The insertion reaction of acetonitrile on aryl nickel complexes stabilized by bidentate N,N′-chelating ligands†

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Organometallic complexes to be used as single component precursors in the catalytic dimerization/polymerization of olefins usually must contain a labile ligand that can easily be displaced by the olefin. This is the first step in the activation of the precursor. One commonly used labile ligand is a nitrile. Here we report an example of incompatibility between the nickel or palladium aryl bond and acetonitrile. Neutral [MBr(Mes)NN] complexes in which Mes = 2,4,6-$Me_3C_6H_2$, NN = diazabutadiene (DAD), pyridinylimine (PIM), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) gave the expected [M(Mes)(3,5-lut)(NN)][BF_4] compounds and the unexpected [Ni(Mes){NH=C(Me)(2,4,6-$Me_3C_6H_2$)}-(NN)][BF_4] complexes in the presence of $TlBF_4$ and 3,5-lutidine or acetonitrile. The sequence of reactions that leads to the imine ligand must include an initial insertion of the nitrile on the σ(Ni–Mes) bond. These ionic complexes remain stable under 20 bar of ethylene.

Introduction

The study of late transition metal olefin oligomerization/polymerization catalysts is an area of interest. The early, important development of the SHOP process for the oligomerization of ethylene used neutral Ni catalysts containing P–O ligands[1] (Chart 1, a). This was followed by the discovery of the Brookhart's system using Ni and Pd α-diimine cationic catalysts[2] (Chart 1, b). Recently, a new family of neutral nickel complexes containing salicylaldimine N–O ligands showed good functional group tolerance, increasing the scope of the catalytic system[3] (Chart 1, c). The commonly used metals are Ni, Pd and Fe[4] (Chart 1, d). The number and type of ligands that have been developed to be applied in this reaction is very large. Some examples are neutral bidentate nitrogen ligands containing a diimine skeleton[5] or mixed P–N phosphine-imine ligands.[6]

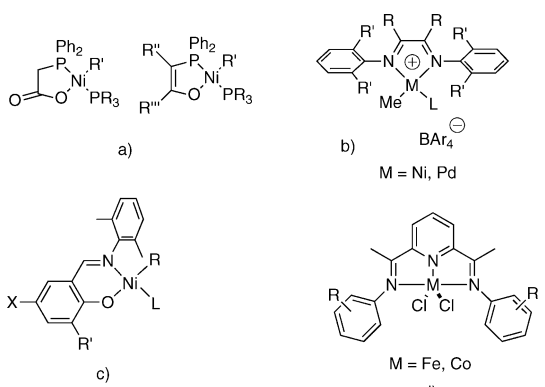

Chart 1

Some catalyst precursors must be activated with a cocatalyst such as MAO, but others are single-component precursors. These precursors are generally ionic or neutral compounds. They contain at least one weakly bonded ligand that could easily be displaced by the olefin, and an M–C bond that after initial insertion of the olefin and a β-elimination reaction will produce hydride catalytic species. One of the commonly used labile ligands is acetonitrile.[7] In most cases and for catalytic purposes, the precursor is generated *in situ* after abstraction of the halide of the neutral complex by a silver or thallium salt. Cationic methylpalladium complexes with bidentate N-donor ligands, such as bipyridine or related diimine ligands, are stable in solution.[8] The X-ray crystal structure of [$Pd(CH_3)(NCCH_3)$(bppy)][PF_6] has also recently been reported.[9] Analogous arylpalladium complexes tend to undergo intermolecular aryl ligand transfer. However when a suitable aryl group and the solvent ligand are chosen several [Pd(Ar)(NN)(solv)]$^+$ can be isolated and characterised.[10,11] Furthermore, the intermolecular aryl ligand transfer reaction in nickel complexes is attributed to cationic intermediate formation.[12] Moreover, the compatibility of the nitrile fragment with a σ-M–C bond in the *cis* position is not always possible. Recently, an unusual insertion of nitriles into a Pd–C bond has been reported.[13] It was assisted by the protonation of the nitrile nitrogen atom by the *ortho*-hydroxy group present in the aryl ligand. The insertion of an acetonitrile ligand into a Pd–aryl bond has been postulated as a key step in the Pd-catalyzed cyanation of aryl halides[14] and in the synthesis of aryl ketones by the reaction of arenes with nitriles.[15] In this paper, we report the synthesis and characterization of neutral and ionic organometallic palladium(II) and nickel(II) complexes of the general formula [MBr(Mes)(NN)] and [M(Mes)(3,5-lut)(NN)][BF_4] (NN = DAD **a**, PIM **b**, bipy **c**, phen **d**). To test the ionic complexes as precursors in the olefin oligomerization reaction we attempted to prepare an analogous compound using CH_3CN instead of 3,5-$Me_2C_5H_3N$ as the stabilizing ligand. However, an unprecedented

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† Electronic supplementary information (ESI) available: Fig. 1S: MS (FAB$^+$) of compounds **7c** and **7c′**. Fig. 2S: ^{1}H NMR spectra of complexes **5a** (500 MHz), **7a** and **7c** (250 MHz). Fig. 3S: MS (CI, NH_3) of imine NH=C(Mes)Me. Scheme 1S: Alternative mechanisms proposed for the evolution of the mesityl–nitrile cationic species. Tables 1S and 2S: ^{1}H NMR spectra of all compounds. See DOI: 10.1039/b608352h

reaction between [NiBr(Mes)(NN)], $AgBF_4$ and CH_3CN led to the isolation of [Ni(2,4,6-$Me_3C_6H_2$){NH=C(Me)(2,4,6-$Me_3C_6H_2$)}(NN)][BF_4], after a sequence of reactions involving the initial formation of azomethine intermediates.

Results and discussion

Synthesis of the dihalo-complexes

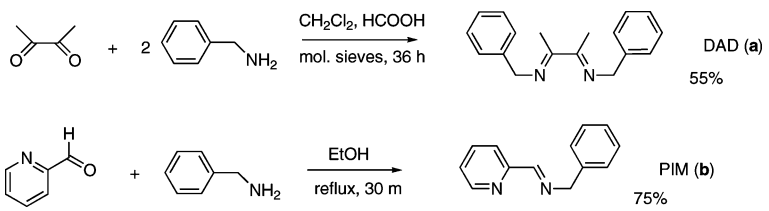
The reported diazabutadiene (DAD)[16] (**a**) and pyridinylimine (PIM)[17] (**b**) were obtained by methods previously described for similar ligands. They were characterized by ^{1}H NMR spectroscopy. 1,4-Diaza-1,3-butadiene (DAD) (**a**) was prepared by condensation between 2,3-butanedione and benzylamine in CH_2Cl_2 in the presence of molecular sieves as drying agents and formic acid as a catalyst.[18] Pyridinylimine (PIM) (**b**) was synthesized by the condensation of pyridine-2-carbaldehyde with the stoichiometric amount of benzylamine in refluxing ethanol[19] (Scheme 1).

The nickel dibromide complexes (**1a**, **1b**) were obtained by the reaction of the organic ligand, DAD (**a**) and PIM (**b**), dissolved in toluene and the equivalent amount of anhydrous nickel bromide. The complexes precipitated almost quantitatively from the reaction mixture as very insoluble pale-yellow solids. The paramagnetic nature of the complexes precluded their characterization by ^{1}H NMR spectroscopy ($\chi T = 1.15$ cm^3 mol^{-1} K, 300 K for **1b**). It has been reported that dibromonickel(II) complexes containing bulky pyridinylimines or diazabutadienes derived from *ortho* mono- or di-substituted phenylamines showed mononuclear or dinuclear structures, with the nickel atom pentacoordinated in a distorted square-planar pyramidal environment.[20–22] Similar complexes with α-dimine ligands[23] have been described as yellow dinuclear solids that transform to violet paramagnetic solids at high temperature. The colour and high insolubility of complexes **1a** and **1b** suggest that these compounds have a dimeric structure in the solid state. This prevents their purification by recrystallization. Palladium complexes **2a** and **2b** were obtained by the reaction of stoichiometric amounts of Li_2[$PdBr_4$] with diazabutadiene (**a**) and pyridinylimine (**b**) ligands in MeOH. The resulting complexes were yellow–orange diamagnetic solids that were insoluble in non-coordinating solvents. They were characterized by elemental analyses and by ^{1}H NMR spectroscopy. ^{1}H NMR data (see Tables 1S and 2S, ESI†) are compatible with a monomeric square-planar structure containing a bidentate coordinated ligand. This is in accordance with other results in the literature.[20,21,24] The respective proton signals of the ligand were shifted to a lower field upon coordination. Of note is the large chemical shift of the methylenic protons. This was particularly notable in compound **2a**, which had a downfield shift of nearly 1 ppm with respect to the free ligand.

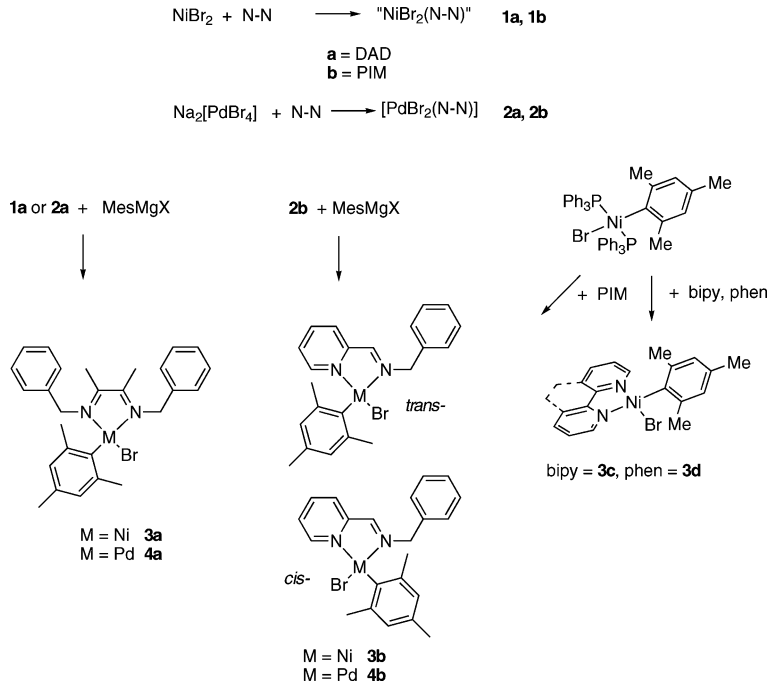
Neutral mesityl nickel and palladium complexes

Bromo(mesityl) nickel complexes, [NiBr(Mes)(NN)], M = Ni; NN = DAD **3a**, PIM, **3b**, bipy, **3c**, phen, **3d**, were obtained either by a substitution reaction of the phosphine ligand in *trans*-[NiBr(Mes)(PPh_3)$_2$] by the NN ligand, according to previously described methods,[25–27] or by the reaction between [$NiBr_2$(DAD)] and mesitylmagnesium bromide in THF solution (Scheme 2). The substitution reaction did not give the desired results in the case of ligand DAD. The complex **3a** must be obtained by the second method because ligand **a** was unable to substitute the PPh_3 in [NiBr(Mes)(PPh_3)$_2$]. For rather basic ligands like bipyridine, phenanthroline and PIM the reaction proceeds very smoothly with high yields. However, the less basic the ligand is, the more the equilibrium tends towards the starting material. Bromo(mesityl) palladium complexes [PdBr(Mes)(NN)], NN = DAD, **4a**, PIM **4b**, were obtained by the reaction between [$PdBr_2$(NN)] and mesityl magnesium bromide in THF solution (Scheme 2). The nickel complexes were purple (**3a**) and deep-red (**3b**, **3c**, **3d**) air stable solids. The palladium complexes (**4a**) and (**4b**) were yellow air stable solids. Nickel complexes **3c** and **3d**, previously described, were obtained for comparison.[25,28] All the new complexes were characterized by elemental analysis, IR spectra and ^{1}H NMR. All assignments are based on their coupling patterns, ^{1}H–^{1}H COSY and NOESY experiments. ^{1}H NMR data for the compounds and the numbering scheme are shown in Tables 1S and 2S (see ESI†).

In the ^{1}H NMR spectra of **3a** and **4a**, two singlets were observed for the methylenic protons, at higher and lower fields than in the free ligand. The signal of the protons of the methylene group *cis* to the mesityl ligand was shifted to higher fields, due to the ring currents. The signal of the methylene protons *cis* to the bromide was shifted to lower fields, due to the strong deshielding effect of the bromide.[8] The ^{1}H–^{1}H NOESY experiment conducted on complex **4a** was entirely consistent with this proposal and permitted the assignment of the remainder of the signals. Selected NOESY correlations are presented in Fig. 1. Exchange contacts between both CH_2 fragments (4.51 and 5.34 ppm) showed the shift of the mesityl group between the two coordination positions opposite the NN ligand. This was probably due to the lability of the bromide ligand in acetone. Since the PIM ligand is non-symmetric, coordination in [MBr(Mes)PIM] compounds can lead to the formation of two isomers, *cis* and *trans*, depending on the relative position of the mesitylene ligand and the iminic nitrogen of the pyridinylimine ligand on the metal atom. This is the case for the Ni(II) and Pd(II) complexes **3b** and **4b**, as can be concluded from the two sets of signals in the NMR spectra. No change in



Scheme 1



Scheme 2

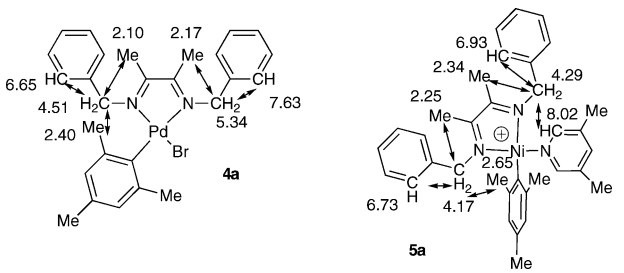
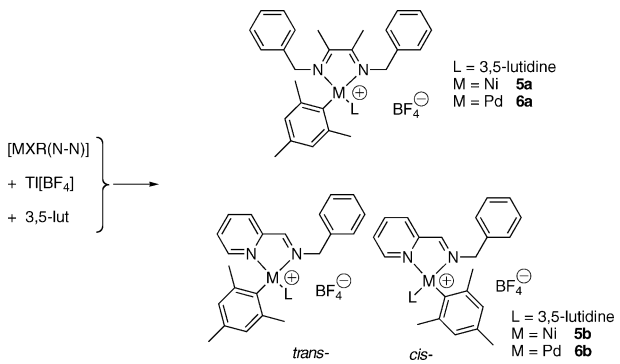


Fig. 1 Details of NOE contacts observed in compounds **4a** and **5a**.

the isomer composition was observed after standing in acetone-d^6 at room temperature for 48 h. The relative *trans* : *cis* ratio of each isomer was 37 : 63 for **3b** and 45 : 55 for **4b**. The *cis* configuration was also found to be the most sterically favourable for the majority of methyl(chloro)palladium complexes of PIM.[8] The most sensitive resonances for the assignment of both isomers were those of the hydrogen atom in the carbon *ortho* of the pyridine ring. In the *cis* isomers, this hydrogen atom had a large chemical shift, owing to the strong deshielding effect of the bromide ligand, which is situated *cis* to the pyridyl group. In the *trans* isomers, it had a considerably lower chemical shift, due to the proximity of the mesityl ring. Isomer interconversion was observed by the exchange signal between 4.13 and 5.19, the two methylene groups of both isomers in the NOESY spectrum of **3b**. The ^{1}H NMR signals of the palladium complex **4b** were assigned by comparison to that of the nickel complex. In addition, the ^{1}H NMR data of both **3c** and **3d** are included (Table 1S, ESI†).

Cationic mesityl nickel and palladium complexes containing 3,5-lutidine

The reaction of bromo(mesityl)palladium and nickel complexes, [MBr(Mes)(NN)], NN = DAD, PIM, with $TlBF_4$ in acetone in the presence of 3,5-dimethylpyridine (3,5-lutidine) yields stable cationic complexes, [M(Mes)(3,5-lutidine)(NN)]BF_4, M = Ni, NN = DAD, PIM, **5a**, **5b**; M = Pd, NN = DAD, PIM, **6a**, **6b** (Scheme 3). The complexes were obtained as orange (**5a**, **5b**) and yellow (**6a**, **6b**) solids that were characterized by elemental analysis and ^{1}H NMR spectra. The ^{1}H NMR data are shown in Tables 1S and 2S (see ESI†).



Scheme 3

The ^{1}H NMR spectra of compounds with DAD showed that the signals of the methylenic and the *ortho* protons of the benzyl groups shifted upfield with respect to free ligand, according to the influence of the ring currents of both the mesityl and the 3,5-lutidine groups. Nevertheless, the assignment of the signals to the corresponding protons can be made with the NOESY spectrum of **5a** (Fig 1). The *ortho*-methyl protons of the mesitylene and the *meta*-methyl protons of the lutidine each appear as singlets, showing the planar symmetry of these molecules. The assignment of the spectra of the palladium complex **6a** was performed by comparing it with that of the nickel complex. The spectra of the ionic compounds containing PIM show, as for the neutral

compounds, the presence of *trans* and *cis* isomers according to the configuration of the mesityl and the iminic nitrogen. Compound **5b** was obtained as a mixture of *trans* and *cis* isomers in a 80 : 20 ratio. Selected correlations observed for the major *trans* isomer were: 4.67 (s, CH_2) with 8.32 (s, H *ortho*, lut) and 2.16 (s, CH_3, *meta*, lut). The isomeric composition of the acetone-d^6 solution was unchanged with time. For the palladium complex **6b**, the two sets of resonances were in an approximate ratio of 10 : 90 for the *trans* and *cis* isomers, respectively, as deduced from NOESY correlation measurements. Selected correlations observed for the major isomer were: 4.60 (s, CH_2) with 2.51 (s, Me *ortho*, Mes), and also 7.98 (d, H *ortho*, Ar) with 8.49 (s, H *ortho*, lut). A significant change in the isomer composition was observed, after leaving the complex at room temperature in acetone-d^6 for a week. The final ratio between the *trans* and *cis* isomers was 75 : 25. The assignment of the signals to the protons of the *trans* isomer was confirmed by the NOESY spectrum. Contacts between 5.01 (s, CH_2), 8.10 (s, H *ortho* lut) and 7.02 (d, H *ortho*, Ar) were observed. No chemical exchange process between the two isomers was revealed in the NOESY spectrum. Therefore, the interconversion between them was slower than the timescale of the NOE experiment. Interestingly, the *trans* configuration is apparently the most favourable configuration for ionic complexes. The opposite has been observed for neutral complexes.

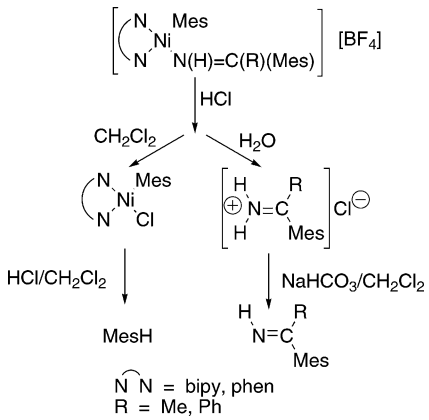
Cationic complexes derived from the reaction with acetonitrile

Our attempts to prepare stable nickel ionic complexes by treating neutral complexes with $TlBF_4$ in the presence of acetonitrile failed. TlBr was formed after addition of $TlBF_4$ to an acetone solution of the neutral complexes **3a**, **3b**, **3c**, **3d** in the presence of an excess of CH_3CN. After filtration and removal of the solvent, orange (**7b**) and reddish (**7a**, **7c**, **7d**) solids were isolated with yields that never reached 40% with respect to the total amount of Ni. The nature of the products obtained was defined after accurate characterization of the products and preparation of the bipy and phen species (**7c**, **7d**), as the ^{1}H NMR spectra were less complex in the alkyl region. The ionic products contained a neutral imine [(Mes)MeC=NH] ligand, the α-diimine ligand and a mesityl group (see Scheme 4).

The structure of the final compounds obtained was proposed after consideration of the elemental analysis, IR spectra (new bands at 3200–3250 and 1635 cm^{-1}, in the range of ν(N–H) and ν(C=N) vibrations), ^{1}H NMR data and FAB data (Table 1). Further identification was by the separation of the neutral imine ligand by reaction with acid and the subsequent recovery of the free ligand by basic treatment (Scheme 5). ^{1}H NMR data showed the

Table 1 FAB^+ data of the compounds [Ni(Mes)(NH=C(Mes)R)-(bipy)]BF_4 (R = CH_3, Ph) in NBA matrix

	7c·MeCN	**7c′** (PhCN)
$M^+ + 1$	495.8 (495.2)	557.4 (557.2)
M^+	494.0 (494.2)	555.9 (556.2)
$M^+ - Mes$	374.9 (375.1)	436.8 (437.1)

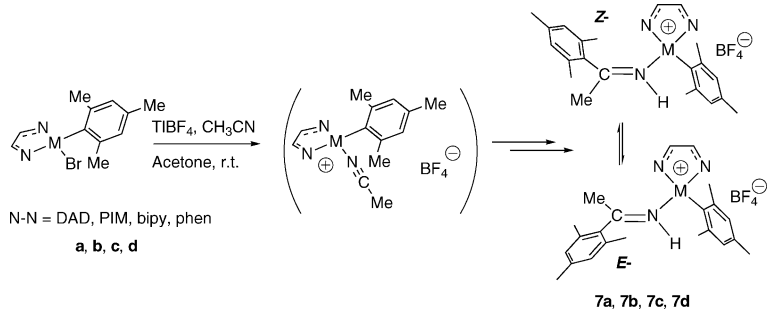


Scheme 5

presence of one (**7a**), two (**7c**, **7d**) or four (**7b**) isomers in solution. Similar behaviour was observed using benzonitrile instead of acetonitrile in the reaction of the nickel bipyridine complex (**7c′**).

For **7a**, {Ni(Mes)[NH=C(Mes)(Me)](DAD)}BF_4, the ^{1}H NMR spectrum showed the presence of only one compound in which the imine [(Mes)MeC=NH] ligand was present in the *E* conformation. This is based on the high chemical shift (2.89 ppm) observed for the methyl group that is close to the metal in the *E* conformation. The same effect was observed in the *ortho* methyl groups of the mesityl ligand that are directly bonded to the metal atom. For **7c**, **7c′** and **7d**, ^{1}H NMR spectroscopy showed the presence of two compounds differing in the *E* or *Z* conformation of the two groups in the imine function. In solution an equilibrium shift to the *E* isomer was shown by NMR spectroscopy in acetone-d^6 at 308 K. Initially the major isomer was in the *Z* conformation, the expected geometry after a *cis*-insertion. However, this evolved to the more sterically favoured *E* isomer. After 60 min the ratio remained constant (Table 2).

The analysis of the spectra of **7b** was more complex, since *cis* and *trans* complexes were obtained due to the asymmetry of the PIM ligand. In addition, the *E* and *Z* conformation of the imine ligand was observed in each case. The ^{1}H NMR spectrum showed the presence of the four isomers. Due to their complexity,



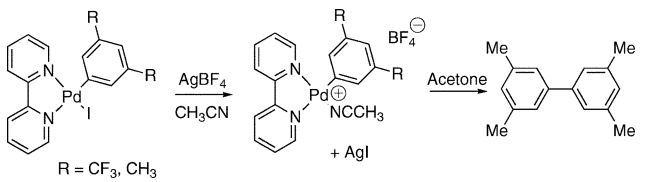
Scheme 4

Table 2 The change in the composition of *Z*-, *E*-isomers observed in acetone-d^6 at 25 °C over 60 min for complexes **7c**, **7c′** and **7d**

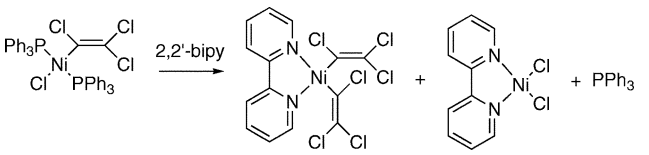
	Initial[a]		Final	
Compound	*Z*	*E*	*Z*	*E*
7c	50	50	15	85
7c′	71	29	37	63
7d	63	37	18	82

[a] Initial composition could vary

the assignment of all the signals was not possible. However, an analysis of the aliphatic region enabled the four singlets of the methylenic groups and those of the methyl groups of the imine ligand to be identified and assigned. The final isomeric composition was, 60 (*trans*, *E*) : 25 (*cis*, *E*) : 9 (*cis*, *Z*) : 6 (*trans*, *Z*). The *trans* form was the most stable, as observed with the ionic complexes **5b** and **6b**. In spite of the fact that the palladium complexes $[Pd(CH_3)(NCCH_3)(PIM)]^+$ are known,[8,29] when we tried to synthesise similar complexes with mesityl instead of the methyl ligand, starting from **4a** or **4b**, similar results to those obtained with the nickel complexes were observed. No further investigation was undertaken. The exact mechanism by which these ionic compounds are obtained is not obvious. The initial cationic species were probably formed, since the expected ionic complexes $[Ni(Mes)(NN)(lut)][BF_4]$ were obtained when lutidine was used. The process implies that the nitrile was inserted in the metal-mesitylene bond giving a azomethine (M–N=CR(Mes)) intermediate, protonation to the final imine neutral ligand and their intermolecular exchange. However, other possibilities could be proposed (see ESI†). The reaction of **3c** in acetone-d^6 with a small amount of D_2O suggests that the hydrogen atom needed for the protonation of the azomethine intermediate comes from water present in the acetone solvent. It is known that the addition of $AgBF_4$ to acetone or THF solutions of [PdI(Ar)(bpy)] (eqn (1)), does not lead to isolation of the cationic aryl palladium complexes and causes intermolecular coupling of the aryl ligands to yield the corresponding biaryls.[10] The symmetrization of a trichlorovinyl nickel complex was observed when a simple substitution of PPh_3 by the bipyridyl ligand was attempted, supporting the proposed mechanism of the formation of biaryls by intramolecular coupling (eqn (2)).[30] Insertion of the CN bond of an organonitrile into a late transition metal–carbon σ bond, is not a common process. However, it has been reported to occur in the palladium–carbon bond giving a free imine (eqn (3)),[14] or trapping the coordinated imine in a N,O-metallacycle (eqn (4)). The process is assisted by the protonation of the nitrile nitrogen atom by the *ortho*-hydroxy group present in the aryl ligand.[13] The reduction of coordinated acetonitrile has been observed in several complexes in which the coordinated nitrile is activated toward nucleophilic attack.[31] Recently, the reduction of nitriles by a catalytic palladium system has been reported.[32]



(1)



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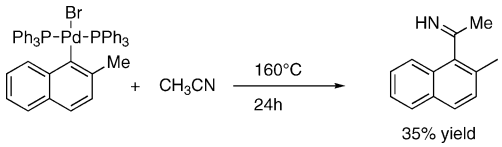

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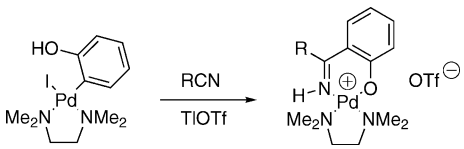

(4)

Reactions with ethylene

Palladium and nickel compounds with α-diimine ligands have been used successfully as precursors of catalytic species in the oligomerization and polymerization of ethylene. Therefore, we studied this reaction with some of the new complexes to evaluate whether the ionic compounds **7** containing the imine ligand could be used as organometallic precursors. In previous work, we described[33] the preparation of ionic complexes containing a tridentate NN′C ligand, derived from modified DAD and PIM backbones, with acetonitrile as a labile coordinated ligand that showed limited activity in the reaction with ethylene. When a THF solution of the cationic **7a** and **7b** complexes were treated with ethylene at 20 bar and 25 °C, the starting compounds were recovered unchanged. Therefore, the imine ligand did not undergo the substitution by ethylene, which is the initial step in the formation of the hydride catalytic species.

Conclusions

The use of nitriles as labile ligands to prepare one component organometallic catalytic precursors of nickel and palladium could be inconvenient in certain conditions. This is because the nitrile fragment is prone to insert into the σ(M–aryl) bond and the resulting imine neutral ligands, which are coordinated when the complex reorganization of the initially desired precursor is complete, are inert with respect to their substitution by ethylene. Therefore, if the process described here occurs, it is impossible to activate the reaction at a medium pressure of ethylene.

Experimental

General remarks

All manipulations of the compounds were carried out under a purified nitrogen atmosphere using standard Schlenk and high-vacuum techniques. The solvents were dried, distilled and stored under a nitrogen atmosphere by standard procedures. All reagents were commercially available. Ethylene (99.95% quality) was used as received. Elemental analyses were carried out by an Eager 1108 microanalyzer. IR spectra were recorded as KBr disks on a Nicolet

520 FT-IR spectrometer. Mass spectra (FAB) were recorded on a Fisons VG-Quattro spectrometer. ^{1}H NMR spectra were recorded with a Bruker DRX 250, Varian XL-500 or Varian Gemini-200 spectrometers. Chemical shifts (in ppm) were measured relative to $SiMe_4$. Coupling constants in Hz, numbering as shown in Tables 1S and 2S (see ESI†). The oligomer products were analyzed on a Hewlett-Packard 5890 equipped with a 50 m ultra-2 cross-linked 5% phenylmethyl silicone capillary column and a FID detector.

Synthesis of the ligands

***N*,*N*′-Dibenzyl-2,3-butanediimine (a).** The ligand was prepared by the same procedure described in the literature[20] for the preparation of related diazabutadienes derived from 2,3-butanedione and aliphatic amines with a secondary α-carbon. 2.0 g (23.2 mmol) of 2,3-butanedione and 4.5 g (42.0 mmol) of benzylamine were dissolved in 20 cm^3 of dichloromethane. To the resulting solution a drop of 98% formic acid and 8 g of molecular sieve (4A) were added. The mixture was stirred at room temperature. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 24–48 h the solution was filtered and the solvent was removed in vacuum. The crude product obtained was recrystallized from MeOH and obtained as an oily material (yield = 55%). ^{1}H NMR (250 MHz, $CDCl_3$), δ 2.25 (s, 6 H, $CH_3^{5,6}$), 4.70 (s, 4 H, $CH_2^{1,7}$), 7.25–7.45 (m, 10 H, Ph).

Benzyl(pyridin-2-yl)methyleneamine (b). This ligand was obtained by the method described for similar ligands.[21] A mixture of 2.0 g (18.6 mmol) of 2-pyridine-2-carbaldehyde and 2.0 g (18.6 mmol) of benzylamine in 20 cm^3 of ethanol were refluxed for 30 min. After cooling, the solvent was removed in vacuum. The crude product obtained was recrystallized in hexane and obtained as an oily material (yield = 75%). ^{1}H NMR (200 MHz, $CDCl_3$), δ 4.88 (s, 2 H, CH_2), 7.27–7.36 (m, 6 H, $H^{7,7',8,8',9}$), 7.72 (t, *J* 7.8, 1 H, H^3), 8.06 (d, *J* 8.0, 1 H, H^4), 8.49 (s, 1 H, H^5), 8.65 (d, *J* 4.8, 1 H, H^1).

Synthesis of the neutral complexes

[$NiBr_2$(DAD)] (1a). A suspension of 4.84 g (22 mmol) of anhydrous $NiBr_2$ and 6.30 g (24 mmol, 10% excess) of ligand **a** in 40 cm^3 of toluene were stirred for 72 h at room temperature. A yellow solid was formed. It was filtered off and washed with hexane, and finally dried in vacuum (yield 75%).

[$NiBr_2$(PIM)] (1b). The complex was prepared following the procedure described for **1a**, by using ligand **b**. The yellow solid was filtered off, washed with hexane and finally dried in vacuum (yield 80%).

[$PdBr_2$(DAD)] (2a). To a solution of 0.40 g (2.25 mmol) of $PdCl_2$ and 0.78 g (9 mmol) of LiBr in 50 cm^3 of methanol at room temperature, 0.63 g (2.40 mmol, 10% excess) of ligand **a** was added. Immediately a yellow–orange solid was formed. It was filtered off and washed with water and methanol and finally dried at vacuum (yield = 87%) (Found: C, 41.2; H, 3.9; N, 5.4. Calc. for $C_{18}H_{20}Br_2N_2Pd$ C, 40.75; H, 3.80; N, 5.28%). ^{1}H NMR (250 MHz, $CDCl_3$), δ: 2.27 (s, 6 H, $CH_3^{5,6}$), 5.63 (s, 4 H, $CH_2^{1,7}$), 7.28–7.40 (m, 6 H), 7.57 (d, *J* 7, 4 H, $H^{2,2',8,8'}$).

[$PdBr_2$(PIM)] (2b). The complex was prepared following the procedure described for **2a**, by using ligand **b** (yield = 90%) (Found: C, 33.2; H, 2.5; N, 5.9. Calc. for $C_{13}H_{12}Br_2N_2Pd$: C, 33.76; H, 2.62; N, 6.06%). ^{1}H NMR (250 MHz, DMSO-d^6), δ 5.21 (s, 2 H, CH_2), 7.3–7.5 (m, 5 H, $H^{7,7',8,8',9}$), 7.86 (t, *J* 5.5, 1 H, H^2), 8.13 (d, *J* 7.6, 1H, H^4), 8.32 (t, *J* 7.6, 1H, H^3), 8.75 (s, CH=N), 9.19 (d, *J* 5.2, 1 H, H^1).

[NiBr(Mes)(DAD)] (3a). Over a suspension of 3.86 g (8.00 mmol) of **1a** in 10 cm^3 of tetrahydrofuran, a solution containing approximately 12 mmol of mesityl magnesium bromide in tetrahydrofuran was added. Immediately the yellow suspension dissolved leaving a deep red solution. After 10 min, the reaction mixture was hydrolysed with 20 cm^3 of 10% NH_4Br solution. The organic phase was extracted with toluene, dried over Na_2SO_4, and filtered off. The solution obtained was evaporated to dryness and the purple solid residue was washed with water and diethyl ether and then dried in vacuum (yield = 50%) (Found: C, 61.4; H, 5.9; N, 5.2. Calc. for $C_{27}H_{31}BrN_2Ni$: C, 62.11; H, 5.98; N, 5.36%). ^{1}H NMR (250 MHz, $CDCl_3$), δ 1.69 (s, 3 H, *p*-CH_3), 1.91 (s, 3 H, CH_3^5), 2.16 (s, 3 H, CH_3^6), 2.75 (s, 3 H, *o*-CH_3), 4.29 (s, 2 H, CH_2^1), 5.37 (s, 2 H, CH_2^7), 6.33 (s, 2 H, *m*-H), 6.68 (br s, 2 H, $H^{2,2'}$), 7.21–7.38 (m, 6 H), 7.65 (d, *J* 6.8, 2 H, $H^{8,8'}$).

[NiBr(Mes)(PIM)] (3b). 0.11 g (0.7 mmol) of ligand **b** were added to a vigorously stirred suspension of 0.46 g (0.6 mmol) of [NiBr(Ms)(PPh_3)$_2$] in 20 cm^3 of diethyl ether. After a few minutes the yellow suspension dissolved leaving a deep red solid precipitate. The solid was filtered off, washed with water and diethyl ether and dried in vacuum (yield = 75%) (Found: C, 58.5; H, 5.2; N, 6.2. Calc. for $C_{22}H_{23}BrN_2Ni$: C, 58.20; H, 5.11; N, 6.17%). ^{1}H NMR (500 MHz, acetone-d^6), obtained from the mixture of the *cis* (65%) and *trans* (35%) isomers. NMR data for the *cis* isomer, δ 9.31 (d, *J* 5.5, 1 H, H^1), 8.62 (s, 1 H, HC=N), 8.18 (td, *J* 7.5 and 1.5, 1 H, H^3), 7.96 (d, *J* 7.5, 1 H, H^4), 7.82 (t, *J* 7.5, 1 H, H^2), 7.38–7.24* (m, 3 H, $H^{8,8',9}$), 6.85 (d, *J* 7.5, 2 H, $H^{7,7'}$), 6.36 (s, 2 H, *m*-H), 4.13 (s, 2 H, CH_2), 2.87 (s, 6 H, *o*-CH_3), 2.17 (s, 3 H, *p*-CH_3). NMR data for the *trans* isomer, δ 8.58 (s, 1 H, HC=N), 8.12 (td, *J* 7.5 and 1.5, 1 H, H^3), 7.85 (d, *J* 7.5, H, H^4), 7.67 (d, *J* 7.5, 2 H, $H^{7,7'}$), 7.44 (t, *J* 7, 1 H, H^2), 7.15 (d, *J* 5.5, 1 H, H^1), 7.40 (d, *J* 7.5 and 1.5, 2 H, $H^{8,8'}$), 7.38–7.24* (m, 1 H, H^9), 6.43 (s, 2 H, *m*-H), 5.19 (s, 2 H, CH_2), 2.96 (s, 6 H, *o*-CH_3), 2.04 (s, 3 H, *p*-CH_3); *overlapped signals of both isomers.

[PdBr(Mes)(DAD)] (4a). According to the procedure described for **3a** by using **2a** (yield = 78%). (Found: C, 56.2; H, 5.4; N, 5.1. Calc. for $C_{27}H_{31}BrN_2Pd$: C, 56.91; H, 5.48; N, 4.92%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 2.10 (s, 3 H, CH_3^5), 2.15 (s, 3 H, *p*-CH_3), 2.17 (s, 3 H, CH_3^6), 2.40 (s, 6 H, *o*-CH_3), 4.51 (s, 2 H, CH_2^1), 5.34 (s, 2 H, CH_2^7), 6.40 (s, 2 H, *m*-H), 6.65 (d, *J* 7.5, 2 H, $H^{2,2'}$), 7.17–7.36 (m, 6 H), 7.63 (d, *J* 7.5, 2 H, $H^{8,8'}$).

[PdBr(Mes)(PIM)] (4b). According to the procedure described for **3a** by using **2b** (yield = 70%). (Found: C, 53.2 H, 4.7; N, 5.2. Calc. for $C_{22}H_{23}BrN_2Pd$: C, 52.67; H, 4.62; N, 5.58%). ^{1}H NMR (500 MHz, acetone-d^6) obtained from a mixture of *cis* (65%) and *trans* (35%) isomers. *cis* Isomer, δ 9.13 (d, *J* 5.5, 1 H, H^1), 8.88 (t, *J* 1.5, 1 H, HC=N), 8.26 (td, *J* 8, 1 H, H^3), 8.12 (d, *J* 8, 1 H, H^4), 7.87 (dd, *J* 5 and 1.5, 1 H, H^2), 7.28 (tt, *J* 7.5 and 1.5, 1 H, H^9), 7.22 (tt, *J* 7.5 and 1.5, 2 H, $H^{8,8'}$), 6.80 (d, *J* 7, 2 H, $H^{7,7'}$), 6.45 (s, 2 H, *m*-H), 4.49 (s, 2 H, CH_2), 2.42 (s, 6 H, *o*-CH_3), 2.02* (s, 3 H, *p*-CH_3). *trans* Isomer, δ 8.69 (t, *J* 1.5, 1 H, HC=N), 8.21 (td, *J* 8 and 2, 1H, H^3), 8.04 (d, *J* 7, 1 H, H^4), 7.70 (d, *J* 7.5, 2 H, $H^{7,7'}$),

7.59 (dd, *J* 5.5 and 1.5, 1 H, H^2), 7.46 (dd, *J* 5.5 and 1.5, 1 H, H^1), 7.40 (tt, *J* 7 and 1.5, 2 H, $H^{8,8'}$), 7.33 (tt, *J* 7.5 and 1.5, 1 H, H^9), 5.23 (s, 2 H, CH_2), 6.55 (s, 2 H, *m*-H), 2.57 (s, 6 H, *o*-CH_3), 2.02* (s, 3 H, *p*-CH_3); *overlapped signals of both isomers.

Synthesis of the ionic complexes

[Ni(Mes)(3,5-lut)(DAD)]BF_4 (5a). 0.30 g (1.03 mmol) of $TlBF_4$ was added over a stirred solution of 0.11 g (1.0 mmol) of 3,5-lutidine and 0.52 g (1.00 mmol) of the neutral complex **3a** in 30 cm^3 of tetrahydrofuran. A reddish suspension containing white insoluble thallium halide was slowly formed. After 14 h the thallium bromide was separated by filtering over Celite. The solvent was then evaporated to dryness and the remaining resin stirred with diethyl ether until a suspension with an orange solid was obtained. The solid was filtered off, and washed several times with water and diethyl ether (yield = 60%) (Found: C, 63.4; H, 6.2; N, 6.6. Calc. for $C_{34}H_{40}BF_4N_3Ni$: C, 64.19; H, 6.34; N, 6.60%). ^1H NMR (500 MHz, $CDCl_3$), δ 2.03 (s, 6 H, *m*-CH_3), 2.06 (s, 3 H, *p*-CH_3), 2.25 (s, 3 H, CH_3^5), 2.34 (s, 3 H, CH_3^6), 2.65 (s, 6 H, *o*-CH_3), 4.17 (s, 2 H, CH_2^1), 4.29 (s, 2 H, CH_2^7), 6.22 (s, 2 H, *m*-H), 6.73 (d, *J* 7, 2 H, $H^{2,2'}$), 6.93 (d, *J* 7.5, 2 H, $H^{8,8'}$), 7.06 (s, 1 H, *p*-H), 7.22–7.40 (m, 6 H), 8.02 (s, 2 H, *o*-H).

[Ni(Mes)(3,5-lut)(PIM)]BF_4 (5b). Compound **5b** was obtained by the same procedure described for complex **5a** by using complex **3b** (yield = 80%) (Found: C, 61.0; H, 5.6; N, 7.5. Calc. for $C_{29}H_{32}BF_4N_3Ni$: C, 61.31; H, 5.68; N, 7.40%). ^1H NMR (250 MHz, acetone-d^6), obtained from the mixture of the isomers *cis* (20%) and *trans* (80%). *trans* Isomer, δ: 8.97 (s, 1 H, *H*C=N), 8.32 (s, 2 H, *o*-H), 8.30 (d, *J* 7, 1H, H^3), 8.16 (d, *J* 7, 1 H, H^4), 7.61 (dd, *J* 5.5 and 1.5, 1 H, H^2), 7.46 (s, 1 H, *p*-H), 7.34–7.33* (m, 3 H, $H^{8,8',9}$), 7.26 (d, *J* 5.5, 1 H, H^1), 7.06–7.07 (m, 2 H, $H^{7,7'}$), 6.49 (s, 2 H, *m*-H), 4.67 (s, 2 H, CH_2), 3.06 (s, 6 H, *o*-CH_3), 2.16* (s, 6 H, *m*-CH_3), 2.12 (s, 3 H, *p*-CH_3). *cis* Isomer, δ 8.76 (s, 2 H, *o*-H), 8.68 (s, 1 H, HC=N), 8.30 (d, *J* 7, 1 H, H^3), 8.19 (d, *J* 7, 1 H, H^4), 7.74 (dd, *J* 5.5 and 1.5, 1 H, H^2), 7.65 (s, 1 H, *p*-H), 7.34–7.33* (m, 3 H, $H^{8,8',9}$), 7.18 (d, *J* 5.5, 1 H, H^1), 6.86 (d, 2 H, $H^{7,7'}$), 6.45 (s, 2 H, *m*-H), 4.23 (s, 2 H, CH_2), 3.01 (s, 6 H, *o*-CH_3), 2.31 (s, 6 H, *m*-CH_3), 2.16* (s, 3 H, *p*-CH_3). * Overlapped signals of both isomers.

[Pd(Mes)(3,5-lut)(DAD)]BF_4 (6a). Obtained by the same procedure described for complex **5a** by using complex **4a** (yield = 70%) (Found: C, 59.1 H, 6.0; N, 6.4. Calc. For $C_{34}H_{40}BF_4N_3Pd$: C, 59.71; H, 5.90; N, 6.14%). ^1H NMR (250 MHz, $CDCl_3$), δ 2.04 (s, 6 H, *m*-CH_3), 2.11 (s, 3 H, *p*-CH_3), 2.32 (s, 6 H, $CH_3^{5,6}$), 2.47 (s, 6 H, *o*-CH_3), 4.51 (s, 2 H, CH_2^1), 4.74 (s, 2 H, CH_2^7), 6.34 (s, 2 H, *m*-H), 6.71 (m, 2 H, $H^{2,2'}$), 6.88 (m, 2 H, $H^{8,8'}$), 7.14 (s, 1 H, *p*-H), 7.16–7.32 (m, 6 H), 7.78 (s, 2 H, *o*-H).

[Pd(Mes)(3,5-lut)(PIM)]BF_4 (6b). The compound was obtained by the same procedure as **5a** using complex **4b** (yield = 83%) (Found: C, 57.2 H, 5.5; N, 7.1. Calc. for $C_{29}H_{32}BF_4N_3Pd$: C, 56.26; H, 5.24; N 6.82%). ^1H NMR (500 MHz, acetone-d^6), obtained from the mixture of the two isomers *cis* (25%) and *trans* (75%). *cis* Isomer, δ 9.05 (s, 1 H, HC=N), 8.49 (s, 2 H, *o*-H), 8.39 (td, *J* 8 and 2, 1 H, H^3), 8.33 (d, *J* 7.5, 1 H, H^4), 7.98 (d, *J* 5, 1 H, H^1), 7.85 (ddd, *J* 7.5, 5 and 1.5, 1 H, H^2), 7.74 (s, 1 H, *p*-H), 7.31 (t, *J* 7.5, 1 H, H^9), 7.24 (t, *J* 5.0, 2 H, $H^{8,8'}$), 6.78 (d, *J* 7.5, 2 H, $H^{7,7'}$), 6.53 (s, 2 H, *m*-H), 4.60 (s, 2 H, CH_2), 2.51 (s, 6 H, *o*-CH_3), 2.33 (s, 6 H, *m*-CH_3), 2.20 (s, 3 H, *p*-CH_3). *trans* Isomer, δ 9.08 (s, 1 H, *H*C=N), 8.40 (td, *J* 8 and 1.5, 1 H, H^3), 8.31 (d, 1 H, H^4), 8.10 (s, 2 H, *o*-H), 7.73 (ddd, 1 H, H^2), 7.64 (d, *J* 5, 1 H, H^1), 7.52 (s, 1 H, *p*-H), 7.31–7.23 (m, 3 H, $H^{9,8,8'}$), 7.02 (d, *J* 7.5, 2 H, $H^{7,7'}$), 6.58 (s, 2 H, *m*-H), 5.01 (s, 2 H, CH_2), 2.68 (s, 6 H, *o*-CH_3), 2.20 (s, 6 H, *m*-CH_3), 2.15 (s, 3 H, *p*-CH_3).

{**Ni(Mes)[NH=C(Mes)(Me)](DAD)**}BF_4 **(7a).** To a solution of 0.40 g (0.91 mmol) of **3a** and 0.11 g of CH_3CN (2.7 mmol, 300% excess) in 50 cm^3 of acetone, 0.27 g (0.94 mmol) of $TlBF_4$ was added. The reaction mixture was stirred for 12 h, during which time a fine precipitate of thallium bromide was formed. The mixture was filtered off through Celite and then concentrated under reduced pressure. The complex was precipitated as an orange–reddish solid by replacing the tetrahydrofuran by toluene. The solid was filtered off and washed with water and ether (yield = 23%, based on nickel) (Found: C, 64.3 H, 6.9; N, 6.7. Calc. for $C_{38}H_{46}BF_4N_3Ni$: C, 66.12; H, 6.72; N 6.09%). ^1H NMR (acetone-d^6, 250 MHz), *E* Isomer, δ 1.54 (s, 6 H, *p*-CH_3), 2.13 (s, 3 H, CH_3^5), 2.15 (s, 3 H, CH_3^6), 2.41 (s, 3 H, *o*-CH_3-imine), 2.46 (s, 3 H, *o*-CH_3-imine), 2.89 (br s, 9 H, *o*-CH_3-Mes and N=CCH_3), 4.48 (s, 2 H, CH_2^1), 4.97 (s, 2 H, CH_2^7), 6.40 (s, 2 H, *m*-H Mes), 6.66 (s, 2 H, *m*-H imine), 6.78 (m, 2 H, *o*-Ph), 7.25–7.70 (m, 8 H), 9.16 (s, 1 H, NH).

{**Ni(Mes)[NH=C(Mes)(Me)](PIM)**}BF_4 **(7b).** Complex **7b** was obtained by the same procedure as **7a** from **3b** as a yellow–orange solid (yield = 30%, based on nickel) (Found: C, 63.3 H, 5.8; N, 6.6. Calc. for $C_{33}H_{38}BF_4N_3Ni$: C, 63.70; H, 6.16; N 6.75%). ^1H NMR (500 MHz, $CDCl_3$), obtained from the mixture of the four isomers. *trans-E* isomer (60%), δ 1.64 (s, 6 H, *o*-CH_3-imine), 2.19 (s, 3 H, *p*-CH_3-imine), 2.20 (s, 3 H, *p*-CH_3Mes), 2.89 (s, 3 H, N=CCH_3), 3.00 (s, 6 H, *o*-CH_3Mes), 4.84 (s, 2 H, CH_2), 6.55 (s, 2 H, *m*-H Mes), 6.70* (s, 2 H, *m*-H imine), 7.21–7.80 (m, 7 H), 8.68 (s, 1 H, CH=N), 10.33 (s, 1 H, NH). *cis-E* Isomer (25%), δ 1.76 (s, 6 H), 2.35 (s, 3 H), 2.18 (s, 3 H), 2.83 (s, 3 H), 2.90 (s, 6 H), 4.18 (s, 2 H), 6.47 (s, 2 H), 6.70* (s, 2 H), 7.2–8 (m, 9 H), 8.11 (s, 1 H, CH=N), 9.20 (s, 1 H, NH); *overlapped signals between the *cis* and *trans* isomers. Most representative signals for the minor isomers, *cis-Z* isomer (9%), δ 3.79 (2 H, s, CH_2), 2.1–2.4 (s, 3 H, N=CCH_3), *trans-Z* isomer (6%), δ 5.00 (2 H, s, CH_2), 2.1–2.4 (s, 3 H, N=CCH_3).

{**Ni(Mes)[NH=C(Mes)(Me)](bipy)**}BF_4 **(7c).** Complex **7b** was obtained by the same procedure as **7a** from **3c** as a yellow solid (yield = 41% based on nickel) (Found: C, 59.4 H, 5.7; N, 6.9. Calc. for $C_{30}H_{34}BF_4N_3Ni$: C, 61.90; H, 5.89; N 7.22%). ^1H NMR (250 MHz, acetone-d^6); *E* Isomer (85%), δ 1.89 (s, 6 H, *o*-CH_3), 2.21 (s, 3 H, *p*-CH_3), 2.22 (s, 3 H, N=CCH_3), 3.06 (s, 3 H, *p*-CH_3), 3.18 (s, 6 H, *o*-CH_3), 6.63 (s, 2 H, *m*-H), 6.81 (s, 2 H, *m*-H), 8.50 (d, 1H), 8.41 (d, 1H), 8.32 (m, 2H), 8.20 (dd, 1H), 7.82 (dd, 1H), 7.42 (d, 2H), 9.45 (s, 1 H, NH); *Z* Isomer (15%), δ 1.70 (s, 6 H), 2.29 (s, 6 H), 2.48 (s, 6 H), 2.54 (s, 3 H), 6.39 (s, 2 H), 6.79 (s, 2 H), 7.20–8.65 (m, 8 H), 11.09 (s, 1 H). Mass spectra FAB$^+$ (NBA): m/z = 495.8 (45), 494.0 (95), 374.9 (8), 332.9 (65), 215.6 (40), 213.7 (100), 161.5 (8).

{**Ni(Mes)[NH=C(Ph)(Mes)](bipy)**}BF_4 **(7c′).** To a solution of 0.164 g (0.40 mmol) of [NiBr(Mes)(bipy)] in 30 cm^3 of THF were added an 300% excess of benzonitrile and 0.137 g (0.47 mmol) of $TlBF_4$. The color of the solution changed slowly from red to yellow, after 30 min of vigorously stirring, TlBr was filtered off

through Celite. The yellow compound which precipitated upon replacement of the THF by toluene, was filtered off and washed with water and ether (yield = 39%, based on nickel) (Found: C, 63.3 H, 5.4; N, 6.5. Calc. for $C_{35}H_{36}BF_4N_3Ni$: C, 65.26; H, 5.63; N 6.52%). ^{1}H NMR (250 MHz, acetone-d^6); *E* Isomer (63%), δ 2.17 (s, 3H, *p*-CH_3), 2.26 (s, 6 H, *o*-CH_3), 2.60 (s, 3 H, *p*-CH_3), 2.81 (s, 6 H, *o*-CH_3), 6.52 (s, 2 H, *m*-H), 6.88 (s, 2 H, *m*-H), 7.50 (m, 5H, Ph), 7.70–7.40 (m, 3H), 8.62–8.22 (m, 5H), 9.83 (s, 1 H, NH); *Z* Isomer (37%), δ 1.57 (s, 6 H), 2.29 (s, 3 H), 2.35 (s, 3 H), 2.60 (s, 6 H), 6.40 (s, 2 H), 6.88 (s, 2 H), 6.70–8.80 (m, 13 H), 11.49 (s, 1 H). Mass spectra FAB$^+$ (NBA): m/z = 557.4 (26), 555.9 (53), 436.8 (8), 332.9 (50), 223.8 (30), 215.6 (40), 213.6 (100), 135.7 (70).

{Ni(Mes)[NH=C(Me)(Mes)](phen)}BF_4 (7d). Complex **7d** was obtained by the same procedure as **7a** from **3d** as a yellow solid (yield = 40%, based on nickel) (Found: C, 61.5; H, 5.6; N, 6.7. Calc. for $C_{32}H_{34}BF_4N_3Ni$: C, 63.41; H, 5.65; N, 6.93%). ^{1}H NMR (250 MHz, acetone-d^6); *E* Isomer (82%), δ 2.02 (s, 6 H, *o*-CH_3), 2.22 (s, 3 H, *p*-CH_3), 2.24 (s, 3 H, N=CCH_3), 3.14 (s, 3H, *p*-CH_3), 3.23 (s, 6H, *o*-CH_3), 6.67 (s, 2H, *m*-H), 6.84 (s, 2H, *m*-H), 7.70–9.00 (m, 8H), 9.57 (s, 1H, NH); *Z* Isomer (18%), δ 1.75 (s, 6H), 2.23 (s, 3H), 2.28 (s, 3H), 2.52 (s, 6H), 2.59 (s, 3H), 6.44 (s, 2H), 6.79 (s, 2H), 7.50–9.05 (m, 8H), 11.22 (s, 1H). Mass spectra FAB$^+$ (NBA): m/z = 520.1 (23), 518.4 (47), 399.5 (8), 357.6 (100), 337.5 (3).

Characterization of the imine [(Mes)MeC=NH] obtained after insertion of CH_3CN

A typical experiment carried out with complex **7b**: to 0.062 g of complex **7b** (0.1 mmol) solved in 15 cm^3 of $CHCl_3$, 15 cm^3 of a 1 M solution of HCl were added. The mixture was stirred at room temperature for 3 h. The neutral imine ligand was recovered from the aqueous phase, after basic treatment with a $NaHCO_3$ solution and extraction with $CHCl_3$, as an oily material. ^{1}H NMR (250 MHz, $CDCl_3$), δ 2.21 (s, 6H), 2,27 (s, 3H), 2.28 (s, 3H), 6.85 (s, 2H). MS (CI NH_3): m/z (relative intensity) 162.3 [M + H]$^+$ (100), 163.4 (16).

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