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Easily available nickel complexes as catalysts for the intermolecular hydroamination of alkenes and alkynes†

Adán Reyes-Sánchez, Ilnett García-Ventura and Juventino J. García*

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A series of nickel complexes of the type [(P–P)NiX$_2$] ((P–P) = bisphospines or bisphosphites, X = chloride, triflate) were used as catalysts for the hydroamination of both activated and unactivated alkenes and alkynes with pyrrolidine. In general, the use of activated unsaturations, such as acrylonitrile, required mild reaction conditions (*e.g.* 100 °C and 4 h) in comparison with other non-activated alkenes. Particularly with a series of alkynes, the use of nickel(II) centers diminished or even inhibited the formation of otherwise undesired homocoupling and/or transfer hydrogenation by-products, such as the ones obtained in the presence of zerovalent nickel. When using less activated substrates, better selectivity was obtained, although harsher reaction conditions were needed. From a general perspective, the results of this report strongly support the potential use of nickel as a good candidate for further application in the hydroamination of organic unsaturations by means of screening of several π acceptor ligands.

1. Introduction

Alkynes and alkenes represent two of the most important building blocks for the synthesis of target compounds with wide applications both in industry and fine chemistry.[1] Besides conventional reactions to functionalize these substrates, hydroamination, defined as the direct addition of amines to alkynes and alkenes,[2,3] represents a route to synthesize N-derivatives such as amines, imines and enamines in one step and with high atom economy. In general, intramolecular hydroamination has been shown to be thermodynamically and kinetically more favored and easier to achieve than the intermolecular manner. In order to afford the hydroamination of C–C unsaturations, catalysts, mainly based on elements of the d and f blocks of the periodic table, have been developed.[2] The found reactivity with such catalysts varies mostly by means of their electronic properties conferred both by the element and its ligands as is briefly described below.

Among the most efficient metal complexes used in the hydroamination stands the use of titanium[4–6] and other early transition metals.[7,8] In most of the reported examples, the corresponding hydroamination products have been obtained in high yields. In the same way, complexes based on rare earth complexes have allowed the hydroamination of alkynes and alkenes mostly in an intramolecular fashion, and in this regard, the extended use of samarium developed by Marks *et al.*[9–12] is noteworthy. Nevertheless, one of the main disadvantages of both early transition and rare earth metal complexes is their high oxophilicity, which eventually limits their use with some oxygen-containing substrates.[3]

Regarding the use of late transition metals, palladium is, by far, the most widely employed metal in hydroamination and other well known relevant organic transformations.[13] Particularly with palladium, there have been some interesting reports related to the effect of variables involving the electronic character of the metal itself and its ligands, which eventually could be applied to neighboring elements. For instance, Hartwig *et al.*[14] have found that in the hydroamination of vinylarenes and dienes, the use of ancillary phosphines bearing wide bite angles (*e.g.* xantphos) allows the formation of the corresponding products more efficiently compared to other phosphines with narrower angles. The same authors adduce this effect to a more favorable nucleophilic attack over the alkene when this is coordinated to a metal center with a wider phosphine. In another example, the Müller group has reported a study[15] describing the enhancement of the rate of hydroamination of aminoalkynes when the counter ion of a cationic palladium catalyst is a sulfonic acid derivative (*e.g.* triflate or tosylate) because of the easiness of replacing them by an alkyne or amine.

There have been some recent efforts to mimic the catalytic activity of palladium, mainly because, when compared to this element, other alternate metals such as copper, nickel and

Facultad de Química, Universidad Nacional Autónoma de México, Circuito Escolar, Ciudad Universitaria, Mexico City 04510, Mexico. E-mail: juvent@servidor.unam.mx

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iron offer lower costs and toxicities as well as a better biocompatibility. In this regard, some recent approaches involve the intermolecular hydroamination of activated alkenes, such as derivatives of acrylonitrile, catalyzed by hydride and NHC complexes of copper,[16,17] the use of silver in the intermolecular hydroamination of alkynes,[18,19] and the iron-catalyzed inter- and intramolecular hydroamination of styrenes[20] and aminoalkenes,[21] respectively. For the particular case of nickel, its use in hydroamination is still scarce, even though it holds great potential as a cheap and biocompatible catalyst, for example, in the hydroamination of activated alkenes,[22–27] dienes,[14] and alkynes.[15,28–31] Recently, our group has reported the hydroamination and transfer semihydrogenation of alkynes catalyzed by the complex $[(dippe)NiH]_2$.[31] In the mentioned work, the hydroamination products of diphenylacetylene and 2-ethynylaniline could be successfully obtained, although in moderate yields (<40%) because of the competing prevalence of both the hydroamination and hydrogenation in the media. Considering these results and in order to avoid or diminish reactions other than the hydroamination, we envisaged the use of a more acidic nickel center to enhance and favor the nucleophilic attack over the coordinated alkyne or alkene also aided by the presence of activating substituents in the substrates. Herein, we present the results of such investigations using different nickel compounds as catalysts in the hydroamination of both activated and unactivated alkynes and alkenes. The facile commercial and/or synthetic availability of the ligands and nickel precursors, as well as the easiness of the procedure, is highlighted.

2. Experimental

2.1 General considerations

Unless otherwise noted, all experiments were carried out using standard Schlenk techniques in a double vacuum-argon manifold or in a glovebox (MBraun Unilab) under high purity argon (Praxair 99.998) and controlled concentrations of water and oxygen (<1 ppm). Catalytic experiments were carried out in Schlenk tubes or in stainless steel Parr (T315SS) reactors. All purchased liquid reagents were of reagent grade and degassed before use. Alkenes **1a–d**, alkynes **1e–p**, pyrrolidine and $[(COD)_2Ni]$ (COD = 1,3-cyclooctadiene) were purchased from Aldrich and stored in the glovebox for further use. Phosphine dippe (1,2-bis(diisopropylphosphino)ethane) was prepared from 1,2-bis(dichloro)ethane (Aldrich) and a solution of isopropylmagnesium chloride (2.0 M, Aldrich) in THF. Phosphines PEt_3, diphos (1,2-bis(diphenylphosphino)ethane), dippf (1,1′-bis(diisopropylphosphino)ferrocene), and dppf (1,1′-bis-(diphenylphosphino)ferrocene) were purchased from Aldrich and used without further purification. Phosphites $P(OEt)_3$ and $P(OPh)_3$ were purchased from Strem Chemicals and stored in the glovebox for further use. Solvents were dried using standard techniques and stored in the glovebox over 4 Å molecular sieves for 24 h prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored under 4 Å molecular sieves for 24 h before use. Complexes $[(dippe)NiCl_2]$, $[(diphos)NiCl_2]$, $[(dippf)NiCl_2]$ and $[(dppf)NiCl_2]$ were prepared from solutions of $NiCl_2{\cdot}6H_2O$ and the corresponding chelating bisphosphine by adapting reported procedures.[32] The nickel dimer $[Ni(dippe)(\mu\text{-}H)]_2$ was synthesized from a stirred suspension of $[(dippe)NiCl_2]$ and Super-Hydride® by the procedure reported in the literature.[33] The complex $[(diphos)Ni](OTf)_2$ was prepared according to reported procedures.[34,35] NMR spectra of complexes and organic products were acquired at room temperature using a 300 MHz Varian Unity Inova spectrometer. Samples and reactions monitored by NMR were manipulated under an inert atmosphere and charged in thin wall (0.33 mm) Wilmad NMR tubes, equipped with J. Young valves and heated in silicon oil baths at the desired temperature. Chemical shifts in ^1H NMR spectra (δ, ppm) are reported according to the residual protio in the solvent. $^{31}P\{^1H\}$ NMR spectra are referred to the 0 ppm signal of external 85% H_3PO_4. $^{19}F\{^1H\}$ NMR spectra are referred to the −76.55 ppm signal of an external solution of CF_3COOH.

2.2 Hydroamination of acrylonitrile mediated by $[(diphos)Ni](OTf)_2$

In a vial, 40 mg (0.053 mmol) of the complex $[(diphos)Ni](OTf)_2$ were dissolved in 0.7 mL of CD_2Cl_2. Then, 2 equiv. (7 μL, 5.8 mg, 0.11 mmol) of acrylonitrile were added. The reaction mixture was transferred into a Wilmad NMR tube with a J. Young valve and stirred and monitored for 24 h. In the $^{31}P\{^1H\}$ NMR spectra a signal assigned to the complex $[(diphos)Ni(\kappa^1\text{-}N\text{-acrylonitrile})_2](OTf)_2$ was observed. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.94 (m, 8H), 7.64 (m, 4H), 7.47 (m), 6.18 (dd, J = 17.8, 0.8 Hz), 6.04 (dd, J = 11.7, 0.8 Hz), 5.62 (dd, J = 17.8, 11.7 Hz), 2.10 (d, $^2J_{PH}$ = 17.4 Hz, 4H). $^{31}P\{^1H\}$ (121.5 MHz) δ 57.2 (s). ^{19}F NMR (282.2 MHz): −77.6 (s).

To this mixture were added 2 equiv. (9 μL, 7.8 mg, 0.11 mmol) of pyrrolidine and the tube containing the reaction mixture was sealed and heated at 60 °C for 4 h. After this time and according to the ^1H NMR spectrum, full conversion of the starting material was observed. ^1H NMR (300 MHz, CD_2Cl_2): δ 2.67 (t, $^3J_{HH}$ = 6.9 Hz, 4H), 2.48 (m, 4H), 1.72 (m, 4H) (Scheme S1, ESI†).

2.3 Catalytic hydroamination of activated alkenes and alkynes with the complex $[(diphos)Ni](OTf)_2$ formed *in situ*

In a typical experiment, a Schlenk tube was charged with 5 mg of $[(diphos)NiCl_2]$ (0.010 mmol), 4.85 mg of AgOTf (0.020 mmol), 0.2 mmol of alkene (10.6 mg, 13 μL in the case of acrylonitrile) and 14 μL (14.2 mg, 0.2 mmol) of pyrrolidine in 5 mL of a solvent (benzonitrile, THF or pyrrolidine). The tube was sealed and heated in an oil bath at 100 °C for 4 h. After this time, the reaction mixture was cooled down to ambient temperature, exposed to the air and passed through a column of celite. The filtrate was diluted 1 : 1 in THF and analyzed by GC-MS.

2.4 Catalytic hydroamination of alkynes with neutral Ni(II)

In a typical experiment, following the above described procedure, a Schlenk tube and/or a Parr reactor was charged with 5 mg of [(dippe)$NiCl_2$] (0.013 mmol), 0.255 mmol of alkyne (26 mg for phenylacetylene) and 5 mL of pyrrolidine without the addition of any other solvent. The tube and/or the reactor was heated at the desired temperature (100 or 180 °C) with constant stirring for 72 h. The reaction mixture was cooled down to ambient temperature and filtered through celite. The filtrate was diluted in THF and analyzed by GC-MS.

2.5 Hydroamination of alkynes at 80 psi catalyzed by complexes of the type [(P–P)Ni$(COD)_2$] and [$((PR_3)_2)$Ni$(COD)_2$] formed *in situ*

In a typical experiment, Ni$(COD)_2$ (2.4 mg, 0.0087 mmol) and the phosphine (dippf: 0.0087 mmol, 3.6 mg) were dissolved separately in 2.5 mL of pyrrolidine. After 20 min of constant stirring, the solution containing the phosphine was added slowly to the [Ni$(COD)_2$] solution and the resulting mixture was kept under constant stirring for 30 min yielding a brown-yellowish solution; later, to this was added 1-phenyl-1-propyne (21.5 mL, 0.1709 mmol). The resulting solution was transferred to a Parr® reactor and this was closed, taken out from the glovebox and pressurized with argon at 80 psi. After this, the reactor was heated in an oil bath at the desired temperature for 72 h. Once the time was over, the reactor was cooled down to ambient temperature and depressurized. Finally, the reaction mixture was exposed to air, filtered and analyzed by GC-MS.

2.6 Hydroamination of alkynes at 80 psi catalyzed by complexes of the type [(P–P)$NiCl_2$]

In a typical experiment, 0.0102 mmol of catalyst (5.0 mg for [(dippf)$NiCl_2$]) was dissolved in 5 mL of pyrrolidine forming a yellow solution. To this was added 1-phenyl-1-propyne (25.5 μL, 0.2039 mmol) with no apparent change in the color of the solution. The reaction mixture was kept under stirring for 5 min, transferred to a Parr® reactor, pressurized with argon (80 psi) and heated at the desired temperature for 72 h. After this time, the reaction mixture was treated as described above.

2.7 Hydroamination of alkynes at 80 psi catalyzed by complexes of the type [$(PR_3)_2NiCl_2$] formed *in situ*

In a typical experiment, 3.2 mg of $NiCl_2{\cdot}6H_2O$ (0.0135 mmol) were dissolved in a minimal amount of ethanol and further were added 7 μL (0.027 mmol) of $P(OPh)_3$ keeping the solution under constant stirring for 30 min. Then 2.5 mL of pyrrolidine and 33.5 μL (0.1871 mmol) of 1-phenyl-1-propyne were added forming a yellow solution, which was transferred to a Parr® reactor, pressurized with argon (80 psi), and heated at the desired temperature for 72 h. After this time, the reaction mixture was treated similarly to the above described procedure.

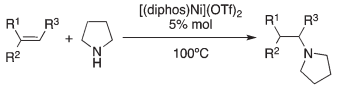
3. Results and discussion

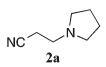
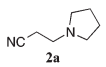
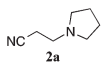
In a first assessment to test the catalytic activity of nickel(II) compounds, complex [(diphos)Ni][$(OTf)_2$ (**1**) was used in stoichiometric amounts to yield the complex [(diphos)Ni(κ^1-acrylonitrile)][$(OTf)_2$ followed by the addition of two equivalents of pyrrolidine to afford the hydroamination of acrylonitrile. The corresponding hydroamination product could be obtained quantitatively (>99% yield in 4 h at 60 °C) in CD_2Cl_2 (Scheme S1, ESI†). After knowing the feasibility of the use of **1** in the hydroamination of acrylonitrile, the same reaction was assayed in a catalytic fashion with acrylonitrile and other closely related substrates as shown in Table 1.

As shown in Table 1, excellent conversions were obtained with acrylonitrile (**1a**) regardless of the solvent (entries 1–3, Schemes S2 and S3, ESI†). Also, there is no significant effect on the yield when the reaction time was shortened from 72 h in dioxane to 3–4 h in THF or benzonitrile. These observations are comparable to similar yields obtained with closely related systems[16,26,36] and are a reflection of the highly activated nature of acrylonitrile. Nevertheless, other substrates related to acrylonitrile, such as alkenes **1b** and **1c** (entries 4 and 5), showed a rather different reactivity due to a remarkable dependence on the steric hindrance. By using **1d**, which bears the same functional groups of acrylonitrile, no conversion was observed possibly because of the lack of conjugation between the cyano group and the π C–C bond, thus inhibiting the transfer of the Lewis acidity of the metal center.

In the light of these results, the same reaction conditions were tested for a group of activated alkynes as shown in Table 2.

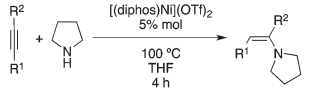
Table 1 Catalytic hydroamination of acrylonitrile and related substrates

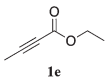
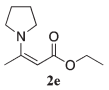
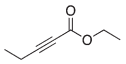
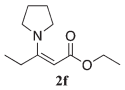
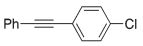
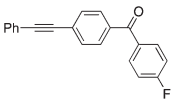


Entry	Alkene	Solvent	Time (h)	Product	Yield[a] (%)
1	 **1a**	Dioxane	72	 **2a**	100
2	 **1a**	Benzonitrile	3	 **2a**	99
3	 **1a**	THF	3	 **2a**	98
4	 **1b**	THF	4	 **2b**	9
5	 **1c**	THF	4	—	0
6	 **1d**	THF	4	—	0

[a] Chromatographic yields.

Table 2 Catalytic hydroamination of activated alkynes



Entry	Alkyne	Product	Yield[a] (%)
1	 1e	 2e	64
2	 1f	 2f	60
3	 1g	—	0
4	 1h	—	0

[a] Chromatographic yields.

With alkynes **1e** and **1f**, the corresponding hydroamination products are obtained in moderate yields (entries 1 and 2, Schemes S4 and S5, ESI†), although not as high as with acrylonitrile, perhaps due to the lower activating effect of the ester moiety compared to the cyano group. It is worth mentioning that the possible steric effect caused by the extra methylene in **1f** does not significantly affect the total conversion because of the lower steric demand of the alkyne toward nucleophilic attack by pyrrolidine compared to the above presented alkenes (*vide supra*). Once again, the lack of reactivity of substrates **1g** and **1h**, when compared with the same behavior of **1d**, suggests that the activating group necessarily must be conjugated to the C–C unsaturation in order to effectively coordinate the substrate to the acidic metal center through a hard donor and then transfer the Lewis acidity to the C–C unsaturation, thus, facilitating the nucleophilic attack by the amine (Fig. 1).[16,27]

In the same manner, successful conversions were obtained for the intramolecular hydroamination of 2-ethynylaniline (**1i**) in 36% yield to the corresponding indole (Scheme 1 and Schemes S6, S7, ESI†), resulting in a comparable result to the one obtained with a nickel(0) center.[31] Nevertheless, when these conditions were applied in the intermolecular hydroamination of phenylacetylene (**1j**), even though there were moderate conversion percentages (45%), we did not observe

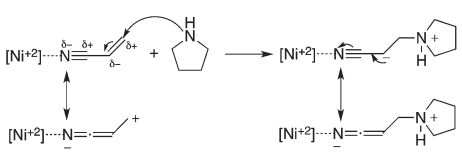
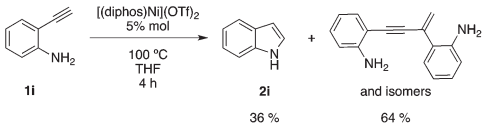


Fig. 1 Proposed effect of the electronic conjugation on the hydroamination of activated alkenes catalyzed by nickel(II) complexes.



Scheme 1 Intramolecular hydroamination of 2-ethynylaniline (**1j**) catalyzed by dicationic Ni(II).

any hydroamination product, in contrast with the high yields for other competing reactions such as cyclotrimerization (8%) and homocoupling (37%) possibly formed *via* a C(sp)–H activation, whenever **1j** is very prone to oligomerize. Additionally, with other terminal alkynes such as 3-phenyl-1-propyne (**1k**) and 4-pentyn-1-ol (**1l**) no products were detected.

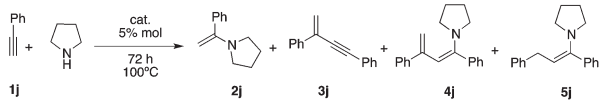
In search of better conditions for the hydroamination of **1j**, the dicationic catalyst was replaced for less acidic nickel centers and in neat conditions using pyrrolidine both as a reagent and a solvent (Table 3).

In the majority of the above-presented cases, the hydroamination products were observed, although the conversions and relative distribution of the products depended on the nature of the catalyst (entries 1 to 3, Schemes S8 and S9, ESI†). In general, the use of neutral nickel(II), an ancillary phosphine – diphos or dippe – and pyrrolidine as a solvent afforded the desired enamine **2j**. Indeed, the yields and distribution of the products are quite similar among the experiments made with these phosphines. On the other hand, even though the conversion using a catalyst without a ligand is high (entry 3), the hydroamination product is formed in a very low yield, hence indicating the strong importance of such an ancillary ligand in the hydroamination of phenylacetylene. By diluting the amount of pyrrolidine in a 1 : 10 pyrrolidine–THF solution (entry 4), no hydroamination was observed showing the imperative use of pyrrolidine or, eventually, a protic solvent, perhaps to form the enamine in a previous step to the closing of the cycle, which involves a [1,3] proton transfer.[37]

Other by-products observed in these experiments include **3j** and its isomers, derived from the above-described homocoupling of phenylacetylene. **3j** is also hydroaminated to form **4j** and this, in turn, undergoes a C–C cleavage to form **5j** (Scheme S10, ESI†), perhaps through a previous C=C transfer hydrogenation by pyrroline[31] followed by the C–C scission.

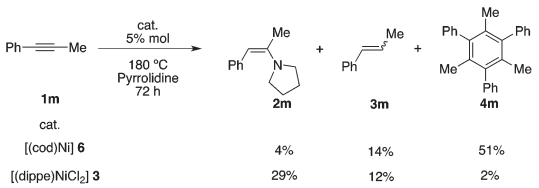
At this point we envisaged the addition of pyrrolidine to unactivated alkynes such as 1-phenyl-1-propyne (**1m**), diphenylacetylene (**1n**) and 2-hexyne (**1o**), yet these attempts were unsuccessful. Even by testing other nickel-based catalysts ranging from dicationic and neutral nickel(II) to nickel(0) precursors such as $[(dippe)Ni(\mu\text{-}H)]_2$ (**5**) and $[(COD)_2Ni]$ (**6**), it was not possible to obtain the expected enamines at 100 °C and 72 h. Nevertheless, when **6** is used in catalytic amounts and at a higher temperature (180 °C), the corresponding enamine was obtained (**2m**, 4%) (Scheme 2). In addition, 1,3,5-triphenylbenzene (**4m**) was also observed as the cyclotrimerization product of the starting material, which indeed is a common product of the reaction of alkynes in the presence of zerovalent nickel.[38] Thereby, the obvious choice was to replace the catalyst

Table 3 Hydroamination of phenylacetylene catalyzed by neutral Ni(II)



Entry	Cat.	Solvent	**2j**[a] (%)	**3j**[a] (%)	**4j**[a] (%)	**5j**[a] (%)
1	[(diphos)$NiCl_2$] **2**	Pyrrolidine	22	12	38	28
2	[(dippe)$NiCl_2$] **3**	Pyrrolidine	25	18	28	27
3	$NiCl_2{\cdot}6H_2O$ **4**	Pyrrolidine	6	11	37	46
4	[(dippe)$NiCl_2$] **3**	Pyrrolidine–THF 1 : 10	0	57	0	0

[a] Chromatographic yield.



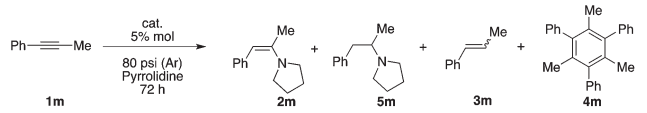
Scheme 2 Catalytic hydroamination of 1-phenyl-1-propyne (**1m**).

by a less basic metal center and, in this regard, the cyclotrimerization by-product was drastically diminished to 3% and, at the same time, the desired enamine was obtained in a considerably higher yield (29%, Schemes S11 and S12, ESI†) by using **3** as a catalyst. These observations evidence, again, the competition between the hydroamination of alkynes and other side reactions.

As depicted in Scheme 2, it was observed that 29% was the best yield for the hydroamination of **1m**. A presumable reason for this was the limited mass transfer in the reaction media, since the boiling point of **1m** is only 5 °C above the temperature reached in these experiments. Therefore, we implemented the use of argon pressure to enhance such a mass transfer by avoiding the evaporation of the starting material. In addition, some other nickel-based catalysts were tested under these conditions. Pertinent results of these experiments are shown in Table 4.

According to what is shown in Table 4, with some catalysts, particularly with **8–10**, **13** and **14**, better yields for the hydroamination product were obtained thus showing a remarkable enhancement of the yield by raising the pressure with argon and using other catalytic precursors. Once again, the selectivity is highly affected with the use of low-valent nickel (entries 1 and 5) or σ-donor phosphines (entry 6), which eventually afford a more basic metal center and, hence, the formation of undesired hydrogenation or coupling products (**3m–5m**). In this context, the hydrogenation products were diminished or even inhibited by slightly lowering the temperature (entries 7 to 9, Scheme S13, ESI†) and the better conditions were found to involve such lower temperatures and a π-acceptor phosphine (entry 9). These optimized conditions were used to achieve the hydroamination of a series of other alkynes as can be seen in Table 5.

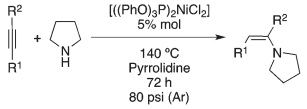
Table 4 Catalytic hydroamination of 1-phenyl-1-propyne (**1m**) under neat conditions and 80 psi of argon

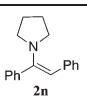
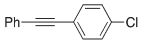
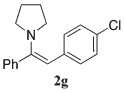
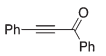
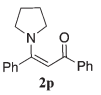
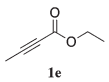
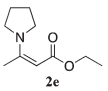


Entry	Cat.	*T* (°C)	**2m**[a] (%)	**5m**[a] (%)	**3m**[a] (%)	**4m**[a] (%)
1	[(dippf)Ni(COD)] **7**	160	12	0	75	0
2	[(dppf)Ni(COD)] **8**	160	51	0	14	0
3	[(dippf)$NiCl_2$] **9**	160	43	0	15	0
4	[(dppf)$NiCl_2$] **10**	160	32	0	26	0
5	[$(P(OEt)_3)_2$Ni(COD)] **11**	160	7	0	58	8[b]
6	[$(PEt_3)_2NiCl_2$] **12**	160	5	16	51	0
7	[$(P(OPh)_3)_2$Ni(COD)] **13**	140	54	10	0	0[c]
8	[$(P(OPh)_3)_2$Ni(COD)] **13**	120	6	3	2	0
9	[$(P(OPh)_3)_2NiCl_2$] **14**	140	42	16	0	0

[a] Chromatographic yield. [b] Additionally, 28% dimerization of **1m** was obtained. [c] 3% dimerization of **1m** was obtained.

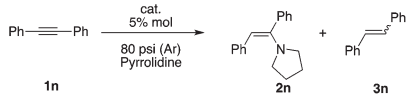
Table 5 Hydroamination of alkynes catalyzed by $[((PhO)_3P)_2NiCl_2]$



Entry	Alkyne	Product	Yield[a] (%)
1	 **1n**	 **2n**	29
2	 **1g**	 **2g**	20
3	 **1p**	 **2p**	78
4	 **1e**	 **2e**	91

[a] Chromatographic yield.

Table 6 Catalytic hydroamination of diphenylacetylene (**1n**)



Entry	Cat.	T (°C)	t (h)	**2n**[a] (%)	**3n**[a] (%)
1	$[(PEt_3)_2NiCl_2]$ **12**	140	72	22	11
2	$[(P(OEt)_3)_2NiCl_2]$ **15**	140	72	39	3
3	$[(PPh_3)_2NiCl_2]$ **16**	140	72	16	0
4	$[(P(OPh)_3)_2NiCl_2]$ **14**	140	72	27	6
5	$[(P(OEt)_3)_2NiCl_2]$ **15**	140	216	36	3
6	$[(P(OEt)_3)_2NiCl_2]$ **15**	160	216	16	25

[a] Chromatographic yield.

The alkynes employed in Table 5 are more activated than 1-phenyl-1-propyne and therefore better yields and selectivities could be successfully obtained (Schemes S14–S21, ESI†). In fact, the hydrogenation of the starting material was completely inhibited. In previous experiments without the additional argon pressure and by using **1**, **3** or **6**, the hydroamination of **1n** and **1g** was not observed at all (*vide supra*). In sharp contrast, with the conditions shown in Table 5, the desired enamines for such alkynes were successfully obtained in moderate yields (entries 1 and 2). In the same way, the yield for the hydroamination of **1e** (entry 4) was dramatically higher (91%) than that with the use of dicationic nickel (**1**) at a lower pressure (Table 2, entry 1, 64%).

In order to improve the yield for the hydroamination of **1n**, several other catalysts and reaction conditions were assessed. Representative results of such experiments are shown in Table 6.

Once again, better yields were obtained with π-acidic phosphines (entry 2 and Scheme S22, ESI†) and, in contrast, the use of not so acidic ligands (**16**) or even σ-donating ligands (**12**) gave lower conversions and/or higher yields for the undesired hydrogenation by-products. Therefore, the best yields for the hydroamination product (**2n**) were obtained with **15** as a catalyst at 140 °C. Using this catalyst at longer reaction times (entry 5) does not significantly improve the transformation to **2n** and a higher temperature (entry 6) ultimately has a negative effect by decreasing the hydroamination and favoring the hydrogenation product (Scheme S23, ESI†).

4. Conclusions

We have successfully developed a methodology for the hydroamination of both activated and unactivated organic unsaturations catalyzed by affordable nickel complexes, which, along with other investigations derived from the use of nickel as a catalyst, could contribute to finding cheaper and more biocompatible alternatives to palladium or other expensive metals. In this particular case, the conversions and selectivities have been shown to be remarkably influenced by the nature of the ancillary ligands and the electronic characteristics of the "(P–P)Ni" fragment (dicationic *versus* neutral) and this fact has given us a better insight aiming to improve the activity and selectivity of this nickel catalyzed process. Current studies are, in fact, underway to enhance such selectivity with other phosphite and phosphonite ligands and aiming to adapt this method for use under a non-inert atmosphere.

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