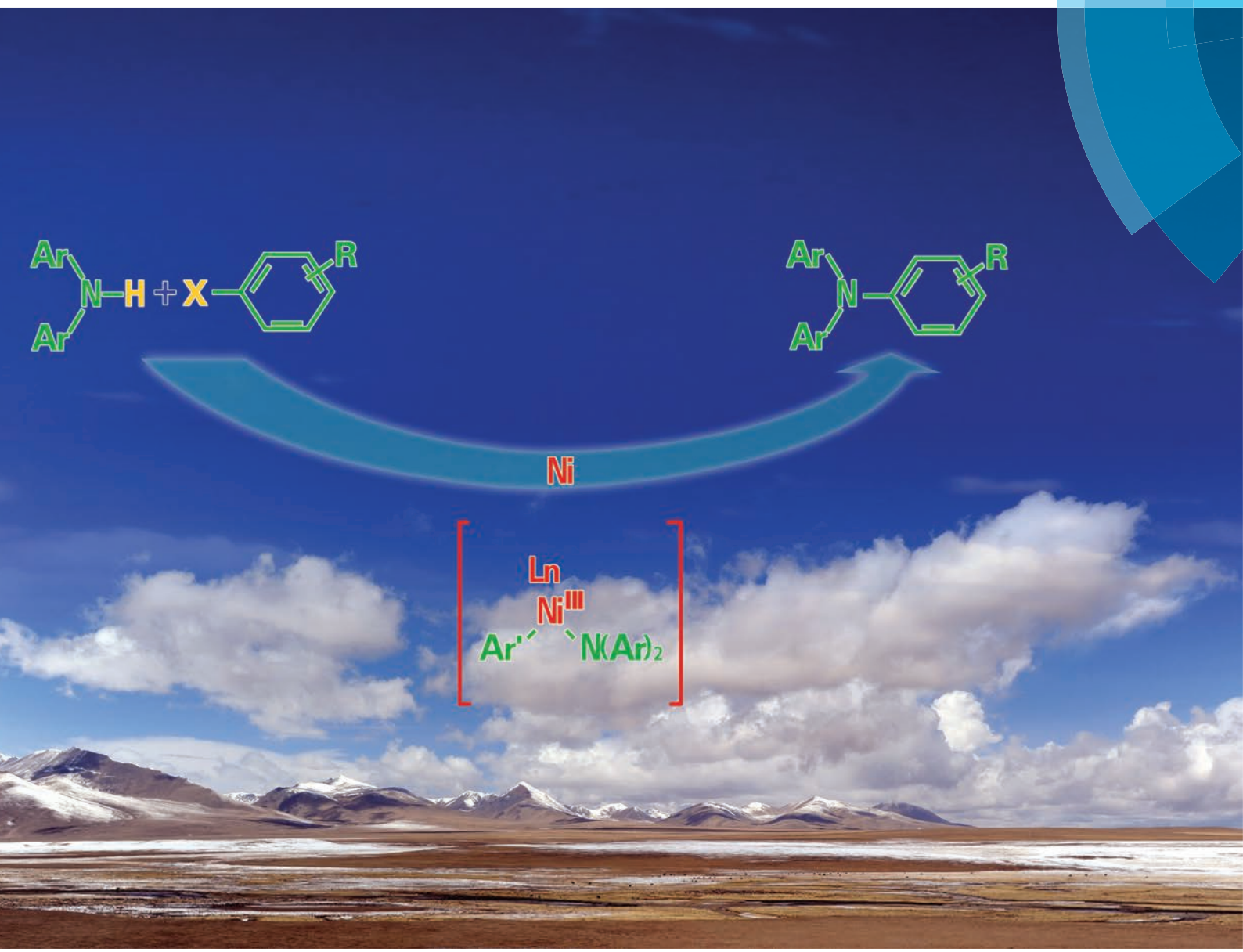
Volume 12 | Number 8 | 28 February 2014 | Pages 1175–1358

Organic & Biomolecular Chemistry

www.rsc.org/obc



ISSN 1477-0520

ROYAL SOCIETY OF CHEMISTRY

PAPER
Xin-Heng Fan, Lian-Ming Yang *et al.*
Nickel-catalyzed triarylamine synthesis: synthetic and mechanistic aspects

Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Nickel-catalyzed triarylamine synthesis: synthetic and mechanistic aspects†

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 1232

Xin-Le Li,[a,b] Wei Wu,[a,b] Xin-Heng Fan*[a] and Lian-Ming Yang*[a]

Received 14th October 2013,
Accepted 27th November 2013

DOI: 10.1039/c3ob42053a

www.rsc.org/obc

An improved protocol was described for the amination of chloroarenes with diarylamines under $NiCl_2(PCy_3)_2$ catalysis in the presence of a Grignard reagent as base. This method fully suits bromo-/iodoarene substrates as well, and even is expanded to certain aryl tosylates. A preliminary investigation into the mechanism suggests that this amination reaction might proceed through Ni^{I} and Ni^{III} intermediates rather than *via* the usually expected Ni^{0}–Ni^{II} cycle.

Introduction

The nickel-catalyzed aromatic C–N coupling reaction represents a major advance in catalytic cross-coupling reactions and constitutes an essential part of modern amination methodologies.[1–14] Highly attractive aspects of nickel catalysts are their economic cost as well as their ability to effectively aminate cheap, readily available electrophilic substrates, such as aryl chlorides[2–4,6–8] and phenolic derivatives,[9–13] with no need for specially tailored ligands. Nickel catalysis has displayed great success in arylations of various aliphatic amines and anilines.[2–13] Curiously, this amination method has been facing a challenge in the synthesis of structurally simple triarylamines,[15] in striking contrast to the development of Pd-[16] and Cu-catalyzed[17] aminations. Until now, there have been only a very few reports involving triarylamine synthesis under nickel catalysis.[14] Hence, further investigation in this regard remains necessary from both synthetic and mechanistic perspectives.

Results and discussion

Our previous communications[14] disclosed the first examples of nickel-catalyzed triarylamine synthesis *via* the amination of bromo-/iodoarenes with metal diarylamides produced *in situ* from diarylamines with a Grignard reagent or sodium hydride as the base. We have since desired to expand the substrate scope of this reaction to chloroarenes or even phenolic derivatives as well as to uncover more mechanistic information about this special type of catalytic amination, and our efforts towards this are the subject of this contribution.

Extensive work on aromatic aminations under nickel catalysis has revealed: that simple anilines are not over-arylated and the reaction proceeds "selectively" to the mono-substitution stage, even in the presence of excess aryl halides; and that a diarylamine is not able to be coupled with an aryl halide under "normal" conditions (*i.e.*, a combination of free amines and inorganic bases).[18] The reasons were presumably that a diarylamine is usually difficult to coordinate to the Ni centre due to its steric bulk and poor nucleophilicity against a relatively small Ni centre.[3c] For metal-catalyzed coupling reactions, this coordination step (*i.e.*, transmetallation) is key in a catalytic cycle. In view of this situation, we still chose a Grignard reagent as base for a model reaction between chlorobenzene (**1a**) and diphenylamine (**2a**). By the Grignard reagent, diphenylamine is readily transformed to a more nucleophilic amide species, which enhances its ability to bind to the Ni centre. In addition, the use of highly air-sensitive Ni^{0} precatalysts is avoided since easy-to-handle Ni^{II} compounds can be reduced *in situ* to Ni^{0} by Grignard reagents.

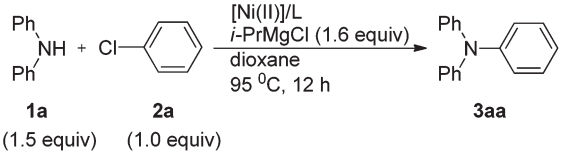
Our screening experiments were focused primarily on nickel catalysts that may be pre-formed or *in situ* generated, with *i*-PrMgCl as base and dioxane as solvent. Several common Ni^{II} systems were surveyed (Table 1). It was found that the type and nature of ligands binding to the Ni centre are closely related to the catalytic activity. Apparently, phosphine-ligated nickel precursors perform better than those bearing other types of ligands (entries 1–3 *vs.* entries 4–6). Among phosphine ligands, tricyclohexylphosphine (PCy_3) offers the relatively highest activity (entry 6). The activation ability of PCy_3 was confirmed by the following observations. Those Ni^{II} precatalysts which performed poorly and even did not work at all dramatically promote the reaction once associated with additional PCy_3 (entries 7–10 *vs.* entries 1, and 3–5). Note that an N-heterocyclic carbene (NHC) ligand (entry 2), although it is

[a]*Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: xinxin9968@iccas.ac.cn, yanglm@iccas.ac.cn; Fax: +8610-62559373*

[b]*Graduate School of Chinese Academy of Sciences, Beijing 100049, P. R. China*

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ob42053a

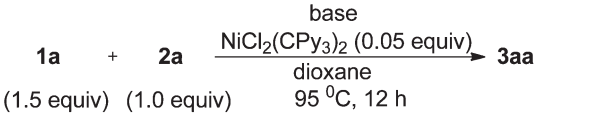
Table 1 Screening of catalyst systems[a]



Entry	[Nickel(II)] (mol%)/L (mol%)	Isolated yield (%)
1	$Ni(acac)_2$ (5)	Trace
2	$Ni(acac)_2$ (5) + IPr·HCl (10)	0[b]
3	$NiCl_2(bpy)$ (5)	0
4	$NiCl_2(PPh_3)_2$ (5)	19
5	$NiCl_2(dppe)$ (5)	35
6	$NiCl_2(PCy_3)_2$ (5)	78 (66[c])
7	$Ni(acac)_2$ (5) + PCy_3 (10)	76
8	$NiCl_2(bpy)$ (5) + PCy_3 (10)	53
9	$NiCl_2(PPh_3)_2$ (5) + PCy_3 (10)	71
10	$NiCl_2(dppe)$ (5) + PCy_3 (10)	73
11	$NiCl_2(PCy_3)_2$ (5) + PCy_3 (10)	78
12	$NiCl_2(PCy_3)_2$ (10)	75[b]
13	$NiCl_2(PCy_3)_2$ (20)	65[d]
14	$NiCl_2(PCy_3)_2$ (3)	70[e]

[a] Reactions performed on a 1 mmol scale. [b] 1.7 equiv. of *i*-PrMgCl used. [c] In toluene. [d] 1.9 equiv. of *i*-PrMgCl used. [e] 1.56 equiv. of *i*-PrMgCl used.

Table 2 Effects of bases[a]



	Base (equiv)	Relative yield[b] (%)
1	*i*-PrMgCl (1.6)	100
2	*t*-BuOM (2) (M = Na, K)	0
3	NaH (2)	0
4	*n*-BuLi (1.6)	35.2
5	EtMgBr (1.6)	95.8
6	PhMgBr (1.6)	98.6

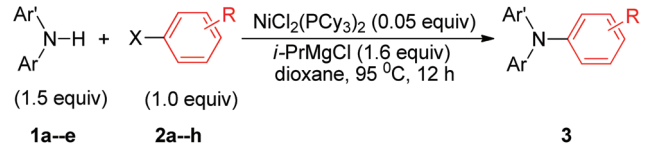
[a] A set of parallel reactions performed on a 0.5 mmol scale. [b] The values of yield calculated relative to the yield obtained using *i*-PrMgCl.

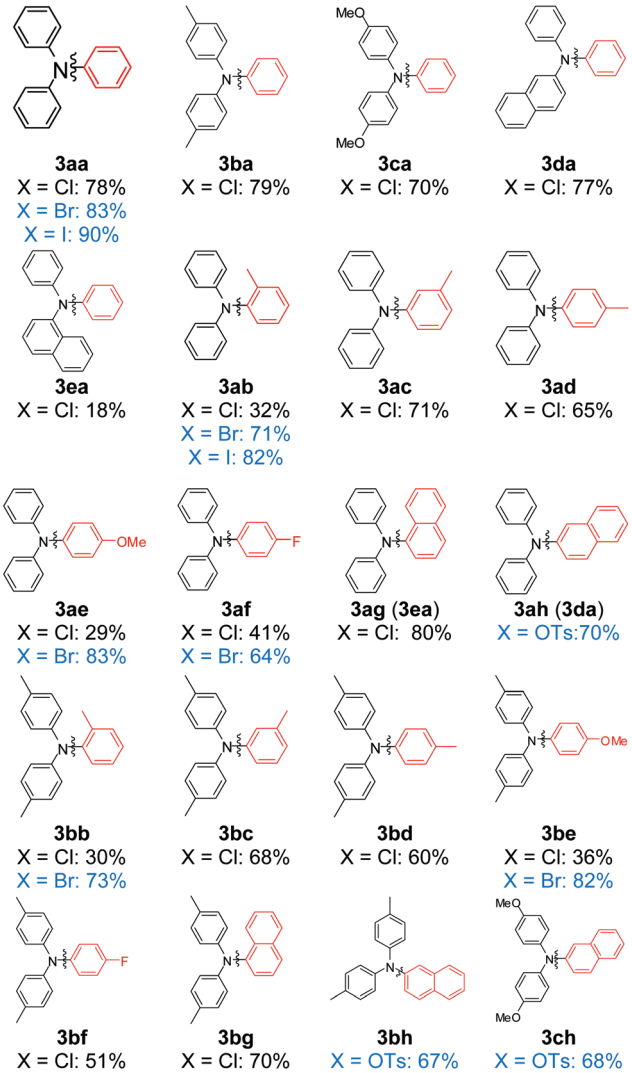
also highly electron-donating and has been utilized widely in nickel-catalyzed aminations, was totally ineffective for this reaction. For the best precatalyst $NiCl_2(PCy_3)_2$, the use of excess PCy_3 seems to be unnecessary since this does not help to further enhance its catalytic efficiency (entry 11 *vs*. entry 6). By a rough analysis of the reaction mixture in entry 6, we found that the starting chlorobenzene was not consumed completely, with small amounts (<5%) of biphenyl as a detectable by-product. Thus, we attempted to increase the catalyst loadings so as to achieve a high conversion and yield. However, the use of double the amount of the Ni precursor did not improve the outcome (entry 12 *vs*. entry 6), and rather, over-loading of the catalyst led to a significantly decreased yield (entry 13). This phenomenon differs completely from the situation in most metal-catalyzed coupling reactions, and the reason may be related to the reaction mechanism (see below). On the other hand, decreasing the catalyst loading, as expected, gave the desired product in a reduced yield (entry 14). As a result, our standard conditions for this reaction were chosen as in entry 5 of Table 1.

The type of bases employed was examined as well (Table 2). Indeed, those bases commonly used in metal-catalyzed aminations do not function (entry 2). Sodium hydride, although it is able to convert diphenylamine into the more nucleophilic diphenylamide, is also ineffective (entry 3). Generally, organometallic reagents are the base of choice by which this reaction could be promoted (entries 1, and 4–6). As we know, organometallic reagents function both as a strong base (deprotonating the N–H of diphenylamine) and as a reducing agent (transforming the Ni^{II} species to the catalytically active Ni^0). In contrast, the Grignard reagent is superior to the organolithium (entries 1, 5, and 6 *vs*. entry 4). Also, aryl or alkyl Grignard reagents may actually provide the same outcome, taking into account possible errors of the isolated yields in individual cases (entries 1, 5, and 6).

To examine the applicability of this protocol, the coupling reaction of representative diarylamines (**1a–e**) with a series of aryl chlorides (**2a–h**) was carried out under the above-mentioned standard conditions. Meanwhile, some typical aryl bromides/iodides or tosylates were selected as electrophiles in this reaction. The results are summarized in Table 3. Regarding the diarylamines, electronic factors did not interfere notably with the reaction, where good yields could be provided (**3aa**, **3ba**, **3ca**, and **3da**); but the reaction was highly sensitive to their steric hindrance, as in the case of *N*-(1-naphthyl)-aniline (**3ea**). As for aryl chlorides, both electronic and steric effects had considerable impact on this reaction. Generally, those chloroarenes which are electron-neutral (**3aa–da**, **3ag**, and **3bg**), with weak electronic effects (**3ac** and **3bc**; **3ad** and **3bd**), as well as with weak steric effects (**3ag** and **3bg**), are suitable substrates, which could be aminated smoothly to give the triarylamine products with satisfactory yields. Either sterically demanding (**3ab** and **3bb**) or highly electron-rich (**3ae** and **3be**) aryl chlorides impeded this reaction. Surprisingly, strongly electron-withdrawing groups, which usually activate electrophilic substrates in metal-catalyzed cross-couplings, did not seemed to be very favourable for this amination reaction (**3af** and **3bf**). Also, two other electron-poor chloroarenes, *p*-chlorobenzophenone and *p*-chlorobenzonitrile, were subjected to this amination reaction with diphenylamine. However, these chlorides quenched the reaction and no expected product was observed. Additionally, it was shown that various aryl bromides/iodides, including electron-neutral (**3aa**), -rich (**3ae** and **3be**) and -poor (**3af**), and sterically hindered (**3ab** and **3bb**), underwent smooth transformations under the standard conditions in good to excellent yields. Of particular note, a particular tosylate, 2-naphthyl tosylate, was found to be suitable for this reaction, and coupled with diarylamines to afford good yields of the triarylamine products (**3ah**, **3bh**, and **3ch**), although most aryl tosylates, such as phenyl and 1-naphthyl

Table 3 Substrate scope[a]



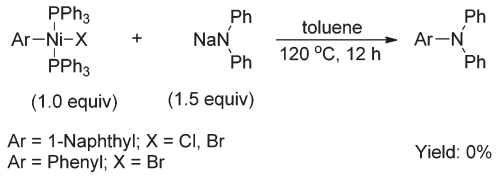


[a] Reaction conditions: **1** (1.5 mmol), **2** (1.0 mmol), dioxane (5 mL), $NiCl_2(PCy_3)_2$ (0.05 mmol), *i*-PrMgCl (0.8 mL, 2 M in THF), 95 °C, 12 h; Isolated yield.

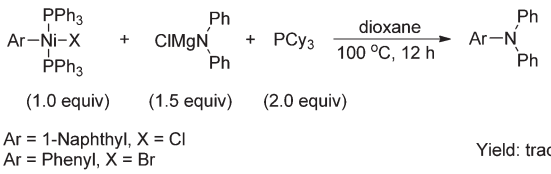
tosylates, have not yet been established as applicable substrates (generally, <30% yields obtained).

Currently two mechanistic pathways have been popularly accepted for nickel-catalyzed aromatic amination.[1,2,3c,5] One, likely more preferred, claims that Ni^0 serves as the catalytically active species and the coupling reactions follow a Ni^0–Ni^{II} cycle involving sequential oxidative addition, transmetallation and reductive elimination; the other suggests that Ni^I, resulting from a single-electron transfer of Ni^0 to an aryl halide, is actually the catalytic species and the reaction proceeds through nickel(I) and nickel(III) intermediates.

According to the mechanistic pathway of a Ni^0–Ni^{II} cycle, arylnickel(II) halides may be regarded as the oxidative adducts of haloarenes to the Ni^0. Some arylnickel(II) halide complexes are readily available and isolable compounds.[19] To examine the intermediacy of arylnickel(II) complexes, we conducted stoichiometric reactions of metal diphenylamides with arylnickel(II) halides, as shown in eqn (1) and (2). As a result, no triarylamine was produced using sodium diphenylamide as nucleophile (eqn (1)), and only a trace of the desired product was detected under more favorable conditions (eqn (2)). These observations led us to conclude that the arylnickel(II) complex might not be a potential intermediate on the catalytic pathway, and thus it would be reasonable to rule out the Ni^0–Ni^{II} mechanism for this nickel-catalyzed triarylamine synthesis.



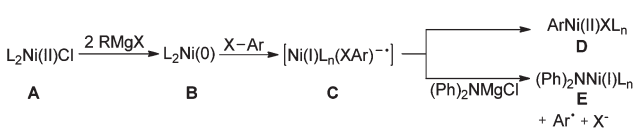
(1)



(2)

Accordingly, the Ni^I species might be actually responsible for the catalytic cycle in this transformation. Kochi *et al.*[20] have investigated in detail the oxidative addition of Ni^0 to aryl halides, and proposed a route to *in situ* formation of the Ni^I species *via* a single-electron transfer from Ni^0 to a haloarene. Based on their studies, we proposed a route to generating the Ni^I intermediate in this reaction (Scheme 1). The Ni^0 (**B**), produced from the reduction of a Ni^{II} precursor (**A**) by the Grignard reagent, undergoes a single-electron transfer to an aryl halide to afford the Ni^I anion radical (**C**) which may decompose into the $ArNi(II)XL_n$ oxidative adduct (**D**) or $(Ph)_2NNi(I)L_n$ (**E**) and an aryl radical. $(Ph)_2NNi(I)L_n$ (**E**) is the catalytically effective species and $ArNi(II)XL_n$ (**D**) the "null and void" for this Ni-catalyzed reaction.

As implied in Scheme 1, since products **D** and **E** are derived from a common intermediate **C**, the two decompositions must compete against each other and a selective conversion can be achieved depending upon the conditions specifically given. It was presumed that under our reaction conditions, **E** might be



Scheme 1 A plausible route to *in situ* generating the nickel(I) species.

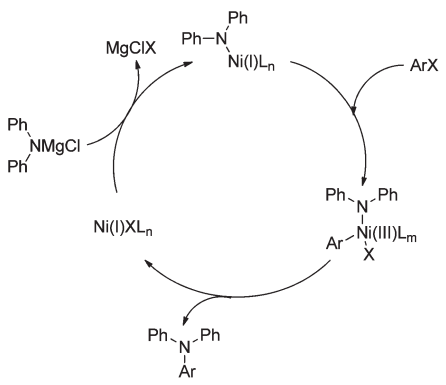
produced predominantly under the aid of a bulky diarylamide ligand. This hypothetical route to generation of the active Ni^{I} species may find supporting evidence from the recent study on the bulky ligand-controlled conversion selectivity of nickel(0) into nickel(I) or nickel(II),[21] and is also consistent with our experimental observations: (1) small amounts of biaryl by-products, which may result from the self-coupling of aryl radicals, are detected in almost all cases; (2) generally the efficacy of the Ni-based catalyst in this transformation is not high enough because a competitive reaction producing the catalytically inactive Ni^{II} species may not be fully suppressed under our current conditions; (3) the reactivity of electrophilic substrates increases in the order chloride ≪ bromide < iodide, with a decrease in the strength of halogen–C_{Ar} bonds; and (4) the reaction is intolerant of functionality like carbonyl and cyano groups which may likely interfere with a single-electron transfer process of the Ni^{0} species.

Hillhouse *et al.*[22] have reported examples of rapid C–N coupling reductive eliminations from oxidation of the nickel(II) amido alkyl complex to the nickel(III). Combining their studies with our viewpoint that the Ni^{I} may be the active species that initiates the reaction, a plausible mechanism is proposed that might follow a catalytic cycle of a Ni^{I}–Ni^{III} shuttle involving sequential oxidative addition, transmetallation, and reductive elimination (Scheme 2). Overall, efficient production of the Ni^{I} species must be the most important factor for this reaction, and oxidative addition, by our current recognition, may be regarded as the rate-determining step in the catalytic cycle.

Experimental

General procedure for the nickel-catalyzed synthesis of triarylamines

An oven-dried 25 mL three-necked flask was charged with $NiCl_2(PCy_3)_2$ (5 mol% relative to the aromatic chlorides, 34 mg), and a diarylamine (1.5 mmol). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Anhydrous dioxane (5 mL) was added *via* syringe. Then *i*-PrMgCl reagent (0.8 mL, 1.6 mmol, 2.0 M solution in THF) was added slowly at room temperature *via* syringe. After stirring for 5 minutes, an aryl halide (1.0 mmol) (if liquid) or its solution in a minimum volume of dioxane (if solid) was added *via* syringe. The mixture was stirred at room temperature for another 10 minutes, and then placed in an oil bath of 95 °C for 12 h. The reaction mixture, after being cooled to ambient temperature, was poured into 20 mL of saturated aqueous NH_4Cl solution and then extracted with ethyl acetate (10 mL × 3). The combined organic phases were concentrated under reduced pressure and the residue purified by column chromatography.



Scheme 2 Proposed mechanism for the nickel-catalyzed amination of haloarenes with diarylamines.

Typical experiment for the reaction of chloromagnesium diphenylamide with arylnickel(II) halides

An oven-dried 25 mL three-necked flask was charged with diphenylamine (256 mg, 1.55 mmol), PCy_3 (560 mg, 2 mmol) and dioxane (10 mL). To the mixture was slowly added *i*-PrMgCl reagent (0.75 mL, 1.5 mmol, 2.0 M solution in THF) *via* syringe, and stirring of the resulting mixture was continued at room temperature for 5 minutes. Then the arylnickel(II) halide (1 mmol) was added into the flask by a solid-addition adapter, and the mixture was heated in an oil bath of 95 °C for 12 h. The reaction mixture was poured to 20 mL of saturated NH_4Cl aqueous solution and then extracted with ethyl acetate (10 mL × 3). Solvents were removed *in vacuo* to afford the residue which was subjected to normal analyses.

Conclusions

In summary, we have first demonstrated the possibility of the nickel-catalyzed amination of chloroarenes for triarylamine synthesis, and more clearly suggested the mechanism of this reaction which might be different from that of a normal Ni^{0}–Ni^{II} cycle. The relative drawback of this protocol may be easily overcome by appropriate choice of the coupling partner pattern of the aryl halide and the diarylamine. Therefore, this simple, inexpensive method for triarylamine synthesis can become a powerful alternative to the corresponding palladium or copper catalysis. Studies are underway to improve the Ni catalyst efficiency by, for example, directly using potential nickel(I) complexes[23] as precatalysts, to overcome the problem of functional group capability by modifying reaction conditions, as well as to further clarify the mechanistic details by kinetic studies, and/or isolating and identifying certain nickel intermediates during the reaction.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Project No. 20872142 and 21102150) for financial support of this work.

Notes and references

1 For the pioneering work, see: R. Cramer and D. R. Coulson, *J. Org. Chem.*, 1975, **40**, 2267.
2 For a seminal study, see: J. P. Wolfe and S. L. Buchwald, *J. Am. Chem. Soc.*, 1997, **119**, 6054.
3 Representative papers from Fort's group: (*a*) E. Brenner and Y. Fort, *Tetrahedron Lett.*, 1998, **39**, 5359; (*b*) E. Brenner, R. Schneider and Y. Fort, *Tetrahedron*, 1999, **55**, 12829; (*c*) C. Desmarets, R. Schneider and Y. Fort, *J. Org. Chem.*, 2002, **67**, 3029.
4 Selected papers with the heterogeneous Ni catalysts used: (*a*) B. H. Lipshutz and H. Ueada, *Angew. Chem.*, 2000, **112**, 4666–4668, (*Angew. Chem., Int. Ed.*, 2000, **39**, 4492); (*b*) S. Tasler and B. H. Lipshutz, *J. Org. Chem.*, 2003, **68**, 1190–1199.
5 K. Matsubara, K. Ueno, Y. Koga and K. Hara, *J. Org. Chem.*, 2007, **72**, 5069.
6 C. Chen and L.-M. Yang, *J. Org. Chem.*, 2007, **72**, 6324.
7 G. Manolikakes, A. Gavryushin and P. Knochel, *J. Org. Chem.*, 2008, **73**, 1429.
8 Under room-temperature conditions: (*a*) M. J. Iglesias, A. Prieto and M. C. Nicasio, *Adv. Synth. Catal.*, 2010, **352**, 1949; (*b*) X.-H. Fan, G. Li and L.-M. Yang, *J. Organomet. Chem.*, 2011, **696**, 2482–2484.
9 Amination of aryl tosylates: (*a*) C. Bolm, J. P. Hildasebrand and J. Rudolph, *Synthesis*, 2000, 911–913; (*b*) C.-Y. Gao and L.-M. Yang, *J. Org. Chem.*, 2008, **73**, 1624.
10 Amination of carboxylates: T. Shimasaki, M. Tobisu and N. Chatani, *Angew. Chem.*, 2010, **122**, 2991, (*Angew. Chem., Int. Ed.*, 2010, **49**, 2929).
11 Amination of aryl phosphates: J.-H. Huang and L.-M. Yang, *Org. Lett.*, 2011, **13**, 3750.
12 Amination of aryl sulfamates/carbamates: (*a*) S. D. Ramgren, A. L. Silberstein, Y. Yang and N. K. Garg, *Angew. Chem.*, 2011, **123**, 2219, (*Angew. Chem., Int. Ed.*, 2011, **50**, 2171); (*b*) L. Ackermann, R. Sandmann and W. F. Song, *Org. Lett.*, 2011, **13**, 1784; (*c*) L. Hie, S. D. Ramgren, T. Mesganaw and N. K. Garg, *Org. Lett.*, 2012, **14**, 4182.
13 Amination of aromatic methyl ether: (*a*) M. Tobisu, T. Shimasaki and N. Chatani, *Chem. Lett.*, 2009, **38**, 710; (*b*) M. Tobisu, A. Yasutome, K. Yamakawa, T. Shimasaki and N. Chatani, *Tetrahedron*, 2012, **68**, 5157.
14 Ni-catalyzed triarylamine synthesis: (*a*) C. Chen and L.-M. Yang, *Org. Lett.*, 2005, **7**, 2209; (*b*) C.-Y. Gao, X. Cao and L.-M. Yang, *Org. Biomol. Chem.*, 2009, **7**, 3922–3925.
15 Triarylamines are important building blocks of organic optoelectronic materials utilized as components in organic light-emitting diodes, dye-sensitized solar cells and organic photoconductors. For reviews, see: (*a*) Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1; (*b*) P. Strohriegl and J. V. Grazulevicius, *Adv. Mater.*, 2002, **14**, 1439; (*c*) Y. Shirota, *J. Mater. Chem.*, 2005, **15**, 75.
16 Selected Pd-catalyzed triarylamine synthesis: (*a*) J. Louie and J. F. Hartwig, *J. Am. Chem. Soc.*, 1997, **119**, 11695; (*b*) J. Louie and J. F. Hartwig, *Macromolecules*, 1998, **31**, 6737; (*c*) M. H. Ali and S. L. Buchwald, *J. Org. Chem.*, 2001, **66**, 2560; (*d*) D. S. Surry and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 10354; (*e*) K. H. Hoi, J. A. Coggan and M. G. Organ, *Chem.–Eur. J.*, 2013, **19**, 843.
17 Selected Cu-catalyzed triarylamine synthesis: (*a*) H. B. Goodbrand and N. X. Hu, *J. Org. Chem.*, 1999, **64**, 670; (*b*) R. K. Gujadhur, C. G. Bates and D. Venkataraman, *Org. Lett.*, 2001, **3**, 4315; (*c*) A. A. Kelkar, N. M. Patil and R. V. Chaudhari, *Tetrahedron Lett.*, 2002, **43**, 7143; (*d*) Y. Zhao, Y. Wang, H. Sun, L. Li and H. Zhang, *Chem. Commun.*, 2007, 3186; (*e*) N. S. Nandurkar, M. J. Bhanushali, M. D. Bhor and B. M. Bhanage, *Tetrahedron Lett.*, 2007, **48**, 6573–6576; (*f*) A. Tlili, F. Monnier and M. Taillefer, *Chem. Commun.*, 2012, **48**, 408–3188.
18 Only one exceptional case was reported in ref. 5, where a triarylamine product can be obtained from the coupling of diphenylamine and *p*-bromobenzophenone under the normal Ni-catalyzed conditions.
19 For the preparation of arylnickel(II) halide complexes used, see: (*a*) L. Cassar, S. Ferrara and M. Foá, *Adv. Chem. Ser.*, ACS, 1974, vol. 132, pp. 252–273; (*b*) J. van Soolingen, H. D. Verkruijsse, M. A. Keegstra and L. Brandsma, *Synth. Commun.*, 1990, **20**, 3153; (*c*) L. Brandsma, S. F. Vasilevsky and H. D. Verkruijsse, *Application of Transition Metal Catalysts in Organic Synthesis*, Springer, New York, 1998, pp. 3–4.
20 (*a*) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 6319; (*b*) J. K. Kochi, *Pure Appl. Chem.*, 1980, **52**, 571.
21 S. Miyazaki, Y. Koga, T. Matsumoto and K. Matsubara, *Chem. Commun.*, 2010, **46**, 1932.
22 (*a*) K. Koo and G. L. Hillhouse, *Organometallics*, 1995, **14**, 4421; (*b*) K. Koo and G. L. Hillhouse, *Organometallics*, 1996, **15**, 2669.
23 Selected publications concerning the preparation, properties and applications of nickel(I) complexes: (*a*) C. J. E. Davies, M. J. Page, C. E. Ellul, M. F. Mahon and M. K. Whittlesey, *Chem. Commun.*, 2010, **46**, 5151; (*b*) ref. 21; (*c*) T. J. Anderson, G. D. Jones and D. V. Vicic, *J. Am. Chem. Soc.*, 2004, **126**, 8100; (*d*) K. D. Kitiachhvili, D. J. Mindiola and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2004, **126**, 10554.

