_2, and transferred *via* syringe under argon into the reactor, which had been previously 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.

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