(NHC-olefin)-nickel(0) nanoparticles as catalysts for the (Z)-selective semi-hydrogenation of alkynes and ynamides

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(NHC-olefin)-nickel(0) nanoparticles as catalysts for the (*Z*)-selective semi-hydrogenation of alkynes and ynamides

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Nickel(0) nanoparticles coordinated to NHC ligands bearing a N-coordinated cynnamyl moiety were readily prepared by reduction of a [NiCpBr(NHC-cynnamyl)] complex with methyl magnesium bromide. The combination of a strong σ-donor NHC ligand with a π-coordinating appended cinnamyl moiety likely prevents nickel(0) nanoparticles aggregation to larger inactive species, and allows the effective and (*Z*)-selective semi-hydrogenation of alkynes and ynamides.

Metal nanoparticles (NPs) are particularly important in catalysis due to their large exposure surface area and because of the unique metal-metal interactions within their core. The major challenge in the application of NPs in catalysis is to design stable NPs under reaction conditions in order to avoid their agglomeration which ultimately results in the loss of their catalytic activity. To achieve that, different strategies have been explored, including the use of: surfactants and micellar catalysis, various supports (with different metal-support interactions) or organic ligands.[1] Whether the latter strategy was initially achieved through the use of ligands such as thiols, amines, cyanides, disulfides, thioethers or phosphines,[2] N-heterocyclic carbenes (NHC) ligands, which are now privileged ligands in organometallic chemistry and homogeneous catalysis, have been established as novel promising stabilisation agents for metal NPs.[3] Thus, several studies have demonstrated the versatility of N-heterocyclic carbene ligands in stabilising and structuring NPs of metals like Ru,[4] Rh,[5] or Pd[6] for significant applications in catalysis, such as the hydrogenation of alkenes and alkynes, the Buchwald-Hartwig amination or the oxidation of alcohols. However, NHC ligands have been much less applied to the stabilisation of NPs of Earth-abundant first-row transition metals, whose development is now a priority in catalysis for obvious economic, environmental and societal reasons.[7]

To the best of our knowledge, there are only three reports on the use of NHC ligands to stabilise Ni NPs.[8,9] In the first two ones, such NHC-Ni NPs proved to be highly active catalysts for Kumada couplings[8a] and the semi-hydrogenation of alkynes[8b] and could be recycled a few times without significant loss of activity. Furthermore, in a recent report, we have shown that a half-sandwich Ni(II)-NHC-picolyl bromide complex effectively catalysed the hydrosilylation of a broad range of aldehydes without additive and of ketones in the presence of KO*t*Bu at 100 °C.[9] Dynamic light scattering, scanning electron microscopy in transmission mode and X-ray photoelectron spectroscopy showed evidence for the involvement of NHC-picolyl Ni particles under the catalytic conditions used for the ketones' reductions.

Beside NHCs, alkenes have also been applied as ligands to low-valent metal species in the last decade and the resulting organometallic complexes and/or NPs displayed interesting catalytic properties.[10] Interestingly, the combination of NHCs with additional alkene ligands allowed the isolation of well-defined organometallics of Ni(0),[11] Pd(0)[12] and Pt(0)[13] which were active in various cross-coupling and reduction reactions.

Herein, we report that the reduction of the [NiCpBr(NHC-cynamyl)] complex **1** with an excess of MeMgBr leads to coordinated Ni(0) nanoparticles (Figure 1). The combination of a strong σ-donor NHC ligand with π-coordinating appended cinnamyl moiety likely prevents Ni(0) particles aggregation to larger inactive species and allows rapid exchanges with reaction substrates. The resulting NHC-olefin-Ni(0) particles effectively catalyse the (*Z*)-selective semi-hydrogenation of alkynes[8b,14] and ynamides, the latter being a rare example of direct hydrogenation of ynamides without the use of any salt or additive.[15] The catalytic semi-hydrogenation of internal or terminal alkynes is useful in numerous organic synthesis by providing alkene building blocks, both at laboratory and industrial scale.[16] In particular, such hydrogenation represents a critical step in polymerization reactions in order to eliminate alkynes and dienes from alkene raw materials.

Our study started with the synthesis of complex **1** from the corresponding imidazolium bromide and nickelocene in refluxing THF for 48 h (Scheme S1). Once isolated in 92% yield and fully characterised by NMR, HRMS, elemental analysis and single-crystal X-ray diffraction analysis (Figure S1, Table S1), complex **1** was readily reduced by reaction with 3 equiv. MeMgBr in toluene at 100 °C for 2 h (Scheme 1). The reduction was characterised by a striking colour change from pink to yellow then brown (Figure S2).

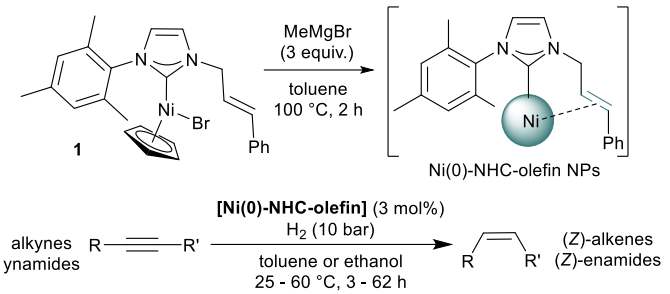
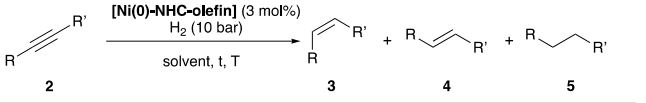


Fig. 1. (*Z*)-selective semi-hydrogenation of alkyne derivatives catalysed by NHC-olefin-Ni(0) nanoparticles

The resulting species (3 mol%) was then applied to the (*Z*)-selective semi-hydrogenation of various alkynes and ynamides under 10 bar H_2, in toluene or ethanol and at temperatures ranging from 25 to 80 °C, depending on the substrate. After optimising all the reaction conditions (Tables S2, S3), all hydrogenations led to the corresponding (*Z*)-alkenes in good to excellent yields (Table 1). The temperature and the solvent were the key parameters to control the activity of these catalyses, ethanol leading to the highest activities due to a better solubility of the substrates and hydrogen. It is worth to note that the substitution of pre-catalyst **1** by nickelocene led to full hydrogenation of alkynes. Regarding terminal alkynes, phenylacetylene **2a**, but-3-yn-1-ylbenzene **2b** and 1-phenylprop-2-yn-1-ol **2c** were readily hydrogenated in 13 h at room temperature in toluene to afford the corresponding alkenes **3a-c** with good selectivities (71 to 87%) and yields. By comparison, 1-ethynyl-3-nitrobenzene **2d** required 62 h at 40°C to afford chemoselectively alkene **3d** in high yield. Regarding internal alkynes, diphenylacetylene **2e$_1$** required a 40 °C heat for 13 h to be fully consumed in toluene (Tables S2, S3), but afforded (*Z*)-stilbene **3e$_1$** with a high selectivity of 91% and good isolated yield (78%). Noteworthy, the semi-hydrogenation of **2e$_1$** proceeded also at the gram scale (5.6 mmol) in 80% yield within 30 h at 40°C in ethanol [**3e$_1$/4e$_1$/5e$_1$** 88/2/10]. By comparison, chloro- or methoxy- substituted derivatives **2e$_2$** and **2e$_3$** needed 80°C for 13 or 48 h in toluene to lead selectively to the related (*Z*)-stilbenes **3e$_2$** and **3e$_3$** in good yields. In contrast, the hydrogenation of ethyl 3-phenylpropiolate **2g** in ethanol was almost quantitative at room temperature for 13 h leading to (*Z*)-alkene **3g** in a good selectivity (78%) with some alkane **5g** (22%). Phenylpropyne **2f**, 3-phenylprop-2-yn-1-ol **2h** and 3-phenylpropiolonitrile **2i** were also quantitatively hydrogenated in ethanol at 25 °C to afford the related (*Z*)-alkenes **3f,h,i** in good isolated yields (81-88 %) and selectivities (84-93 %) with only minor amounts of the (*E*)-isomers **4f** and **4i** (2 %) and alkanes **5f,h,i** (5-14 %). On the whole, by comparison to "P-2 Ni" catalyst, our Ni catalyst was somehow less (*Z*)-selective and universal but more chemoselective as aryl chloride moiety of **2e$_2$** the nitro and nitrile functions of **2d** and **2i** were preserved.[16] In addition, it displayed a modular reactivity for semi- and full hydrogenations (see Table S3) and, to the best of our knowledge, allowed for the first time the effective and selective semi-hydrogenation of various ynamides without any additive.[15] Indeed, Ms, Ts, Boc and Moc protected derivatives **2j-m** were hydrogenated to the desired (*Z*)-enamides in high selectivities (85-92 %) and good isolated yields (72-80 %) within 48 to 62 h in ethanol at 60 °C.

Table. 1 Catalysis scope – Yields and selectivities by GC and ^{1}H NMR for alkenes **3a-i** and by ^{1}H NMR for enamides **3j-r**. Isolated yields in parenthesis (average of at least 2 runs on a 0.5 mmol scale).



Substrate **2**	Solvent	T (°C)	t (h)	Yield (%)	Ratio **3/4/5**
Ph— **2a**	toluene	25	13	100	71/0/29
Ph— **2b**	toluene	25	13	89	87/0/13
HO, Ph **2c**	toluene	25	13	100	75/0/25
O_2N **2d**	toluene	40	62	95	85(63)/0/15
Ph—Ph **2e$_1$**	toluene	40	13	100	91/(78)/0/9
Cl— Ph **2e$_2$**	toluene	80	13	100	90(75)/0/10
MeO— Ph **2e$_3$**	toluene	80	48	87	100(69)/0/0
Ph—Me **2f**	ethanol	25	3	100	84/2/14
Ph—CO_2Et **2g**	ethanol	25	13	95	78(63)/0/22
Ph—CH_2OH **2h**	ethanol	25	4.5	100	88(81)/0/12
Ph—CN **2i**	ethanol	25	13	100	93(88)/2/5
$Ph(CH_2)_2$— N(Ms)(Me) **2j**	ethanol	60	48	100	88(74)/12/0
$Ph(CH_2)_2$— N(Ts)(Me) **2k**	ethanol	60	62	100	92(80)/6/2
$Ph(CH_2)_2$— N(Boc)(Me) **2l**	ethanol	60	62	100	92(72)/0/8
$Ph(CH_2)_2$— N(Moc)(Me) **2m**	ethanol	60	48	100	85(79)/15/0
$Ph(CH_2)_2$— N,O **2n**	ethanol	60	13	100	89(72)/4/7
Ph— N(Ts)(Me) **2o**	ethanol	60	62	100	94(84)/6/0
Me— N(Ts)(Me) **2p**	ethanol	60	36	100	74(62)/13/13
$Ph(CH_2)_2$— N(Ac) **2q**	ethanol	60	13	70	97(61)/0/3
$Ph(CH_2)_2$— N(Ms) MeO_2C **2r**	ethanol	70	13	81	94(72)/6/0 (ethylester **3r'** and **4r'**)

Under similar conditions, the hydrogenation of the ynamide **2n** bearing isoindolinone and phenylethyl moieties was completed in only 13 h with a good isolated yield (72 %) and a high selectivity in **3n** (89 %) and only minor amounts of **4n** and **5n**. With the tosyl substituted ynamides **2o** and **2p**, the phenyl derivative **2o** required more time to be reduced than the methyl derivative **2p** and afforded the (*Z*)-enamide **3o** with a higher selectivity of 94 % (*vs.* 74 % for **3p**), isolated yields remaining good (84 % for **3o** and 62 % for **3p**). The ynamide **2q** substituted by an indole fragment afforded almost exclusively **3q** after 13 h reaction at 60 °C, with a fair isolated yield of 61 %. Finally, ynamide **2r** led selectively to **3r'**, the ester moiety being changed from methyl to ethyl due to concomitant trans-esterification with the solvent.

To gain some insights into the nature of the probable Ni(0) active species, a sample solution was first analysed by DLS and particles with an average size of 110 nm ±21 were observed (Figure S3). Evaporation to dryness of a similar sample afforded a residue which was washed with dry pentane under argon and dried under vacuum. Noteworthy, the remaining solid, i.e.: our catalyst, proved still active although with a lower activity than an in situ-generated catalyst (Table S3). X-ray diffraction (XRD) in the reflexion mode was performed on the isolated catalyst placed on a glass support in open air but no diffraction patterns were observed, most likely due to the poor crystallinity of the sample (Figure S4). Therefore, no Ni(111) plan (i.e. Ni(0) species), nor NiO one could be observed.[17a] As XRD is mainly a bulk technique, we then analysed our isolated catalyst by XPS in order to determine the chemical composition at the topmost surface (i.e.: 9-2 nm) of the particles. The survey scan and high-resolution spectra of a freshly prepared sample revealed the core levels of C1s, Mg1s, O1s, N1s, Ni2p and Br3d elements (Figure S5). More specifically, the peaks values for Ni2p3/2 and 2p3/2 satellite of the Ni2p region were found at 854.8 and ca. 861.9 eV, respectively (Figure S6). These values are consistent with the presence of NiO, which likely results from the oxidation of the Ni(0) species during the transfer of the sample in air.[17] Furthermore, XPS provided the % surface ratio of all the elements and confirmed the presence of C, O, N, Si, Br and Ni elements in the catalyst sample (Table S6). The observed Ni/N ratio of ca. 1:3 suggested the presence of NHC-cinnamyl-coordinated Ni particles. Noteworthy, Raman spectroscopy, carried out on a catalyst sample whose exposure to air was avoided, showed no evidence of Ni oxides (150–430 cm^{-1}) and Ni hydroxides (3100–3650 cm^{-1}) (Figure S7). The catalyst was then characterised by SEM, TEM and HR-TEM microscopies. At low magnification, piles with stacked layers of various sizes and thicknesses were observed (Figures 2a-d, S8 and S9). According to SEM-EDX chemical analysis, they could be attributed to the Ni-based material, as the observed piles were composed of C, N, O, Ni, Br and Mg elements, at least on their surface (Figure S8). At higher magnification, some domains appeared to be partially crystalline but no diffraction patterns were observed (Figures 3c, S9). The most visible NPs corresponded to a lattice spacing of 0.65 nm which is rather different from the uniform lattice spacing of 0.203 nm of the pure Ni(111) plane.[17a] Other structures appeared to be finer but, due to the presence of organic matter, the contrast was too weak to allow other measurements. The dispersion of the elements was then studied by STEM EDS elemental mapping without quantification and sizing (Figure 2e-g, S10). A homogeneous dispersion of Ni, N, C and other observed elements was hereby confirmed. Finally, to get a reliable estimation of the number of NHC-cinnamyl ligands that remain bound to the Ni, two samples were then analysed by ICP-AES and CHN elemental analyses. Mass percentages of 7.10±0.1 (Ni) and 3.51±0.2 (N) were measured, which corresponds to a Ni:N molar ratio of 1:2, thus to a Ni:NHC ratio of 1:1 as in the precursor complex **1**. These results strongly suggest the coordination of NHC ligands and their appended π-accepting cinnamyl moiety to the Ni(0) NPs.

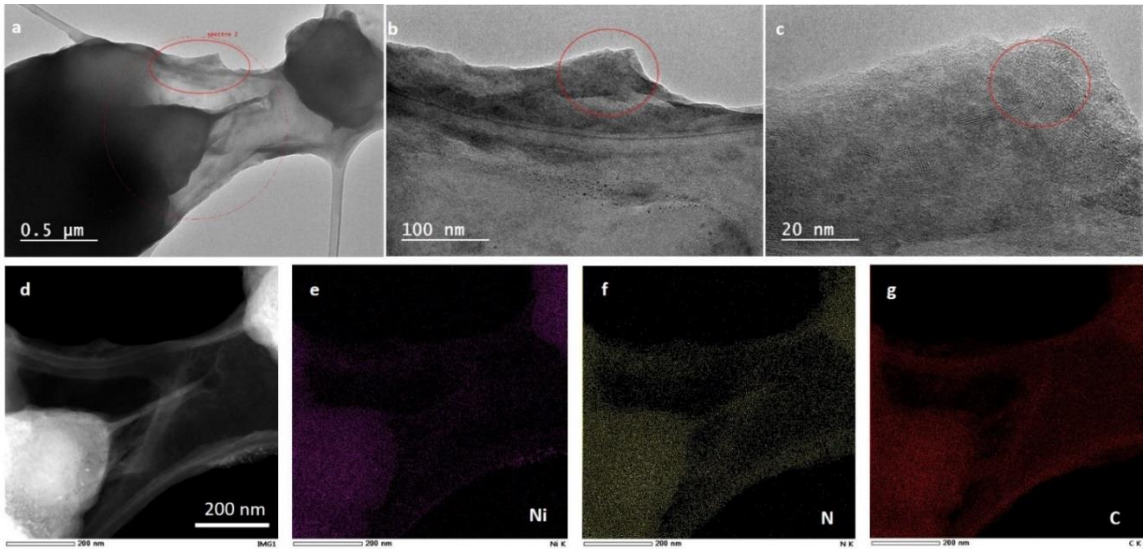


Fig. 2 TEM analyses of reduced complex **1** used as catalyst. (a), (b), (c) and (d) TEM and HR-TEM images; (e), (f) and (g) elemental mapping for Ni, N and C by STEM-EDS

The reusability of the catalyst was next studied for the hydrogenation of alkynes **2b** and **2f** over 6 runs (Tables S4, S5). Though the terminal alkene **3b** was recovered in good yields and selectivities until the 5th run, a gradual deactivation of the catalyst over long reaction times resulted in a decrease of yields in internal alkene **3f** while keeping a high selectivity. SEM and TEM analyses of the spent catalyst revealed features which were similar to the fresh catalyst but without crystalline domains and with lower Ni and N contents (Figures S11-12).

In summary, we report here the half-sandwich Ni(II)-NHC complex **1** bearing an appended cinnamyl moiety can readily be reduced by MeMgBr to lead to a first example of NHC-olefin-coordinated Ni(0) nanoparticles. The resulting catalyst allowed the effective and (*Z*)-selective semi-hydrogenation of alkynes and, most impressively, of ynamides without any additive. Further developments on such NHC-olefin-Ni nanocatalysts are currently under study in our laboratories and will be reported in the future.

Conflicts of interest

There are no conflicts to declare.

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