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Study of the reactivity of 2-methyl-3-butenenitrile with Ni(0)-*N*-heterocyclic carbene complexes

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ABSTRACT

The catalytic isomerization of 2-methyl-3-butenenitrile (2M3BN) was performed in the presence of Ni(0) with *N*-heterocyclic carbene (NHC) ligands. On using bulky aromatic substituents on the NHC nitrogen atoms, the isomerization reaction proceeded at room temperature within 15 min: a total conversion of such substrate into the *E*- and *Z*-isomers of 2-methyl-2-butenenitrile (2M2BN), being confirmed to take place as a result of governing C–H bond activation, at the catalytic proportion of substrates used. The presence of fluorinated substituents on the heterocyclic carbene ligand results in low catalyst stability, resulting in rapid decomposition of the catalysts. The use of stoichiometric amounts of nickel complex in this reaction did show that C–CN bond cleavage is feasible, allowing isolation and characterization of the allyl complex [Ni(NHC)$_2$(η^3-1Me-allyl)(CN)] (**2**).

1. Introduction

The isomerization of the branched cyano-olefin 2-methyl-3-butenenitrile (2M3BN) to the linear 3-pentenenitrile (3PN) is a key intermediate step for the catalytic process addressing the synthesis of adiponitrile (AdN), which is the major nylon-6,6 precursor [1]. The isomerization reaction is typically achieved using nickel complexes with phosphorus-donor (P-donor) ancillary ligands such as phosphines [2–6], phosphonites [4], and phosphates [7], all of which depict σ-donation/π-acceptance capabilities intended to assist and enhance the selectivity towards a C—CN bond cleavage in the starting 2M3BN from which 3PN is to be ultimately obtained in catalysis. The presence of σ-donation however, inevitably favors a C—H bond activation over the C—CN bond cleavage of 2M3BN and thus, the formation of the undesired branched by-product 2-methyl-2-butenenitrile (2M2BN), cannot be prevented as a competing process of the overall catalytic cycle.

For a number of years, our group has been interested in the activation of C—CN bonds of nitriles, using for this purpose the key 14e fragment [(L_2)Ni] (L_2 = bidentate alkyl diphosphine, such as 1,2-bis(di-isopropyl)phosphino-ethane, dippe) in the presence of several different aromatic [8], *N*-heterocyclic [8a] and aliphatic nitriles [9]. The bridging-hydride nickel(I) compound [Ni(L_2)(μ-H)]$_2$ has typically been the source of choice in the initial activation of all those nitriles, the η^2-coordination of the CN bond in them to nickel(0) occurring as the first step, a result of a reductive elimination of di-hydrogen [8,9]. Altogether, the formation of *side-on* [Ni(L_2)(η^2-NCR)] (R = alkyl, aryl and heteroaryl) compounds has been established to be entirely general. This type of coordination leads to reactivity including the hydration of bound nitrile moieties [10].

A second distinctive feature of these type of compounds is their ability to effect the cleavage of the C–CN bond producing the respective nickel(II) compounds [Ni(L_2)(η^1-*C*N)(R)] (R = alkyl, aryl and heteroaryl). This cleavage is dependent on the nature of the particular substituent (i.e. chain length in the case of aliphatic nitriles, or the substituents in the aryl nitriles) [9]. Studies have proven that C—CN cleavage can occur under thermal and/or photochemical conditions, and that it is reversible for some compounds [8,9]. This prompted us to exploit use of these Ni(0) compounds in the C—CN isomerization process, the choice of 2M3BN as a substrate being a natural choice for this type of reaction study.

The use of L_2 = 1,2-bis(dicyclohexyl)phosphino-ethane, dcype [2b], for instance, has permitted the isolation and characterization of all the intermediates depicted in the catalytic cycle

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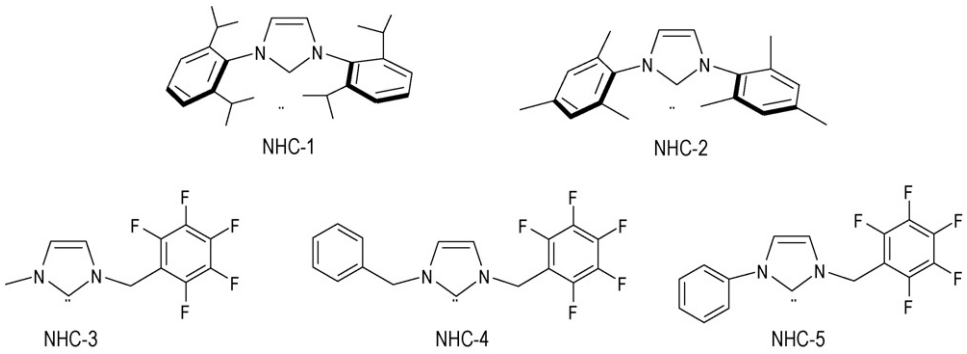


Fig. 1. NHC ligands used for the catalytic isomerization of 2M3BN.

proposed by Sabo-Etienne and co-workers, at the time based only on DFT calculations [5]. The use of a ferrocenyl diphosphine such as 1,2-bis(diphenylphosphino)ferrocene, dppf, has rendered the best yield of 3PN so far, with a high selectivity (83%) and total conversion (100%) being observed to take place under catalytic conditions [2c]. More recently, the use of 1-diphenylphosphine-1′-(di-*tert*-butylphosphino)-ferrocene, *t*Buppf, in the presence of $ZnCl_2$ has permitted the isolation and complete characterization of a novel key intermediate within the catalytic process, the latter being found to exhibit hemilability [2a]. Single-crystal X-ray diffraction determinations were performed on the above-mentioned intermediate, its direct use as catalyst resulting in a selectivity towards 3PN ranging from 70 to 76%. Additional studies involving the use of the $[Ni(dippe)(\mu\text{-}H)]_2$ dimer for related C–CN bond activations in allylnitriles have also been reported [11]. A nickel(0) compound [Ni(dippe)(η^2-*C*,*C*-allylnitrile)], exhibiting a coordinated C—C double bond was detected at low temperature. Upon warming to room temperature, an isomerization reaction led to a mixture of nickel(0) and nickel(II) compounds, namely *cis*- and *trans*-[Ni(dippe)(η^2-*C*,*C*-crotonitrile)], formed via C—H bond activation, and [Ni(dippe)(η^3-allyl)(CN)], formed via C—CN bond cleavage.

In the recent years, the use of *N*-heterocyclic carbene ligands (NHC) over nickel(0), namely Ni(0)–NHC [12], has been applied for a variety of reactions involving the C—F bond activation of aryl fluorides. The use of the same type of compounds has also been reported in catalysis involving Kumada cross-coupling reactions [13]. The use of NHC as ancillary ligands for transition metal complexes in catalysis is well known [14], the most representative examples involving olefin polymerization processes using ruthenium (NHC-Ru) [15] and palladium (NHC-Pd) catalysts [16], exceeding by far the rest of the chemistry explored using these ligands. In particular, the *N*-heterocyclic carbenes depict distinctive characteristics *vs*. other nitrogen donor systems, the latter being known to stabilize complexes with transition metals in both high and in low oxidation states [14b]. The former ligands are known to act as σ-donor ligands that are capable of π-acceptance also, properties that have been well established on both an experimental and computational basis [17,18].

Of relevance to the current studies, the synthesis of nickel(0) and nickel(II) compounds bearing *N*-heterocyclic carbene ligands and coordinated olefins or allyls, namely Ni(0)–NHC-η^2-olefin [19], or $[Ni(NHC)(\eta^3\text{-allyl})(L)]^+$ (L = H_2O or MeCN); [20] – the latter, used in catalytic polymerization reactions involving 1,3-butadiene and styrene – have been reported. These reports, accompanied with the similarity depicted between NHC ligands and P-donor ligands (*vide supra*), allowed us to speculate on the possibility of using the former as ligands for the isomerization of 2M3BN using nickel. Ni(0)–NHC species are expected to behave similarly to the $[Ni(L_2)]$ species involving diphosphines, as has been established in the reaction of aryl nitriles with $[(NHC)_2Ni^0]$ [21].

We have prepared a series of Ni(0)–NHC complexes and tested them for the isomerization of 2M3BN. This manuscript presents a summary of our findings with this substrate, under both stoichiometric and catalytic conditions.

2. Results and discussion

The isomerization of 2M3BN was undertaken using $[Ni(COD)_2]$ as a catalyst precursor and each of the NHC ligands illustrated in Fig. 1, typically using a 1:1 stoichiometric proportion of ligand to nickel, and a 0.9 mole percent relationship with respect to the substrate, 2M3BN (Table 1, entries 1–14). Entries 15 and 16 in Table 1 show the effect of using 2 equiv. of the NHC ligand per nickel center. The isomerization reaction was explored both in the absence and the presence of Lewis acids as well. The results of these experiments are all summarized in Table 1.

The use of the bulky *N*-aryl NHC ligands NHC-1 and NHC-2 generally afforded very active catalytic systems. While little branched to linear isomerization was observed, a 100% conversion to a distribution of branched isomers *E*- and *Z*-2M2BN and in some cases also *cis*-2-pentenenitrile (*cis*-2PN) was reached after only 15 min in most cases, either under neat conditions (entries 1–2, Table 1) or dissolved in THF or hexanes (entries 11–14) at room temperature. Similar activities were also observed at low temperature (entries 17 and 18). The experiments performed at −68 °C showed small differences in the final distribution of products in the case of hexane, in which case a greater yield of the *Z*-isomer was observed. The isomerization of 2M3BN to 3PN was not achieved in any of these cases, therefore indicating that the rate of C—H bond activation exceeds that of C—CN cleavage, leading selectively to the *E*- and *Z*-2M2BN isomers as the major products of catalysis. The fact that small amounts of *cis*-2PN were obtained in some cases, particularly using the *N*-heterocyclic carbene ligands NHC-3 and NHC-4 under neat conditions (entries 3 and 5), suggests that the C—CN bond cleavage is also dependent on the degree of π-acceptance from the carbene ligand, whose ultimate selectivity still differs from that of the P-donor systems normally used for this reaction [2–7]. The use of 2 equiv. of NHC ligand (NHC-1 or NHC-2) per nickel center was also examined, intending to alter the kinetics of catalysis and presumably its outcome (entries 15 and 16). The results obtained, however, showed no significant difference with respect to the experiments with 1 equiv. of NHC, with the preferential formation of the branched *Z*-2M2BN isomer still being observed. Addition of Lewis acids to the reaction media (entries 7–10) did not influence the kinetics for C–CN cleavage, despite evidence that Lewis acids are known to assist the C—CN bond cleavage reaction leading to the linear 3PN isomer [5]. In the experiments with Lewis acid,

Table 1
Catalytic isomerization of 2M3BN

Entry	System	T (°C)	t (min)	Solvent	Conversion (%)	E-2M2BN (%)	Z-2M2BN (%)	*cis*-2PN (%)
1	[Ni]/NHC-1	r.t.	15	Neat	100	46	53	1
2	[Ni]/NHC-2	r.t.	15	Neat	100	59	38	3
3a	[Ni]/NHC-3	r.t.	15	Neat	47	25	0	22
4a	[Ni]/NHC-4	r.t.	15	Neat	0	–	–	–
5a	[Ni]/NHC-4	r.t.	180	Neat	38	22	0	16
6a	[Ni]/NHC-5	r.t.	15	Neat	0	–	–	–
7b	[Ni]/NHC-1/BEt_3	r.t.	15	Neat	47	28	15	4
8b	[Ni]/NHC-2/BEt_3	r.t.	15	Neat	58	40	14	4
9b	[Ni]/NHC-1/$ZnCl_2$	r.t.	15	Neat	100	51	44	6
10b	[Ni]/NHC-2/$ZnCl_2$	r.t.	15	Neat	100	71	27	3
11	[Ni]/NHC-1	r.t.	15	THF	100	69	28	3
12	[Ni]/NHC-2	r.t.	15	THF	100	70	27	3
13	[Ni]/NHC-1	r.t.	15	Hexanes	100	80	14	6
14	[Ni]/NHC-2	r.t.	15	Hexanes	100	80	16	4
15c	[Ni]/2 NHC-1	r.t.	15	Neat	100	50	48	2
16c	[Ni]/2 NHC-2	r.t.	15	Neat	100	76	23	1
17	[Ni]/NHC-1	−68	15	THF	100	69	28	3
18	[Ni]/NHC-2	−68	15	Hexanes	100	56	42	2

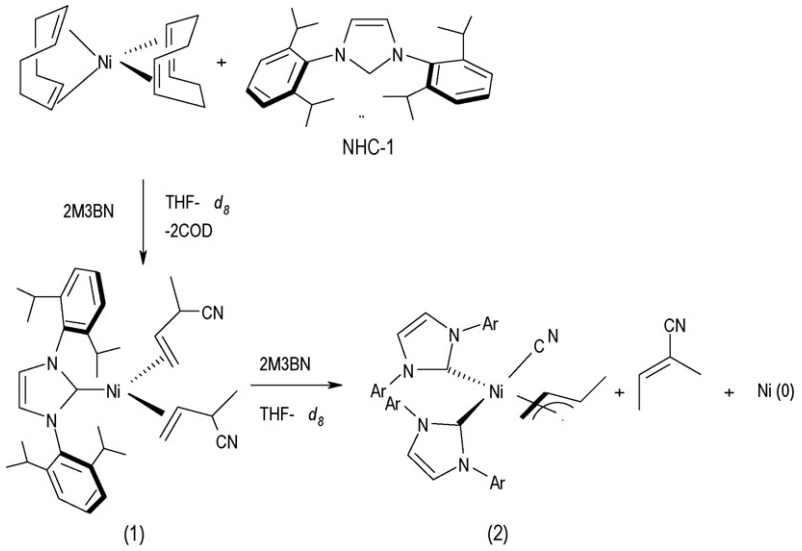
Substrate:ligand:[Ni] = 110:1:1. [Ni] = $Ni(COD)_2$. 2M3BN conversion percent and yield were obtained by GC–MS and confirmed by ^{1}H NMR spectroscopy. (a) Decomposition of the catalytic system and presence of metallic nickel was observed at the end of the reaction. (b) Substrate:ligand:[Ni]:Lewis acid = 110:1:1:1. [Ni] = $Ni(COD)_2$. (c) 2 equiv. of NHC ligand were used per nickel.

a drop in catalytic activity was observed as reflected by the total conversion when BEt_3 was employed. It is clear that the kinetic preference for C—H activation was not changed by the presence of the Lewis acid; a distribution of branched isomers similar to that seen in experiments without the Lewis acid was obtained. This is again an indication of the strong effect that the NHC ligands exert on the nickel catalyst. The choice of Lewis acid is also important as far as the extent of conversion is concerned, with $ZnCl_2$ showing neither slowing of the reaction nor a change in product distribution (entries 9 and 10).

Indications of catalyst stability in these reactions were also obtained. In the case of the *N*-benzyl-fluorinated carbene ligands, NHC-3 and NHC-4, which possess the greatest π-acceptance (and reciprocally, least σ-dative) character, the presence of metallic nickel particles was observed at the end of reaction, presumably due to catalyst decomposition (entries 3–6). These systems showed small to moderate activities for the conversion of 2M3BN, as expected for less nucleophilic catalysts. Branched products, a result of C—H bond activation, still dominated with these NHC ligands. In fact, no isomerization was observed to take place in the case of the pentafluoro phenyl analogue, NHC-5, after a considerably longer reaction time (180 min) than any of the other NHC ligands, fluorinated or not. Nickel complexes of this carbene therefore appear to be incapable of even C—H bond cleavage.

The isomerization reaction using NHC carbene ligands was also studied under stoichiometric conditions and followed by ^{1}H NMR and GC–MS. In a typical reaction, a mixture of [$Ni(COD)_2$], NHC-1, and 2M3BN in 1:1:2 ratio was dissolved in THF-d_8 in a closed NMR tube. The formation of the *side-on* coordination compound [Ni(NHC-1)(η^2-*C*,*C*-2M2BN)$_2$], **1**, was observed immediately on the basis of ^{1}H NMR spectroscopy (see Scheme 1).

Closely related olefinic complexes similar to **1**, have been observed and fully characterized by X-ray determinations by Cavell and co-workers [19]. Two additional equiv. of 2M3BN were added to the same reaction mixture and after 24 h stirring at room temperature, these were observed to completely isomerize into *E*-2M2BN. In the olefinic region, the ^{1}H NMR spectrum displays the presence of the free COD ligand, but no coordinated COD. Also during this time, **1** was transformed into a different compound exhibiting allyl signals [Ni(η^1-*N*HC-1)$_2$\{η^3-*C*,*C*,*C*-1-(Me-allyl)\}(η^1-*C*N)], **2**.



Scheme 1.

The presence of metallic Ni was indicated by a precipitate on the inner walls of the NMR tube. The ^{1}H NMR spectrum of the system at this stage displayed four different methyl resonances as doublets attributed to the carbene ligand in **2**, centered at δ 1.59, 1.35, 1.14 and 1.11 ($^3J_{H-H}$ = 6.89 Hz) and two more methyne resonances as septuplets, at δ 3.17 and 2.86 ($^3J_{H-H}$ = −6.89 Hz). The latter sets indicate the presence of two distinct NHC ligands coordinated to the nickel center in **2**. The C*H* resonances for the NHC ligand in the ^{1}H NMR spectrum yielded a multiplet located at δ 7.33, whereas the signals for the bound allyl ligand were observed at δ 4.23 (m, central C*H*), 2.68 (m, C*H*), 2.50 (dd, $^3J_{H-H}$ 7.19 Hz and 1.79 Hz, C*H*H), 1.30 (d, $^3J_{H-H}$ = 6.59 Hz, CH_3) and 0.89 (m, CH*H*).

The ^{13}C{^{1}H} NMR spectrum of this compound yielded complimentary information regarding its features, the presence of the two distinct coordinated NHC ligands with each displaying resonances for each carbon atom in the heterocycle. In the case of the bound allylic carbons, four distinctive signals were observed at δ 111.9 (central *C*H), 80.3 (*C*H), 48.6 (*C*H_2) and 18.3 (–Me), whereas the bound cyano moiety was located at δ 125.9. The coordinated carbene carbon produces a broad signal at δ 189.5. The latter NMR assignments were further corroborated by a series of 1D and 2D experiments (see Supporting Information).

Clearly, from the observation of **2**, it follows that C—CN bond activation is feasible under stoichiometric conditions. Under catalytic conditions, however, the C—H bond activation pathway is favored, even at low temperature or in the additional presence of Lewis acids (*vide supra*). Consequently it appears that an interaction between the Ni–NHC catalyst and the excess substrate may be present in the catalytic reaction, such that selectivity towards C—CN bond cleavage is in fact hampered by excess substrate, either by slowing C—CN cleavage or by accelerating C—H cleavage. A similar effect has been seen in [Ni(dippe)] catalyzed reactions of 2M3BN [22]. It is now clear from these studies that the use of NHC ligands do not appear to present any advantage over the P-donor ligands used for the isomerization of 2M3BN by our group or others [2–7], even if in principle they might be expected to exhibit similar properties in terms of σ-donation/π-acceptance.

3. Conclusions

The use of Ni–NHC compounds possessing varied σ-donor/π-acceptor characteristics were assessed for the catalytic isomerization of 2M3BN. The activity of the catalysts was found to be very high, yet with almost zero selectivity toward linear 3PN, producing mainly mixtures of *E*- and *Z*-2M2BN. These products are the result of a C—H bond activation process which is dominant under catalytic conditions with an excess of substrate. Under stoichiometric conditions, evidence for C—CN bond cleavage was obtained, and consequently one must conclude that important effects associated with the choice of NHC ligand and the presence of excess substrate can alt C—H/C—CN cleavage selectivities. The C—H bond activation pathway shows a dependence on the strong σ-donating character.

4. Experimental section

All manipulations were carried out using standard Schlenk and glove box techniques under argon (Praxair, 99.998). THF and hexanes (J.T. Baker) were dried and distilled from dark purple and blue solutions of sodium/benzophenone ketyl, respectively. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were stored over 3 Å molecular sieves in an MBraun glove box (<1 ppm H_2O and O_2). [Ni(COD)$_2$] was purchased from Strem and purified from a THF solution, filtered through Celite, and dried in a vacuum manifold until a yellow crystalline solid was obtained. It was dried for an additional 3 h *in vacuo*. BEt_3 and imidazolium salts and were purchased from Aldrich and were used as received. NHC-1 and NHC-2 were prepared according the reported procedure using ^{t}Bu-ONa; [23]; NHC-3, NHC-4 and NHC-5 ligands were prepared analogously from their corresponding imidazolium salts [24]. 2M3BN (86.5% by GC–MS) was purchased from TCI America, purged and stored in the glove box before use. $ZnCl_2$ was purchased from J.T. Baker. ^{1}H and ^{13}C{^{1}H} and NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in THF-d_8 or toluene-d_8. ^{1}H chemical shifts (δ) are reported relative to the residual proton resonances in the deuterated solvent. ^{13}C{^{1}H} chemical shifts (δ) are reported relative to the resonance of the deuterated solvent. All NMR spectra and catalytic reactions were carried out using thin wall (0.38 cm) WILMAD NMR tubes fitted with J. Young valves. Mass determinations (FAB+) were performed using a JEOL SX-102A, in nitrobenzilic alcohol matrix and GC–MS determinations were done using a Varian Saturn 3 instrument, equipped with a 30 m DB-5MS capillary column.

4.1. Catalytic isomerization of 2M3BN in the absence of Lewis acid (LA)

A mixture of neat 2M3BN (0.4 mL, 4.00 mmol) and the corresponding ligand was added to yellow crystalline [Ni(COD)$_2$] (10 mg, 0.036 mmol), at room temperature in the glove box. The mixture of reagents resulted in orange solutions. The mixture was stirred at room temperature for 15 min, after which time three aliquots were extracted. Two were dissolved separately in THF-d_8 or toluene-d_8, and transferred to closed NMR tubes for ^{1}H NMR analyses. The third aliquot was analyzed by GC–MS to determine the composition of nitrile isomers present.

4.2. Catalytic isomerization of 2M3BN in the presence of LA

A neat mixture of 2M3BN (0.4 mL, 4.00 mmol) a Lewis acid (BEt_3 or $ZnCl_2$, 0.036 mmol), and an NHC ligand (0.036 mmol), was added to yellow crystalline [Ni(COD)$_2$] (10 mg, 0.036 mmol) at room temperature in the glove box. The mixture was stirred for 15 min and then analyzed following the procedure described above.

4.3. Catalytic isomerization of 2M3BN at low temperature

A colorless THF (2 mL) solution of 2M3BN (0.4 mL, 4.00 mmol) and NHC (0.036 mmol) was added to a pre-cooled THF (1 mL) solution (−78 °C) of [Ni(COD)$_2$] (10 mg, 0.036 mmol), using the double manifold argon line, dropwise adding the first solution to the second via canula. A bright orange solution was obtained, which was stirred for 15 min at the low temperature. Aliquots were then extracted and analyzed by ^{1}H NMR and GC–MS as above.

4.4. Preparation of [Ni(NHC-1)(η^2-C,C-2M3BN)$_2$] (1) and [Ni(NHC-1)$_2$(η^3-1Me-C_3H_6)(CN)] (2)

THF (2 mL) solutions of NHC-1(21 mg, 0.0545 mmol) were dropwise added to a second THF (3 mL) solution of [Ni(COD)$_2$] (15 mg, 0.0545 mmol) with stirring. A brown solution of [Ni(COD)(NHC-1)] was obtained. Following further stirring for 15 min, 2M3BN (10 μL, 0.109 mmol) was added to the mixture. The brown solution was observed to immediately turn yellow. The solvent was evaporated from the mixture and the remaining crude residue redissolved in THF-d_8 (750 μL) and analyzed by ^{1}H NMR spectroscopy, indicating the formation of compound **1**. The mixture was left to stir overnight at room temperature during which time metallic nickel was observed to be formed on the walls of the tube. The remaining solution was transferred to a Schlenk flask and was taken to dryness

using a vacuum manifold (<10^{-4} mmHg, for 3 h), yielding an orange solid. ^{1}H and ^{13}C{^{1}H} NMR analyses of this compound showed the formation of compound **2**. Isolated yield = 52%. Ni(NHC-1)(η^2-*C*,*C*-2M3BN)$_2$] (**1**) ^{1}H NMR (299.7 MHz, THF-d_8): δ (ppm) 7.4–6.9 (m, 8H, C*H*–Ar and C*H*–imidazole), 4.31 (br m, 4H, =C*H*$_2$), 2.67 (m, 2H, =C*H*). [Ni(NHC-1)$_2$(η^3-1Me-C_3H_6)(CN)] (**2**) FAB+ = 919 (M+2). ^{1}H NMR (299.7 MHz, THF-d_8): δ (ppm) 7.48 (d, $^3J_{H-H}$ = 8.69 Hz, 4H, C*H*-meta), 7.42 (t, $^3J_{H-H}$ = 7.79 Hz, 2H, C*H*-*para*), 7.31(m, 4H, CH-imid), 4.23 (m, 1H, central C*H*), 3.17 (septuplet, 2H, $^3J_{H-H}$ = 6.89 Hz, C*H*Me$_2$), 2.86 (septuplet, $^3J_{H-H}$ = 6.89 Hz, 2H, C*H*Me$_2$), 2.68 (m, 1H, C*H*), 2.50 (dd, $^3J_{H-H}$ = 7.19 Hz, and 1.79 Hz, 1H, C*H*H), 1.59 (d, $^3J_{H-H}$ = 6.89 Hz, 6H, CH*Me*$_2$), 1.35 (d, $^3J_{H-H}$ = 6.89 Hz, 6H, CH*Me*$_2$), 1.30 (d, $^3J_{H-H}$ = 6.59 Hz, 3H, C*H*$_3$), 1.14 (d, $^3J_{H-H}$ = 6.89 Hz, 6H, CH*Me*$_2$), 1.11 (d, $^3J_{H-H}$ = 6.89 Hz, 6H, CH*Me*$_2$) 0.89 (m, 1H, CH*H*). ^{13}C{^{1}H} NMR (75.4 MHz, THF-d_8): δ (ppm) 189.5 (br, NCN), 147.5 (*ipso*-CN_a), 147.3 (*ipso*-CN_b), 139.2 (*ipso*-C-^{i}Pr$_a$), 137 (*ipso*-C-^{i}Pr$_b$), 130.7 (C*H*-*para*$_a$), 130.6 (C*H*-*para*$_b$), 126.3 (C*H*-*meta*), 125.9 (–C*N*), 124.7 (C*H*-imid$_a$), 124.6 (C*H*-imid$_b$), 111.9 (C*H*=), 80.3 (C*H*), 48.6 (C*H*$_2$=), 29.4 (C*H*Me$_2$), 26.8 (s), 26.4 (s), 23.4 (s), 23.3 (CH*Me*), 18.3 (C*H*$_3$).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.03.024.

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