

The catalytic hydration of 1,2-, 1,3- and 1,4-dicyanobenzenes using nickel(0) catalysts

Carmela Crisóstomo, Marco G. Crestani, Juventino J. García*

Facultad de Química, Universidad Nacional Autónoma de México, México, D.F. 04510, México

Received 4 October 2006; received in revised form 25 October 2006; accepted 25 October 2006

Available online 6 December 2006

Abstract

The homogeneous catalytic hydration of 1,2-, 1,3- and 1,4-dicyanobenzenes using organometallic nickel(0) catalysts of general formula [(dippe)Ni(η^2 -*N,C*-1,*n*-(CN)₂-benzene)] (*n* = 2–4; complexes **2–4**, respectively) was achieved under heating, the products of hydration, at least in the case of 1,3- and 1,4-dicyanobenzene being strongly dependent on the temperature used for the process; the production of the respective 1,3- and 1,4-cyanobenzamides been observed at 120 °C, while catalysis at 180 °C resulted in the quantitative formation of the 1,3- and 1,4-dicarboxylic acids. In the case of 1,2-dicyanobenzene, catalysis at either temperature yielded the hemihydration product 1,2-phthalamide, implying an important difference in overall reactivity for this system. All the hydration products were obtained in excellent selectivity and yield, using 0.5 mol% loadings of the corresponding nickel(0) catalyst and thus, the current work provides important evidences that could be of use for both synthetic organic chemistry and in the eventual production of polyamides.

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Keywords: Homogeneous; Catalysis; Dinitriles; Hydration; Nickel

1. Introduction

The catalytic hydration or hydrolysis of nitriles is a very active field in contemporary chemistry, given that the products obtained from this process (either amides or their parent carboxylic acids) present a large practical use in synthesis, pharmacology and in industry in general [1]. In the case of polyamides (nylons), their large-scale production for the manufacture of high performance synthetic fibers, films, insulators, etc., is of considerable technical [2] and economical [3,2b,2c] importance. Fabrics and materials made of nylon are widely known for fire-retardancy application. Also, most polyamides are biologically inert and offer no toxicological problems to the point of being used as suture materials; these are also non-leaching polymers and as such, compacted sanitary landfills pose no danger to subsurface water [2d,2e]. Thus, the straightforward preparation of these products either through one-pot reactions or from their precursor monomers (*e.g.* cyanobenzamides [4], aromatic dicarboxamides [5], etc.) in separate hydration processes (batch

production), in high yield and selectivity, through environmentally friendly routes, have become major issues in modern production techniques and in this instance, the use of inorganic [6] or enzymatic [7] catalysts to assist the direct hydration of the starting dinitriles are particularly attractive strategies [8].

For a number of years, our group has been interested in the activation of aryl-, heteroaryl- and alkyl-substituted nitriles, using nickel(I) precatalysts of the formula [(P–P)NiH]₂; (P–P), a chelating bisphosphine ligand such as dippe (dippe = 1,2-bis(di-isopropylphosphino)ethane) [9]. In all cases, the reactions that occur with nitriles yield nickel(0) complexes of the type [(P–P)Ni(η^2 -*N,C*-R)] (R = aryl-, heteroaryl- or alkyl-), in which the corresponding nitrile is π -bonded to the [(P–P)Ni] moiety through a *side-on*, η^2 -*N,C* coordination [10], and may undergo thermal or photochemically induced oxidative addition of the C–CN bond to produce the respective nickel(II) complexes [(P–P)Ni(CN)(R)]. In the case of aryl- and heteroaryl-nitriles, the oxidative cleavage of the C–CN bond is thermally driven and occurs upon gentle heating (50 °C) [9b,9c]. In the case of alkyl-nitriles, the oxidative addition is inhibited with longer chain lengths even when subjecting the corresponding complex to irradiation with a UV source as was the case of the adamantyl cyanide system [9a]. A similar stabilization

* Corresponding author. Tel.: +52 55 56223514; fax: +52 55 56162010.
E-mail address: juvent@servidor.unam.mx (J.J. García).

effect was also observed with the smaller ethyl-, *n*-propyl-, *i*-propyl-, *t*-butyl-, *c*-propyl- and *c*-butyl-analogs, which did not undergo oxidative addition under heating, but could only be converted into their respective nickel(II) derivatives upon photolysis ($\lambda = 300$ nm). The results are in contrast to the acetonitrile complex $[(\text{dippe})\text{Ni}(\eta^2\text{-}N, C\text{-CH}_3)]$, in which the C–CN oxidative addition reaction was observed to take place even at room temperature after 2 h in solution.

In the above-described nickel(0) complexes (aryl-, heteroaryl- and alkyl-substituted), the coordinated carbon atoms undergo a significant increase in their electrophilic character due to the σ -donation into the nickel(0) center. This is confirmed from $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complexes that exhibit chemical shifts of the coordinated carbon atoms around 160 ppm as doublets of doublets (dd), which are significantly downfield from those of the free nitrile ligands, typically singlets (s) around 120 ppm [9]. These facts have prompted us to explore the chemistry of these nickel(0) complexes in a number of nucleophilic substitution reactions, which in the case of water as nucleophile gives the nitrile hydration reaction. Our previous findings using benzo- and acetonitrile have been published [11]. The catalytic hydration of these substrates are proposed to occur over the $[(\text{P-P})\text{Ni}(\eta^2\text{-}N, C\text{-R})]$ (R = phenyl-, methyl-) complexes by a concerted *N,N*-dihydro-*C*-oxo-biaddition of water to the *side-on* coordinated nitrile moieties. In the current work, we have extended the scope of the hydration reaction to some industrially important substrates such as the aromatic dinitriles 1,2-, 1,3- and 1,4-dicyanobenzene (1,2-DCB, 1,3-DCB, 1,4-DCB). To the best of our knowledge, few examples of the catalytic hydration of these three substrates, incorporating at least one-water molecule into the corresponding dinitrile (production of cyanobenzamides) have been reported [4,5,7c,12]. On the stoichiometric level, the situation is similar and few examples of the activation of dicyanobenzenes – all of them depicting *end-on* η^1 -coordinated nitrile moieties – have been reported [13].

2. Results and discussion

2.1. Catalysis of dinitrile hydration

The catalytic hydration of 1,2-DCB, 1,3-DCB and 1,4-DCB was successfully achieved with heating using 0.25 mol%

of $[(\text{dippe})\text{NiH}]_2$ (**1**) as catalyst precursor. The respective hydrations were performed using water suspensions of the corresponding dinitrile and the nickel(I) precatalyst at the 50:1 mole proportion of water to the corresponding dinitrile; the effect of THF solvent was also investigated. Table 1 summarizes the results obtained for the three substrates at 120 and 180 °C.

As indicated in the table, the selectivity of the overall catalytic hydration may be affected by the substrate that is used, the temperature of the process and the characteristics of the reaction media (illustrated in the table by the use of THF or water; entries 6 and 7). In the cases of the 1,3- and 1,4-DCB, the hydrations are strongly temperature-dependent and thus, catalysis at 120 °C led only to the partial hemihydration products 1,3- and 1,4-cyanobenzamide (entries 4, 6, 7), while catalysis at 180 °C yielded the total hydrolysis products 1,3-isophthalic and 1,4-terephthalic acids along with the corresponding amounts of ammonia (entries 3 and 5). In the case of 1,2-DCB (entries 1 and 2), the hemihydration product 1,2-phthalamide was obtained at both 120 and 180 °C, without any influence over product selectivity, yield, turnover number (TON) or frequency (TOF), therefore, suggesting a dramatic difference with respect to the other two systems, probably due to steric constraint afforded by the adjacent amido substituents in the 1,2-phthalamide product, that prevents further hydrolysis of this compound (*vide infra*).

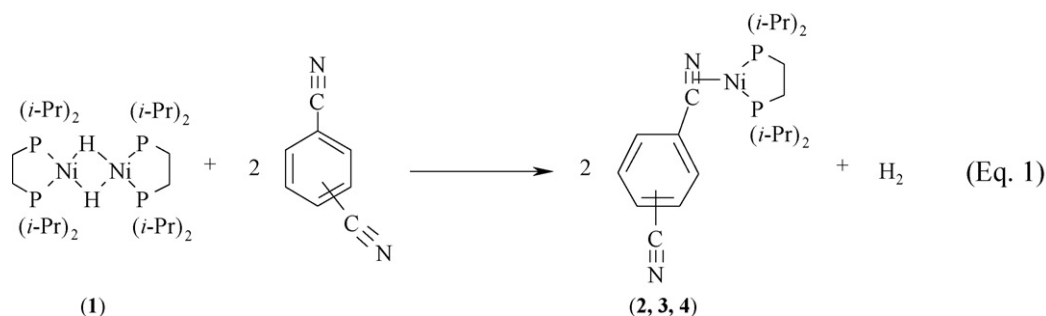
2.2. Mechanisms for dinitrile hydration

As in the cases of benzo- and acetonitrile [11], the catalytic hydrations of dicyanobenzenes are expected to be effected by nickel(0) complexes that exhibit a η^2 -coordination of a –CN bond to a $[(\text{dippe})\text{Ni}]$ moiety [9]; the immediate formation of monocoordinated nickel(0) complexes with the general formula $[(\text{dippe})\text{Ni}(\eta^2\text{-}N, C\text{-}1, n\text{-(CN)}_2\text{-benzene})]$ ($n = 2\text{--}4$; complexes **2–4**, respectively) been confirmed to take place in THF-*d*₈ and toluene-*d*₈, on using a 2:1 ratio of the respective dinitrile versus **1**. The results are in agreement to what is expected to occur at the larger mole proportion of organic substrate that is used in catalysis and thus, they strongly support the premise of a nickel(0)-assisted catalytic reaction. Eq. (1) illustrates the reactions that occur in the presence of stoichiometric amounts of the dinitrile substrate, over the nickel(I) dihydride dimer.

Table 1
Catalytic hydration of dicyanobenzenes using nickel(0)

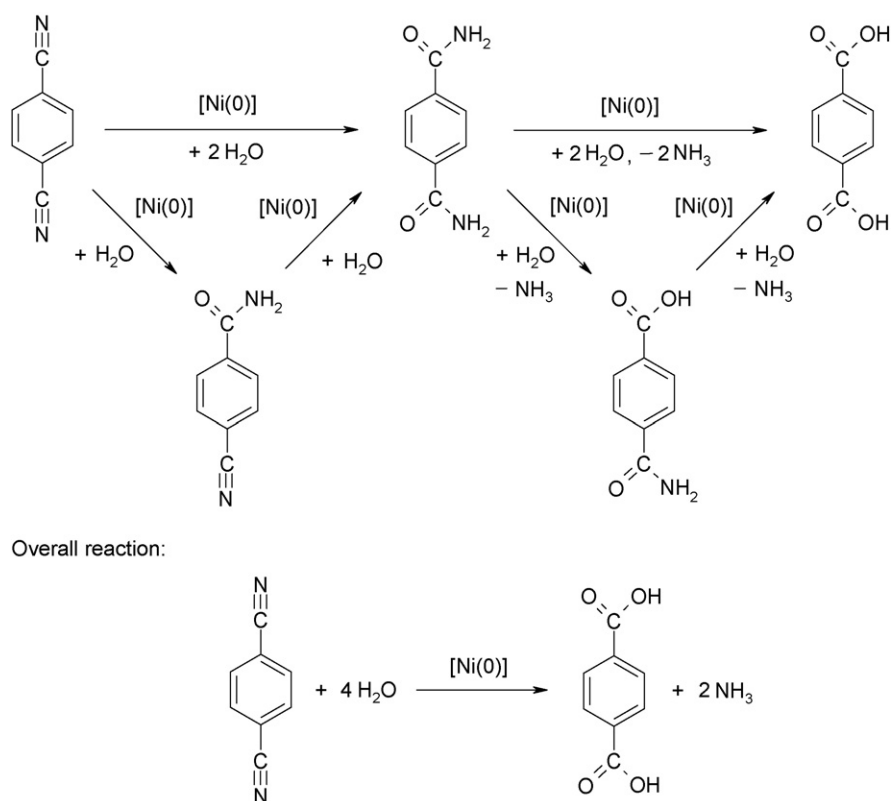
Entry	Substrate	<i>T</i> (°C)	THF	Product	TON	TOF (TON/h)	Yield ^a (%)
1	1,2-DCB	120	No	1,2-Phthalamide	135	2	71
2	1,2-DCB	180	No	1,2-Phthalamide	135	2	71
3	1,3-DCB	180	No	1,3-Isophthalic acid + ammonia	259	4	68
4	1,3-DCB	120	No	1,3-Cyanobenzamide	82	1	86
5	1,4-DCB	180	No	1,4-Terephthalic acid + ammonia	325	5	86
6	1,4-DCB	120	No	1,4-Cyanobenzamide	64	1	68
7	1,4-DCB	120	Yes	1,4-Cyanobenzamide	83	1	87

^a All yields indicated in this table have been obtained on the basis of isolated product after work-up.



Complexes **2–4** depict archetypical features that are characteristic of complexes in which nitriles are η^2 -coordinated to a metal center [9] and in this instance, examination of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **2–4** (see Table 2), has confirmed the presence of two slightly broadened asymmetric doublets with $^2J_{\text{P-P}}$ coupling constants of 63 Hz, characteristic of two types of phosphorus environments; the magnitude of the coupling constant being consistent with a monocoordination of the dicyanobenzenes as is illustrated in Eq. (1) [9b]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the pure compounds is also consistent with this description, and thus the apparition of two doublets of doublets (dd) in the surroundings of δ 165 in all spectra has confirmed the presence of a η^2 -coordinated $-\text{CN}$ bond to a $[(\text{dippe})\text{Ni}]$ moiety; the uncoordinated nitrile substituents in complexes **2–4** appearing as singlets usually around δ 117 [14]. Table 2 summarizes the key spectroscopic information, for the three nickel(0) complexes.

Complexes **2–4** are reasonably stable under argon at room temperature in THF or toluene solutions and in this instance, no evolution of these complexes into their respective nickel(II) derivatives $[(\text{dippe})\text{Ni}(\text{CN})(1,n\text{-(CN)-benzene})]$ ($n=2\text{--}4$), was observed to occur on standing in these media, prior to 24 h (see Section 4). Addition of water prevents this reaction and in this instance, the suppression of the oxidative addition by water is consistent with the fact that no inhibition of catalysis was observed at the temperatures used for the processes. The results are similar to those of benzo- and acetonitrile [11] using nickel(0) catalysts of the type $[(\text{dippe})\text{Ni}(\eta^2\text{-}N,C\text{-R})]$ ($R = \text{-Me, -Ph}$), and in this instance, the catalytic hydration of dicyanobenzenes is also expected to occur by concerted N,N -dihydro- C -oxo-biadditions of water to the *side-on* coordinated nitriles in complexes **2–4**, respectively. The degree of hydration is temperature- and substrate-dependent and as such, the



Scheme 1. Progressive hydration of dinitriles using nickel(0) catalysts [11]: 1,4-terephthalonitrile.

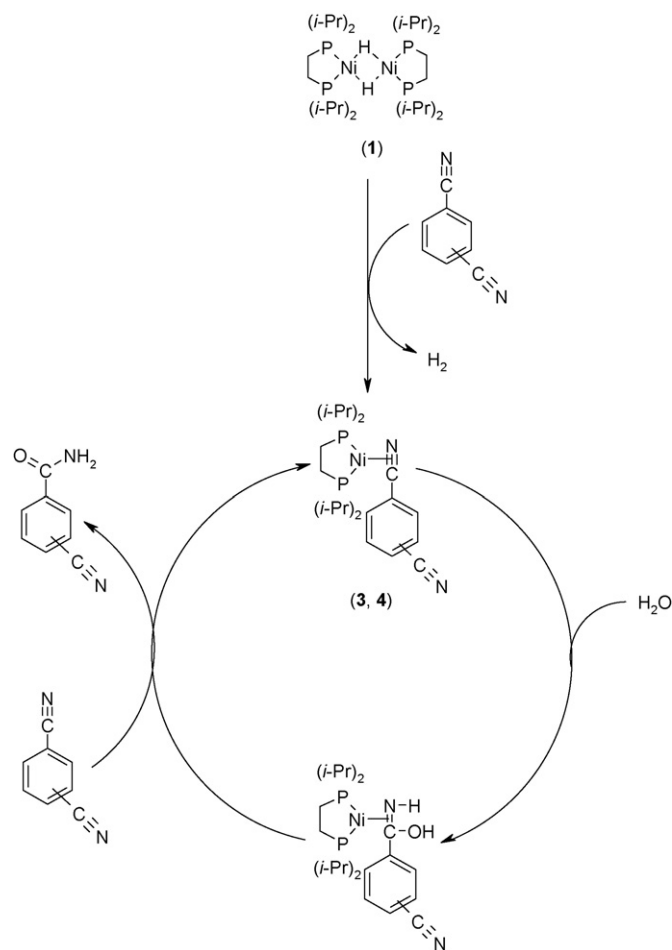
Table 2
Distinctive $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of complexes **2–4**

Complex	$^{31}\text{P}\{^1\text{H}\}$	$^{13}\text{C}\{^1\text{H}\}$		
		Coordinated CN	Uncoordinated CN	
2	80.2 (d, $^2J_{\text{P-P}} = 63$ Hz)	69.4 (d, $^2J_{\text{P-P}} = 63$ Hz)	169.9 (dd, $J_1 = 72.4$ Hz, $J_2 = 28.2$ Hz)	118.6
3	77.6 (d, $^2J_{\text{P-P}} = 63$ Hz)	65.9 (d, $^2J_{\text{P-P}} = 63$ Hz)	162.9 (dd, $J_1 = 73$ Hz, $J_2 = 28.5$ Hz)	117
4	77.5 (d, $^2J_{\text{P-P}} = 63$ Hz)	65.7 (d, $^2J_{\text{P-P}} = 63$ Hz)	169.9 (dd, $J_1 = 30$ Hz, $J_2 = 9$ Hz)	119.4

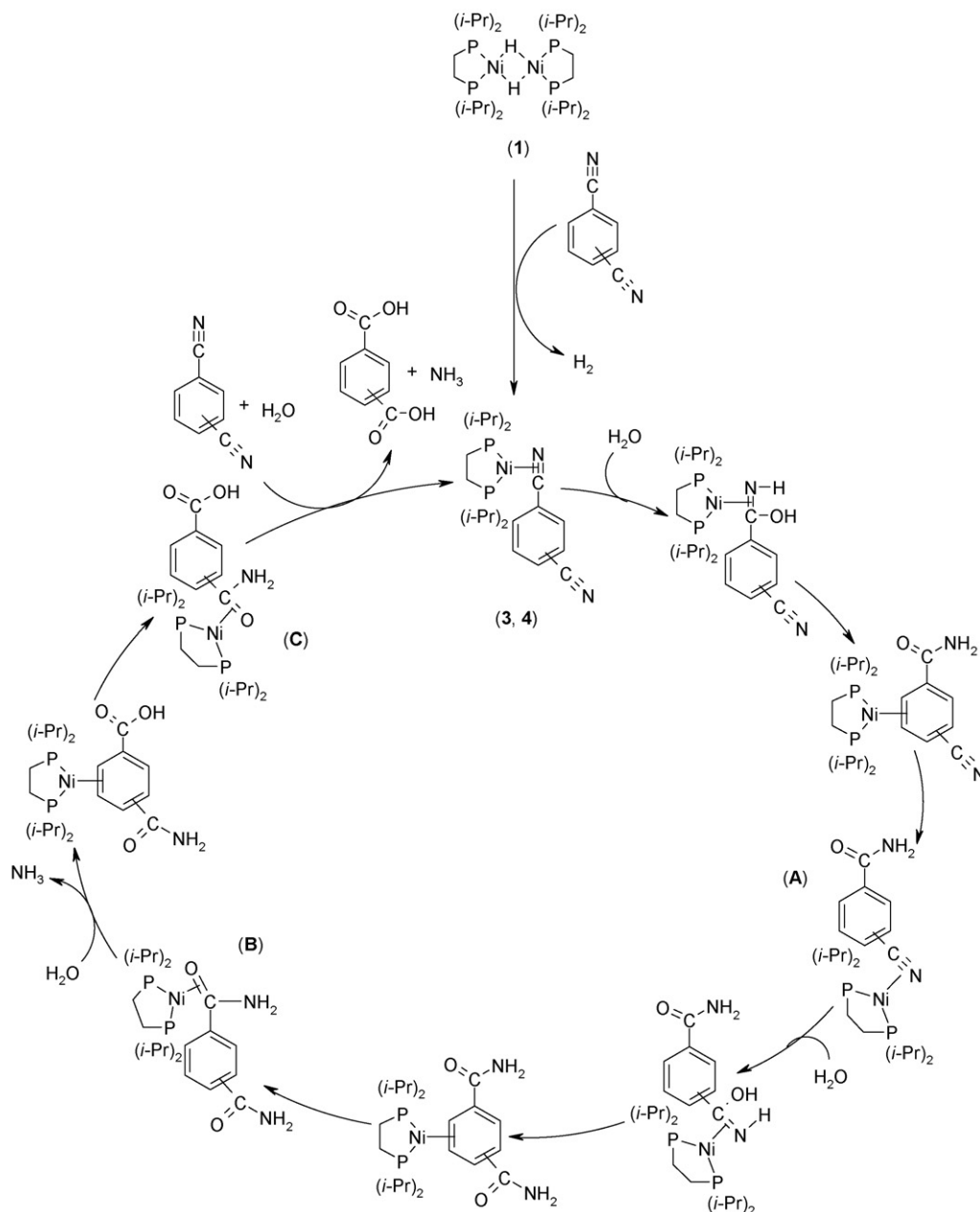
distribution of products may range from the *one-water-addition* process yielding cyanobenzamides, to the total hydration of the dicyanobenzene substrate, producing dicarboxylic acids. The conclusion that can be brought from these instances is that the catalytic hydration of each nitrile in a dicyanobenzene substrate can be rationalized as if *occurring independently of the eventual hydration of the other* and as such, a series of intermediates involving the progressive hydration of the substrate can be established [15]. A general scheme that describes this conclusion is depicted in Scheme 1.

Implicit in Scheme 1, the incorporation of water molecules into the organic functionalities—nitriles or carbonyls [16], is always assumed to take place over the η^2 -coordinated functions and thus a number of related nickel(0) intermediates besides of complexes **2–4** can be envisioned, depending on the stage of hydration catalysis they assist. The additional complexes are proposed to form within the catalytic cycles according to the temperature and the substrate used and in this instance, a number of catalytic proposals that describe these intermediates have been included in Schemes 2–4 (vide infra). The proposed intermediates could be described as having amido/cyano moieties, only amides or amido/carboxyl, depending of the particular stage of catalysis occurring and thus, their complexes could be formulated following these leads as [(dippe)Ni(η^2 -*N,C*-1,*n*-(CN)(C(O)NH₂)-benzene)] (**A**) for the amido/cyano [(dippe)Ni(η^2 -*C,O*-1,*n*-(C(O)NH₂)₂-benzene)] (**B**) for the double amido complex and [(dippe)Ni(η^2 -*C,O*-1,*n*-(C(O)NH₂)(C(O)OH)-benzene)] (**C**) for the amido/carboxyl derivative; presumably the last intermediate before the total hydration is achieved (see Scheme 3). In the cases of the 1,3- and 1,4-dicyanobenzenes, the catalytic cycle at 120 °C (Scheme 2) would require only one additional intermediate, namely [(dippe)Ni(η^2 -*N,C*-1,*n*-(C(O)NH)(CN)-benzene)] (for *n* = 3, 4) to produce the corresponding cyanobenzamides, while catalysis at 180 °C would require all the other nickel(0) intermediates to be formed as well. At this temperature, the migration of the [(dippe)Ni] moiety over the arene ring through a series of stepwise η^2 -bonded [(dippe)Ni(η^2 -*C,C*-2-(X)(Y)-benzene)] (X, Y = -CN, -C(O)NH₂, -C(O)OH) intermediates – alternatively to intermolecular catalysis, involving decoordination and re-coordination of the nickel(0) catalyst – could be proposed to take place, shifting the position of the nickel(0) catalyst from one organic function to the other (amido to cyano, amido to amido and amido to carboxyl), therefore, linking the series of intermediates mentioned above within the same catalytic cycle [17]. The selectivities to 1,3-isophthalic and 1,4-terephthalic acids at 180 °C are indicative of such premise: a non-sequential hydration process (such as that involving the

nickel catalyst going on and off for catalysis) being expected to yield mixtures of partially and fully hydrolysed products, which was not the case [18]. Interestingly, the migration process (or alternatively, the first -CN hydration, assuming a completely intermolecular reactivity by which free [(dippe)Ni] fragments were to coordinate randomly to these substrates) should be temperature-dependent provided that only one water molecule is transferred into the organic substrate at 120 °C, as only cyanobenzamides are produced at this temperature (see Table 1) and as such, a high energy barrier limiting the migration of the [(dippe)Ni] moiety undergone through an intramolecular pathway at such temperature, could be presumed to exist in order to prevent any further hydrolysis of the two dicyanobenzenes (1,3- and 1,4-DCB). At 180 °C however, the



Scheme 2. Mechanistic proposal for the partial hemihydration of 1,3- and 1,4-DCB at 120 °C, using nickel(0) catalysts.



Scheme 3. Mechanistic proposal of the total hydration of 1,3- and 1,4-DCB at 180 °C, using nickel(0) catalysts.

temperature would be enough to overcome such energy barrier and as a result, the two nitriles in each dicyanobenzene substrate become fully hydrolysed.

The mechanistic proposals that illustrate the premise of an intramolecular migration of [(dippe)Ni] moieties to yield the hemi- and complete hydration of the 1,3- and 1,4-DCB are included in Schemes 2 and 3, as follows. To note, the mechanistic proposal of sequential dinitrile hydrations afforded by the stepwise migration of the nickel(0) catalyst [(dippe)Ni] over each arene ring, have also been reported by Tfouni et al. using penta-ammineruthenium complexes [13a]: an *N*-amide to *N*-nitrile linkage isomerization reaction been predicted to take place (~55%), producing the corresponding

end-on coordinated nitrile complex [(NH₃)₅Ru(η¹-*N*,*C*-1,4-(CN)(C(O)NH₂)-benzene)]. The reaction was proposed to occur through a series of stepwise η²-bonded (NH₃)₅Ru(II) 1,4-cyanobenzamide complexes, consistent with previous references using isonicotinamide [19].

In the case of 1,2-DCB – and in contrast with the 1,3- and 1,4-DCB mechanistic proposals illustrated above – the catalytic hydration of this substrate resulted in the formation of 1,2-phthalamide at both 120 and 180 °C, selectively: catalysis was thus found to be independent of the temperature and in this instance, the product was also unique (the expected 1,2-dicarboxylic acid not formed at 180 °C). A number of possibilities to explain this issue have been thought and in this

instance, one possible conclusion that was raised, regardless of the mechanistic pathway by which hydration is accomplished, is to presume the steric hindrance of the adjacent amides in 1,2-phthalamide to be responsible of stopping any further hydrolysis, limiting the effective re-coordination of the [(dippe)Ni] moiety to the carbonyl functions in it. The mechanistic pathway by which hemi-hydrolysis of 1,2-DCB takes place is clearly also open for discussion, but given the experimental results obtained thus far, we are inclined to trust this process not be driven by a stepwise migration of the [(dippe)Ni] catalyst over the arene ring, but rather by an intermolecular *nitrile-to-nitrile* shift over this substrate, provided that the two organic functions are so close to each other: the corresponding 1,2-diamide been obtained even at 120 °C, where the high energy barrier predicted by analogy with the other two systems might have been expected to limit the intramolecular migration of the [(dippe)Ni] moiety producing 2-cyanobenzamide, instead. A mechanistic proposal that summarizes these conclusions for the catalytic hydration of 1,2-DCB at 120 and 180 °C using nickel(0) catalysts, is presented in Scheme 4.

To note, the fact that 1,2-phthalamide could be obtained selectively from 1,2-DCB in this work is also important: the

previous studies using 2-cyanobenzamide in the presence of stoichiometric amounts of ruthenium and cobalt complexes been found to result in the intramolecular cyclization of coordinated 2-cyanobenzamide, therefore yielding 3-imino-1-oxo-isindole complexes [13].

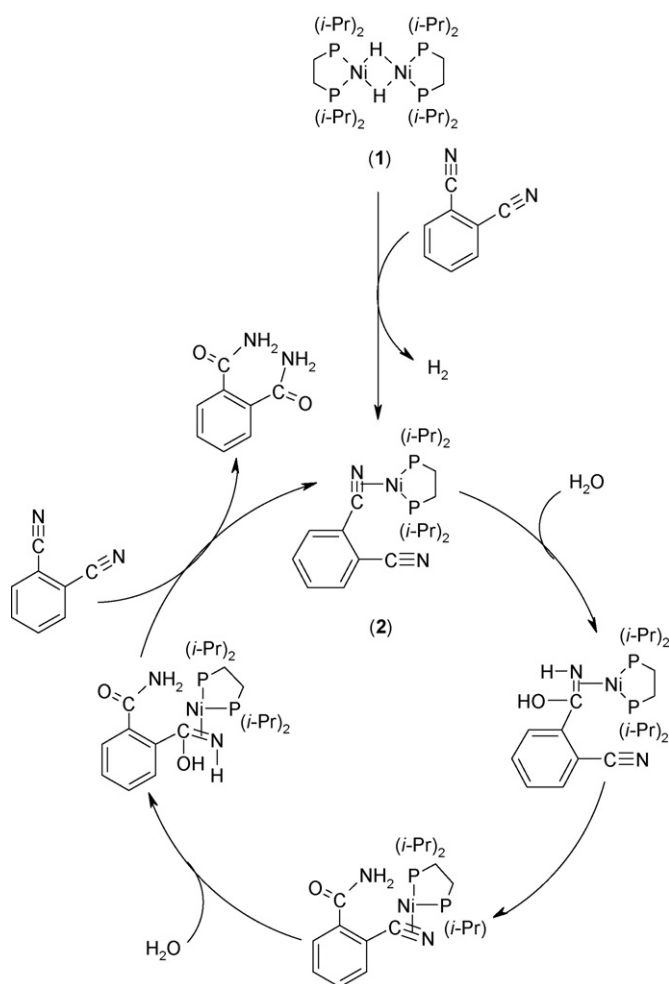
3. Conclusions

The catalytic hydration of 1,2-, 1,3- and 1,4-dicyanobenzenes was achieved under thermal conditions, using monocoordinated nickel(0) complexes with general formula [(dippe)Ni(η^2 -*N,C-1,n*-(CN)₂-benzene)] (*n*=2–4). For these systems, the experimental distributions of products show that there is an important dependence on the isomer that is chosen and on the temperature that is used for catalysis. The hydration products are obtained in excellent selectivity and thus, the potential use of these catalysts in organic synthesis could be envisioned. Current studies are in progress to extend this reaction to dicyano-alkyl substrates.

4. Experimental

4.1. General considerations

Unless otherwise noted, all manipulations were performed using standard Schlenk techniques in an inert-gas/vacuum double manifold or under argon atmosphere in an MBraun glovebox (<1 ppm H₂O and O₂). Catalysis experiments were conducted in a 300 mL stainless steel Parr Series 4560 Bench Top Mini Reactor or alternatively in a 100 mL stainless steel Parr Series 4590 Micro Bench Top Reactor; the catalytic mixtures were loaded in the reactor inside the glovebox. All argon used in this work was supplied by Praxair in high purity grade (99.998%). Solvents were purchased from J.T. Baker in reagent grade and in the case of THF and hexane, that were used in the preparation of [(dippe)NiH]₂ (**1**) (vide infra), these were additionally dried and distilled from sodium/benzophenone ketyl; THF used in catalysis experiments distilled likewise. Ethyl acetate and acetone were used for the chromatographic separation of the hydration products, and were used as received. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and were stored over 3 Å molecular sieves in the glovebox for at least 24 h before their use. NMR spectra of complexes and products were recorded at ambient temperature on a 300 MHz Varian Unity spectrometer. ¹H, ³¹P{¹H} NMR spectra of all nickel complexes were obtained using concentrated solutions of the pure nickel complex (30 mg) in an inert solvent such as toluene-*d*₈ or THF-*d*₈, unless otherwise stated. All the samples were handled under argon, using thin wall – 0.38 mm – WILMAD NMR tubes with J Youngs valves. ¹H and ¹³C{¹H} chemical shifts (δ , ppm) are reported relative to either the residual protiated solvent or deuterated-carbon resonances of the solvent, respectively. ³¹P{¹H} NMR spectra were recorded in units of parts-per-million (ppm) relative to external 85% H₃PO₄. ¹H and ¹³C{¹H} NMR spectra of the hydration products were obtained in DMSO-*d*₆. Complex **1** was prepared from Super-Hydride and [(dippe)NiCl₂]



Scheme 4. Mechanistic proposal for the hemihydration of 1,2-DCB at 120 and 180 °C, using nickel(0) catalysts.

[20] suspended in hexane as previously reported [21]; the neutral alumina used for the preparation of the nickel(I) di- μ -hydride dimer was heated to 200 °C under vacuum for 2 days and stored in the glovebox, prior to its use. The chelating bisphosphine ligand, 1,2-bis(di-isopropylphosphino)ethane (dippe) was synthesized from 1,2-bis(dichlorophosphino)ethane (Strem) and isopropylmagnesium chloride (2.0 M solution in THF, Aldrich), following the reported procedure [22]. The dinitrile reactants 1,2-DCB (98%), 1,3-DCB (98%), and 1,4-DCB (98%) were purchased from Aldrich and were used without further purification. The water used for all hydrations was distilled and was purged with argon for at least 30 min prior to use. All other chemicals used, filter aids and chromatographic materials were reagent grade and were used as received. The catalytic experiments were performed by the in situ preparation of the respective nickel(0) complex [(dippe)Ni(η^2 -N,C-1,*n*-(CN)₂-benzene)] (*n* = 2–4), unless otherwise stated. The total amount of nitrile used, was calculated on the basis of 0.5 mol% of the corresponding nickel(0) catalyst, as calculated on the basis of the total mole amount of nickel(0) versus the total mole amount of nitrile functionalities available, such that every mole of dinitrile substrate affords two moles of nitrile functionalities that may be subject to hydration. All the hydration products were purified by column chromatography, unless otherwise stated and the quoted yields are isolated yields. Characterization of these was made by direct comparison of the ¹H and ¹³C{¹H} NMR spectra and melting points of the products, with those of expressly prepared standards and available literature [23]. Elemental analyses and mass spectra (MS-EI⁺) of the purified organics were carried out by USAI-UNAM using an EA 1108 FISONs Instruments analyser and a Jeol SX-102A mass spectrometer, respectively. Infrared spectra were obtained using a Perkin-Elmer 1600 FT spectrophotometer. All the ammonia produced from catalysis experiments at 180 °C was bubbled from the reactor into concentrated hydrochloric acid before opening the reactor vessel; the resulting acid solution been neutralized after, using NaHCO₃. The mixture of ammonium chloride (NH₄Cl) and sodium chloride (NaCl) produced from this procedures, was then filtered in buchner, dried and analysed by X-ray powder diffraction (Powder XRD); the results of which are included in the Supporting Information of this work. All Powder XRD analyses were performed using graphite monochromatized Cu K α radiation (λ = 1.5406 Å) in a Siemens D5000 diffractometer; by USAI-UNAM. All experimental melting points were obtained by closed capillary methods, using an Electrothermal Digital Melting Point Apparatus. All the turnover numbers (TON) for the catalytic hydrations in this work were calculated as moles of isolated product over moles of nickel(0) catalyst, multiplied by a factor of 1 in the case of cyanobenzamides, 2 for diamides, and 4 for dicarboxylic acids, according to the degree of hydration achieved in each product. Turnover frequencies (TOF) are calculated as TON over reaction time. All the calculated ¹H and ¹³C{¹H} NMR spectra in this work were obtained using ACD/HNMR Predictor [24] and ACD/CNMR Predictor [25], respectively; the chemical formulas for all the calculated structures in these spectra, obtained using ACD/ChemSketch [26].

4.2. Reaction of [(dippe)NiH]₂ (1) with 1,2-DCB: preparation of [(dippe)Ni(η^2 -N,C-1,2-(CN)₂-benzene)] (2)

The reaction of [(dippe)NiH]₂ (0.020 g, 0.031 mmol) and a 2:1 excess of 1,2-DCB (0.008 g, 0.062 mmol), yielded the formation of the monocoordinated nickel(0) complex [(dippe)Ni(η^2 -N,C-1,2-(CN)₂-benzene)] (2). The reagents were mixed at room temperature, adding the 1,2-dicyanobenzene to a dark red THF-*d*₈ solution (1 mL) of the nickel(I) dimer. After mixing, a strong effervescence was observed to occur; all the released gas was vented to the glovebox. The mixture was left under stirring for 1 h, after which time it was examined by NMR. On standing in solution for 24 h at room temperature, in the absence of additional water, the oxidative addition complex [(dippe)Ni(CN)(2-CN-phenyl)] (5) gradually forms. NMR spectra of 2 in THF-*d*₈ solution: ¹H, δ 7.64 (m, 1H, CH), 7.45 (m, 1H, CH), 7.29 (m, 1H, CH), 7.07 (m, 1H, CH), 2.2–1.9 (m, 4H, CH), 1.85–1.6 (m, 4H, CH₂), 1.2–0.92 (m, 24H, CH₃). ¹³C{¹H}, δ 169.9 (dd, *J*₁ = 72.4 Hz, *J*₂ = 28.2 Hz, coordinated CN), 137.8 (s, C), 134.5 (s, CH), 132.6 (s, CH), 129.5 (s, CH), 128.1 (s, CH), 118.6 (s, CN), 110.6 (s, C), 25.9 (d, *J*_{C-P} = 22.6 Hz, CH), 24.5 (d, *J*_{C-P} = 24 Hz, CH), 23.0–22.5 (m, CH₂), 20.4 (s, CH₃), 20.2 (s, CH₃), 19.6 (s, CH₃), 19.2 (s, CH₃). ³¹P{¹H}, δ 80.2 (d, ²*J*_{P-P} = 63 Hz), 69.4 (d, ²*J*_{P-P} = 63 Hz). NMR spectra of 5 in THF-*d*₈ solution: ³¹P{¹H}, δ 86.2 (d, ²*J* = 25 Hz), 74.3 (d, ²*J* = 25 Hz).

4.3. Reaction of [(dippe)NiH]₂ (1) with 1,3-DCB: preparation of [(dippe)Ni(η^2 -N,C-1,3-(CN)₂-benzene)] (3)

The reaction of [(dippe)NiH]₂ (0.020 g, 0.031 mmol) and a 2:1 excess of 1,3-DCB (0.008 g, 0.062 mmol), yielded the formation of the monocoordinated nickel(0) complex [(dippe)Ni(η^2 -N,C-1,3-(CN)₂-benzene)] (3). The reagents were mixed at room temperature, similarly to the procedures described for 1,2-dicyanobenzene, adding the amount of 1,3-dicyanobenzene to a dark red toluene-*d*₈ solution (1 mL) of the nickel(I) dimer. On standing in solution for 24 h at room temperature, in the absence of additional water, the oxidative addition complex [(dippe)Ni(CN)(3-CN-phenyl)] (6) gradually evolves. NMR spectra of 3 in toluene-*d*₈ solution: ¹H, δ 7.82–7.97 (m, 1H, CH), 7.09 (m, 2H, CH), 7.2–6.88 (m, br, 1H, CH), 2.12–1.7 (m, 4H, CH), 1.6–1.4 (m, 4H, CH₂), 1.2–0.9 (m, 24H, CH₃). ¹³C{¹H}, δ 162.9 (dd, *J*₁ = 73 Hz, *J*₂ = 28.5 Hz, coordinated CN), 142.3 (s, CH), 140.4 (s, CH), 135.5 (s, CH), 135.3 (s, CH), 126.5 (s, C), 117 (s, CN), 114 (s, C), 25.9 (d, *J*_{C-P} = 22.1 Hz, CH), 24.5 (d, *J*_{C-P} = 24 Hz, CH), 22.9–22.3 (m, CH₂), 20.41 (s, CH₃), 20.38 (s, CH₃), 19.2 (s, CH₃), 18.05 (s, CH₃). ³¹P{¹H}, δ 77.6 (d, ²*J*_{P-P} = 63 Hz), 65.9 (d, ²*J*_{P-P} = 63 Hz). NMR spectra of 6 in THF-*d*₈ solution: ³¹P{¹H}, δ 81.9 (d, ²*J*_{P-P} = 24.5 Hz), 70.9 (d, ²*J*_{P-P} = 24.5 Hz).

4.4. Reaction of [(dippe)NiH]₂ (1) with 1,4-DCB: preparation of [(dippe)Ni(η^2 -N,C-1,4-(CN)₂-benzene)] (4)

The reaction of [(dippe)NiH]₂ (0.020 g, 0.031 mmol) and a 2:1 excess of 1,4-DCB (0.008 g, 0.062 mmol), yielded

the formation of the monocoordinated nickel(0) complex [(dippe)Ni(η^2 -C,N-1,4-(CN)₂-benzene)] (**4**). The reagents were mixed at room temperature, similarly to the procedure described for 1,2-dicyanobenzene, adding the amount of 1,4-dicyanobenzene to a dark red toluene-*d*₈ solution (1 mL) of the nickel(I) dimer. No oxidative addition of the C–CN bond to the nickel(0) center in **4** was obtained at room temperature, after 24 h in solution; however, as reported before in Ref. [9b], on warming a solution of this complex to 50 °C for 12 h in the absence of additional water, the oxidative addition complex [(dippe)Ni(CN)(4-CN-phenyl)] (**7**) was indeed obtained. Also, as reported in that same reference, the use of an equimolecular mixture of [(dippe)NiH]₂ (0.040 g, 0.062 mmol) and 1,4-terephthalonitrile (0.008 g, 0.062 mmol) in solution, allowed the production of the doubly coordinated dinitrile complex [(dippe)Ni₂(η^2 -, η^2 -C,N-1,4-(CN)₂-benzene)] (**8**) [9b]. Recrystallisation of **8** from hexanes precipitates this product in pure crystalline form. NMR spectra of **4** in toluene-*d*₈ solution: ¹H, δ 7.6 (d, J = 8 Hz, 2H, CH), 6.98 (d, J = 8.0 Hz, 2H, CH), 2.01–1.88 (m, 4H, CH), 1.85–1.71 (m, 4H, CH₂), 1.28–1.09 (m, 24H, CH₃). ¹³C{¹H}, δ 169.9 (dd, J_1 = 30 Hz, J_2 = 9 Hz, coordinated CN), 134.2 (s, C), 132.6 (s, CH), 130.1 (s, CH), 119.4 (s, CN), 112.3 (s, C), 26.2–25.2 (m, CH), 23.6–22.4 (m, CH₂), 20.5 (s, CH₃), 20.2 (s, CH₃), 19.5 (s, CH₃), 19.3 (s, CH₃). ³¹P{¹H}, δ 77.5 (d, ² J_{P-P} = 63 Hz), 65.7 (d, ² J_{P-P} = 63 Hz). NMR spectra of **7** in toluene-*d*₈ solution: ³¹P{¹H}, δ 81.7 (d, ² J_{P-P} = 23.5 Hz), 70.9 (d, ² J_{P-P} = 23.5 Hz). NMR spectra of **8** in THF-*d*₆: ¹H, δ 7.82–7.97 (m, 1H, CH), 7.09 (m, 2H, CH), 7.2–6.88 (m, br, 1H, CH), 2.12–1.7 (m, 4H, CH), 1.6–1.4 (m, 4H, CH₂), 1.2–0.9 (m, 24H, CH₃). ¹³C{¹H}, δ 169.2 (dd, J_1 = 30 Hz, J_2 = 10 Hz, coordinated CN), 133 (s, C), 130.5 (s, CH), 26.7 (d, J_{C-P} = 22.6 Hz, CH), 26.5 (d, J_{C-P} = 24 Hz, CH), 26–25.5 (m, CH₂), 20.6 (s, CH₃), 19.99 (s, CH₃), 19.53 (s, CH₃), 19.2 (s, CH₃). ³¹P{¹H}, δ 79.9 (d, ² J_{P-P} = 68 Hz), 67.9 (d, ² J_{P-P} = 68 Hz).

5. Catalysis

5.1. Hemihydration of 1,2-DCB at 180 and 120 °C: production of 1,2-phthalamide

The reactor vessel was loaded in separate runs with [(dippe)NiH]₂ (0.0801 g, 0.124 mmol), 1,2-DCB (3 g, 0.023 mol) and water (21 mL, 1.17 mol). The resulting mixtures were heated at 180 and 120 °C for 72 h, similarly to the procedures already described. In either case, a green crude solid residue was removed from the reactor vessel with the aid of additional water. The aqueous solutions were each filtered through a frit. Water was removed from the residues by evaporation and these were recrystallised from hot methanol, precipitating a white crystalline solid in each case, using hexane. Yield of 1,2-phthalamide at 180 °C, after work-up: 71% (2.6 g, 0.016 mol) with a TON of 135 and a TOF of 2 cycles per hour. Yield of 1,2-phthalamide at 120 °C, after work-up: 71% (2.6 g, 0.016 mol) with a TON of 135 and a TOF of 2 cycles per hour. Mp of 1,2-phthalamide: 222–225 °C. NMR spectra for 1,2-phthalamide in DMSO-*d*₆: ¹H, δ 8.04 (m, 2H, CH), 7.54 (m, 2H, CH), 7.12 (s, br, 4H,

NH₂). ¹³C{¹H}, δ 166.3 (carbonyl), 134.4 (s, C), 131.4 (s, CH), 130.5 (s, CH).

5.2. Total hydration of 1,3-DCB at 180 °C: production of 1,3-isophthalic acid

The reactor vessel was loaded in the glovebox with [(dippe)NiH]₂ (0.0801 g, 0.124 mmol), 1,3-DCB (3 g, 0.023 mol) and water (21 mL, 1.17 mol). The mixture was heated at 180 °C, under vigorous stirring for 72 h, after which time the reactor vessel was left to cool down and opened in a hood prior to work-up; all the ammonia produced in the reactor during the hydration process was bubbled into a concentrated hydrochloric acid before opening the reactor vessel. A brown crude solid residue was removed from the reactor vessel and subjected to acid/base purification, dissolving it in a concentrated solution of NaOH, which was then filtered through a frit. Dropwise addition of concentrated HCl until a neutral pH, precipitated a white powder, that was recovered as a pure material after repeated washings using distilled water. The washed product was vacuum dried overnight ($P < 10^{-4}$ mmHg). Yield of 1,3-isophthalic acid after work-up: 68% (2.61 g, 0.016 mol), with a TON of 259 and a TOF of 4 cycles per hour. Mp of 1,3-isophthalic acid: >250 °C (sublimes). MS (EI⁺): m/z = 166.7 (molecular ion). Losses: m/z = 149 (–OH), 121 (–COOH). Anal. Calcd. for C₈H₆O₄ (1,3-isophthalic acid): C 57.8, H 3.6. Found: C 57.9, H 3.8. NMR spectra for 1,3-isophthalic acid in DMSO-*d*₆: ¹H, δ 13 (s, br, 2H, OH), 8.4 (m, 1H, CH), 8.2 (m, 2H, CH), 7.6 (m, 1H, CH). ¹³C{¹H}, δ 166.7 (carbonyl), 133.5 (s, CH), 131.3 (s, CH), 130.1 (s, CH), 129.2 (s, C).

5.3. Partial hemihydration of 1,3-DCB at 120 °C: production of 1,3-cyanobenzamide

The reactor vessel was loaded in the glovebox with [(dippe)NiH]₂ (0.0801 g, 0.124 mmol), 1,3-DCB (3 g, 0.023 mol) and water (21 mL, 1.17 mol). The mixture was heated at 120 °C, under vigorous stirring for 72 h, after which time the reactor vessel was left to cool down and opened in a hood prior to work-up, which was performed following the procedure described infra for 4-cyanobenzamide. Yield of 1,3-cyanobenzamide after work-up: 86% (2.92 g, 0.020 mol) with a TON of 82 and a TOF of 1 cycle per hour. Mp of 1,3-cyanobenzamide: 225–228 °C. Anal. Calcd. for C₈H₆N₂O₁ (1,3-cyanobenzamide): C 65.1, H 4.1, N 19.1. Found: C 65.1, H 3.9, N 19.1. NMR spectra for 1,3-cyanobenzamide in DMSO-*d*₆: ¹H, δ 8.22 (m, 1H, CH), 8.08 (m, 1H, CH), 8.0 (m, 1H, CH), 7.64 (m, 1H, CH), 7.63 (br, s, 2H, NH₂). ¹³C{¹H}, δ 166.4 (carbonyl), 135.3 (s, C), 134.8 (s, CH), 132.3 (s, CH), 131.1 (s, CH), 129.8 (s, CH), 118.4 (s, CN), 111.5 (s, C).

5.4. Total hydration of 1,4-DCB at 180 °C: production of 1,4-terephthalic acid

The reactor vessel was loaded in the glovebox with [(dippe)NiH]₂ (0.0801 g, 0.124 mmol), 1,4-DCB (3 g, 0.023 mol) and

water (21 mL, 1.17 mol). The mixture was heated at 180 °C, under vigorous stirring for 72 h, after which time the reactor vessel was left to cool down and opened in a hood prior to work-up; all the ammonia produced in the reactor during the hydration process was bubbled into a concentrated hydrochloric acid before opening the reactor vessel. A white crude solid residue was removed from the reactor vessel and subjected to acid/base purification, following the procedure for 1,3-isophthalic acid, described above. Yield of 1,4-terephthalic acid after work-up: 86% (3.36 g, 0.020 mol), with a TON of 325 and a TOF of 5 cycles per hour. Mp of 1,4-terephthalic acid: >300 °C (sublimes). NMR spectra for 1,4-terephthalic acid in DMSO-*d*₆: ¹H, δ 13.3 (s, br, 2H, OH), 8.0 (s, 4H, CH). ¹³C{¹H}, δ 166.7 (carbonyl), 134.5 (s, C), 129.5 (s, CH). IR (KBr disc, cm⁻¹): 3111.2 (OH), 1715 (carbonyl), 1428–1570, 700 (Ar).

5.5. Partial hemihydration of 1,4-DCB at 120 °C: production of 1,4-cyanobenzamide

The reactor vessel was loaded in two separate runs with [(dippe)NiH]₂ (0.0801 g, 0.124 mmol), 1,4-DCB (3 g, 0.023 mol) and water (21 mL, 1.17 mol); the second run been additionally charged with 50 mL of THF. Each mixture was then heated at 120 °C, under vigorous stirring for 72 h, after which time the reactor vessel was left to cool down and opened in a hood prior to work-up. A white crude solid residue was removed from the reactor vessel in both occasions and purified by column chromatography eluting over neutral alumina. Unreacted 1,4-DCB was recovered as the first fraction, eluting with ethyl acetate only. 4-Cyanobenzamide was recovered as the second fraction, eluting with a 1:1 (v/v) mixture of ethyl acetate and acetone. Solvent evaporation yielded a white crystalline powder from the two experiments, which was characterized as 1,4-cyanobenzamide. Yield of 1,4-cyanobenzamide produced in the absence of THF, after work-up: 68% (2.34 g, 0.016 mol) with a TON of 64 and a TOF of 1 cycle per hour. Yield of 1,4-cyanobenzamide produced in the presence of THF, after work-up: 87% (3 g, 0.020 mol) with a TON of 83 and a TOF of 1 cycle per hour. Mp of 1,4-cyanobenzamide: 225–228 °C. MS (EI⁺): *m/z* = 146 (molecular ion). Losses: *m/z* = 130 (–NH₂), 102 (–CONH₂), 44 (–C₇H₄N). Anal. Calcd. for C₈H₆N₂O₁ (1,4-cyanobenzamide): C 65.1, H 4.1, N 19.1. Found: C 65.0, H 3.9, N 18.9. NMR spectra for 1,4-cyanobenzamide in DMSO-*d*₆: ¹H, δ 8.22 (s, br, 1H, NH), 8.02 (m, 2H, CH), 7.86 (m, 2H, CH), 7.64 (s, br, 1H, NH). ¹³C{¹H}, δ 166.5 (carbonyl), 138.3 (s, C), 132.4 (s, CH), 128.3 (s, CH), 118.4 (s, CN), 113.7 (s, C). IR (KBr disc, cm⁻¹): 3448–3176 (NH₂), 2226 (CN), 1702 (carbonyl), 1428–1570, 700 (Ar).

Acknowledgements

We thank DGAPA-UNAM (IN-205603) and CONACYT (C02-42467) for their support to this work. MGC also thanks CONACYT for a Ph.D. grant.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.10.054.

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- [14] The smaller magnitudes of the ${}^2J_{C-P}$ coupling constants for the coordinated $-CN$ group in complex **4** have been attributed to the electron withdrawing effect that is imposed by the other cyano substituent that is present in 1,4-DCB. In this instance, previous Hammett studies with a number of electron donating and electron withdrawing substituents in the *para*-position of the benzene ring (the case of 1,4-DCB been addressed in such studies) have shown that the latter ones induce the localization of negative charge around the ipso carbon of the coordinated $-CN$ moiety (see Ref. [9b]). In the light of such results, one possible outcome is that the magnitude of π -back bonding to the nickel(0) center may be expected to diminish as a consequence of this $Ni^{\delta+}-C^{\delta-}$ polarization, therefore, affecting the magnitude of the ${}^2J_{C-P}$ coupling constants; an effect that is seemingly most dramatic in the case of complex **4**.
- [15] An activating effect over the coordinated $-CN$ group towards the *N,N*-dihydro-*C*-oxo-biaddition of water promoted by the second $-CN$ is expected to exist in all DCB substrates. The extent of such effect is expected to be particularly dramatic in the case of complex **4** as it shows the smaller ${}^2J_{C-P}$ coupling constants from the series (indicated in Table 2) and in this instance, it seems reasonable to conclude that from all DCB substrates, it is this complex that would depict the more electron poor character at the coordinated $-CN$ moiety and thus probably, the faster hydration rate.
- [16] The η^2-C,O coordination of the carbonyl from an amide or carboxylic acid derivative to the [(dippe)Ni] moiety is proposed on the basis of its similarity with an imine; the hydroxy *N*-protonated imines that result from the concerted *N,N*-dihydro-*C*-oxo-biaddition of water to η^2-C,N coordinated nitriles to this nickel(0) entities (validated from experimental results described in Ref. [11]), being examples of η^2 -coordinated double bonds to nickel(0) in resemblance to the η^2 -coordinated carbonyls, proposed herein.
- [17] Structural and spectroscopic evidences of the η^2 -coordination of arene rings to [(dippe)Ni] moieties have already been found upon reacting quinoline in the presence of complex **1**, the resulting complex been characterized as [(dippe)Ni(η^2 -quinoline)] [9b]. Even more related with this work, when the otherwise similar 2- and 3-cyanoquinolines were reacted with this complex, the formation of [(dippe)Ni($\eta^2-C,C-2-CN$ -quinoline)] and [(dippe)Ni($\eta^2-C,C-3-CN$ -quinoline)] were also confirmed; the former complex been found to evolve in THF solution only after an initial coordination of the nitrile to the corresponding [(dippe)Ni] moiety. (see Scheme 1, also in Ref. [9b]).
- [18] The alternative of nickel(0) going on and off for catalysis would imply that all nickel(0) intermediates required to yield the complete hydration of 1,3- and 1,4-DCB would have been formed within 72 h, at 180 °C. In the case of 1,2-DCB the same premise might imply additionally, that at the same temperature the free nickel catalysts should coordinate to the 1,2-phthalamide produced in situ in a fashion not conducive towards further hydration, therefore, not producing the corresponding dicarboxylic acid. Still, the selectivity and yield afforded at 120 °C for such product and not to 2-cyanobenzamide which would be expected to form otherwise, specially if free [(dippe)Ni] catalysts were to react randomly, an explanation based on an intramolecular migration of these species was found to be reasonable, at least for the time being.
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