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ARTICLE

Ni(I)-Ni(III) Cycle in Buchwald-Hartwig Amination of Aryl Bromide Mediated by NHC-ligated Ni(I) Complexes

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Intermediate amide complexes of NHC-ligated monovalent nickel in Buchwald-Hartwig amination of aryl halides were isolated and structurally characterized. The amide complexes reacted with aryl bromide to form a cross-coupled product. Low-temperature observation of the oxidative addition product of Ni(I) amide complex with aryl bromide indicated the presence of Ni(III) intermediate. The results showed that a well-defined mononuclear NHC-Ni(I) complex can act as a key intermediate in homogeneous catalysis.

Introduction

Nickel-catalysed organic transformations involving active nickel intermediates with odd-valence numbers have been challenging targets in recent chemistry of catalysis.[1] This has become an intriguing unsolved problem, occurring with chemical advances such as the search for catalytically active species and analysis of reaction mechanisms by computational chemistry. Although monovalent nickel complexes are thermally stable and can be easily isolated under an inert-gas atmosphere,[2] direct involvement of Ni(I) in catalytic cycles has not been observed for decades. Recently, however, several reports have proposed catalytic pathways that involve mononuclear Ni(I)-L and dinuclear L-Ni(I)-Ni(I)-L complexes, where L is monodentate or bidentate ligand, such as phosphine and N-heterocyclic carbine (NHC).[3-7] Depending on the structure of the ligands or the type of reactions, mononuclear Ni(I) is generated as an off-cycle product or can act as a key intermediate in the cycle. If it is revealed that Ni(I) complexes can act as a true active intermediate, development of new types of reactions using nickel catalysts could be possible. Furthermore, a Ni(I)-Ni(III) cycle can be considered to be analogous to a Pd(0)-Pd(II) cycle, where various highly efficient catalytic reactions have been developed. That is because a Ni(0) complex is easily oxidised to the corresponding Ni(II) and hardly reduced back to Ni(0), while a 2e-oxidation of Ni(I) into Ni(III) can be relatively difficult but 2e-oxidised intermediate Ni(III) can be easily reduced.[3]

As shown in Chart 1, one of the possible pathways involving Ni(I) intermediates is (1) an active Ni(0) intermediate couples with Ni(II) into a stable Ni(I) dimer reaching a resting state equilibrium,[4] (2) monomeric Ni(I) forms *in situ* to become a deactivated complex as an off-cycle product,[5] and (3) unsaturated Ni(I) dimer promotes the catalytic cycle as a key intermediate.[6] Alternatively, (4) an active mononuclear Ni(I) intermediate in a catalytic cycle is also proposed using stable Ni(I) complexes.[7] However, it is quite difficult to experimentally prove that a Ni(I) complex acts as a true active intermediate in a catalytic cycle, because (5) it sometimes disproportionates into Ni(0) and Ni(II), which can be the real active species in catalysis.[8] There are several theories that support the Ni(I)-Ni(III) cycle but no clear experimental evidence to the best of our knowledge.[9]

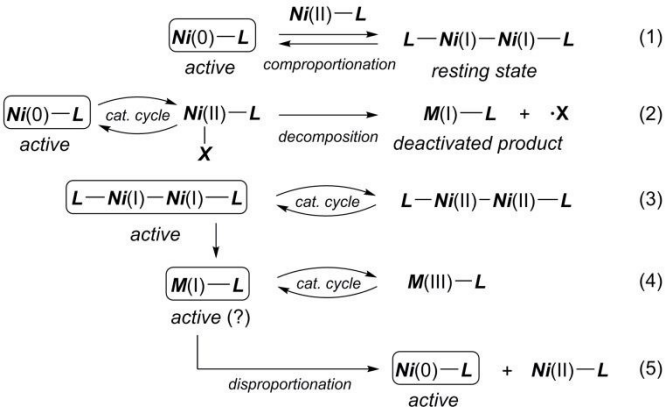

Chart 1. Various pathways of the active intermediates in nickel-catalysed systems involving monomeric Ni(0), Ni(I), and Ni(II) complexes and Ni(I) dimer.

Dinuclear L-Ni(I)-Ni(I)-L often forms a mononuclear active catalyst in literature.[10-12] Based on theoretical calculations, Chirik et al. proposed the generation of a mononuclear Ni(I)

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hydride complex in catalytic hydrosilylation which can be formed from a dinickel(I) hydride complex bearing redox-active ligands as a result of a one-electron reduction of the ligand.[10] Hazari et al. showed that a Ni(I) dimer, $[Ni(NHC)]_2(\mu\text{-}Cl)(\mu\text{-}\eta^3\text{-}Cp)$, and its disproportionation product, monomeric Ni(I) complex CpNi(IPr), where Cp is a η^5-cyclopentadienyl, and IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidne, were catalytically active in the Suzuki-Miyaura cross coupling of 4-chlorotoluene.[11] They concluded that homolytic cleavage of the Ni(I)-Ni(I) bond into the monomer complexes is necessary to activate the dimer for catalysis. Our group also reported that the Sigman's Ni(I) dimer, $[Ni(IPr)]_2(\mu\text{-}Cl)_2$,[12] cleaves its Ni(I)-Ni(I) bond in the presence of phosphines and pyridine to give mononuclear Ni(I) complexes.[13] Both monomer and dimer complexes can catalyse Kumada-Tamao-Corriu coupling and Buchwald-Hartwig amination of aryl halides. However, even in these reactions, it is unclear how the monomeric Ni(I) complexes behave in catalysis, as the real intermediate such as Ni(III) species, have not been detected or isolated experimentally.

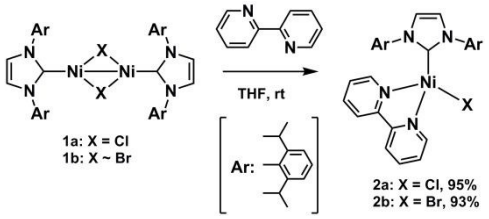
Generally, an unpaired electron on the monovalent nickel promotes facile elimination of ligands and/or products, and smooth single electron transfer (SET) enables facile activation of substrates. Therefore, if coordinatively-unsaturated mononuclear Ni(I) complexes can be appropriately used not as a deactivator but as active key catalyst, it will be a very important finding, potentially leading to development of new catalytic transformations.

Recently, based on our and other groups' studies using nickel complexes bearing bulky NHCs, thermally stable nickel(I) complexes have been defined and applied to several catalytic processes.[13,14] Electron-donating NHC ligands may destabilize low-valent metal species such as Ni(0), probably by supressing competing Ni(0)-catalysed systems. However, a recent study showed that IPr-Ni(0) system can also catalyse Ni(0)-Ni(II) systems in the amination of pyridyl chloride.[15] Therefore, clear evidence is needed to show that Ni(I) complexes can act as key intermediates in such catalytic reactions.

Herein, monomeric IPr-Ni(I) complexes are found to be the active species in the Buchwald-Hartwig amination of aryl bromide. The ligand 2,2'-bipyridyl (Bipy) provided the air-stable mononuclear tetrahedral IPr-Ni(I) complexes at least in the solid state, for more than several minutes. Experimental and theoretical studies also suggested that easy elimination of Bipy forms a linear two-coordinate (13e) IPr-Ni(I) complexes as the active species, one of which was isolated and well determined. Furthermore, the paramagnetic intermediates were successfully detected in a X-band EPR spectrum at low temperature, upon oxidative addition of aryl bromide to the IPr-Ni(I), indicating the existence of the Ni(I)-Ni(III) cycle in the NHC-Ni-catalysed system for the first time experimentally.

Results and discussion

Preparation and Structures of Ni(I) Bipyridyl Complexes. Addition of Bipy to a pale-yellow solution of di-Ni(I) halides $[Ni(iPr)]_2(\mu\text{-}X)_2$ [**1a** (X = Cl) and **1b** (X = Br)] bearing a bulky N-heterocyclic carbene, IPr, immediately afforded monomeric tetra-coordinate Ni(I) halides Ni(IPr)X(Bipy) [**2a** (X = Cl) and **2b** (X = Br)] (Scheme 1). Compounds **2a** and **2b** were successfully isolated as dark purple crystals upon recrystallization in 95 and 93% yields, respectively. Although the previously reported three-coordinated 15e Ni(I) complexes Ni(IPr)Cl(L), where L was pyridine, triphenylphosphine, and triphenylphosphite, were very unstable in the air and rapidly oxidised even in the solid state, the complex **2a** is rather stable, at least in the solid state. The half-lives of the crystals were about 15 minutes at room temperature. The corresponding bromide analogue **2b** was more stable than the chloride analogue **2a**. It should be noted that the ^{1}H NMR spectra for **2a** and **2b** did not show any signals assigned as the starting materials **1a** and **1b**, even though the analogous three-coordinate Ni(I) complexes readily regenerate the dimeric nickel complexes **1a** and **1b** in equilibrium.[13] This result indicated that chelating Bipy ligand in **2a** and **2b** can stabilize the Ni(I) complexes, compared to monodentate pyridine and phosphines in three-coordinate Ni(I) complexes.[13]



Scheme 1. Preparation of monomeric Ni(I) halides with 2,2'-bipyridyl.

These complexes were characterised by NMR spectroscopy, ESI-TOF MS, SQUID, and elemental analysis. The ^{1}H NMR spectra of **2a** and **2b** showed characteristic broadened signals due to paramagnetic nature of nickel (See ESI). The spin states of the complexes were studied based on SQUID measurements. The SQUID measurements supported the existence of an unpaired electron on the nickel atom. In our previous reports, the three-coordinate Ni(I) complexes had S = 1/2 ($\chi_{mol}T$ = 0.34 - 0.52 cm^3 K mol^{-1} at 20 K, where χ_{mol} is molar magnetic susceptibility). In complexes 2a and 2b, the values were 0.68 and 0.72 at 20 K, respectively, higher than those of the three-coordinate complexes and the theoretical χ_{mol}/T value, which is 0.375 cm^3 K mol^{-1} when S = 1/2. The large difference of the χ_{mol}/T values in **2a** and **2b** could be attributed to the spin state of the unpaired electron in nickel, probably in the degenerate electron orbitals, composed of the pseudo-tetrahedral nickel orbitals. Additionally, the χ_{mol}/T values did not depend on temperature T even at 10 K, suggesting that other electronic structures, such as high-spin Ni(II) and a bipyridyl anion radical, can be ruled out according to Curie's law.

Suitable crystals suitable for X-ray crystallography were obtained from a THF/hexane solution at −30 °C, enabling the confirmation of the crystal structures of these complexes (Figure 1). The representative bond distances and angles of **2a** and **2b** are listed in Table 1. These complexes have distorted tetrahedral geometry around the nickel atoms. The distances

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of nickel-carbene bonds for **2a** and **2b** were 1.982(5) and 1.959(4) Å, respectively, similar to those of the analogous 15e complexes of Ni(IPr)Cl(L).

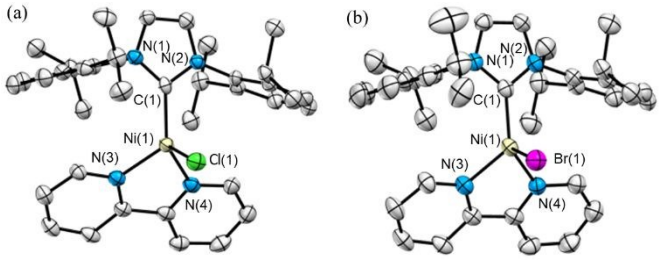
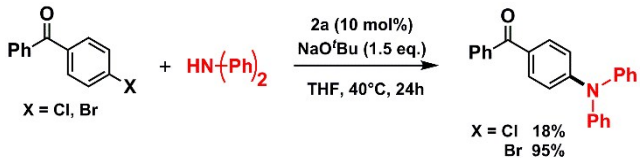


Figure 1. ORTEP drawings of complexes (a) **2a** and (b) **2b** with 50% thermal ellipsoids. Hydrogen atoms and two co-crystallised THF molecules were omitted for clarity.

Table 1. Representative bond distances (Å) and angles (°) of **2a** and **2b**.

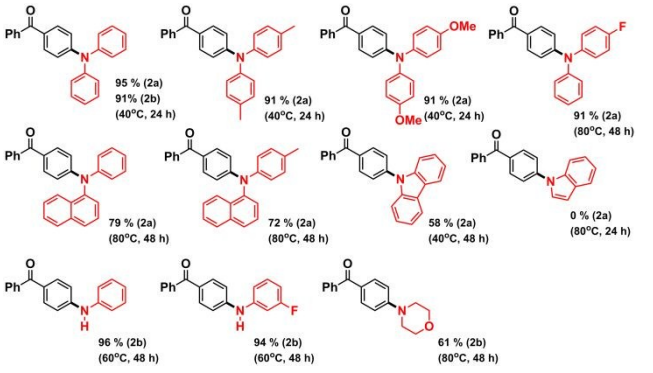
2a		**2b**	
Bond Distances (Å)			
Ni(1)-C(1)	1.982(5)	Ni(1)-C(1)	1.959(4)
Ni(1)-Cl(1)	2.3399(17)	Ni(1)-Br(1)	2.4450(8)
Ni(1)-N(3)	1.984(4)	Ni(1)-N(3)	1.968(4)
Ni(1)-N(4)	1.995(4)	Ni(1)-N(4)	1.972(4)
Bond Angles (°)			
C(1)-Ni(1)-Cl(1)	112.99(13)	C(1)-Ni(1)-Br(1)	111.46(13)
N(3)-Ni(1)-Cl(1)	102.94(13)	N(3)-Ni(1)-Br(1)	108.07(11)
N(4)-Ni(1)-Cl(1)	112.75(12)	N(4)-Ni(1)-Br(1)	106.81(10)

Buchwald-Hartwig Amination of 4-Halobenzophenone Using 2a and 2b. The well-defined complex **2a** catalysed the Buchwald-Hartwig amination of 4-chloro- and 4-bromo-benzophenone with diphenylamine even at 40°C to yield 4-N,N-diphenylamino-benzophenone in 18 and 95% yields, respectively (Scheme 2). The results encouraged us to search the scope of amines as listed in Table 2 for the reaction with 4-bromobenzophenone mediated by **2a** and also **2b** under the similar conditions. Most of the triarylamines were obtained in good to excellent yields, 58–96%. Electron-donating and withdrawing substituents on the diarylamines did not affect the yields of the products. However, sterically demanding groups, such as a naphthyl group deactivated the process. The reaction with carbazole gave several by-products in contrast to the other reactions, reducing the yield of the amination product to 58%. The reaction with indole, (4-cyanophenyl)phenylamine, and (4-nitrophenyl)phenylamine resulted in recovery of the starting materials. In these unsuccessful reactions, the colour of the solution of the reaction mixture was different from those providing the desired products. For instance, the successful conditions gave dark green solutions of nickel, whereas the addition of the unsuccessful substrates provided yellowish brown or reddish brown solutions, suggesting that the nickel complexes were deactivated in the presence of these substrates. Electron-withdrawing groups on aryl halides can accept an electron from electron donor Ni(I) to form an ion pair consisting of anionic radical species and cationic Ni(II), which may lead to inactivated nickel species. Therefore, nitrobenzene was added to **2a** in THF solution of at 40°C for 24 h. The colour of the solution changed to black, and the reaction was completely inhibited as expected (see ESI).



Scheme 2. Buchwald-Hartwig amination of 4-chloro- and 4-bromo-benzophenone with diphenylamine.

Table 2. Buchwald-Hartwig amination of 4-bromobenzophenone with diarylamines mediated by **2a** and **2b**.[a]



[a] All yields were determined after column chromatography.

Isolation of intermediary compounds. According to our previous reports studying catalytic amination of 4-bromobenzophenone, the catalytic activity of **2a** is comparable to those of the three-coordinate Ni(I) complexes, NiCl(IPr)L (L = PPh3, pyridine).13 The two-coordinate Ni(I) complex, Ni(IPr)Cl, is proposed as the key intermediate in the catalytic cycle, because the ligands L in the three-coordinate analogues can be removed easily. However, coordination of Bipy to Ni(I) is stronger than the phosphorus ligands or pyridine, as noted above. Therefore, we are interested in how these efficient reactions occur using **2a** as the catalyst.

Addition of diphenylamine to the dark-purple solution of **2a** in the presence of sodium *tert*-butoxide at ambient temperature immediately gave a dark-blue solution, containing Ni(I) amide complex Ni(IPr)(NPh_2)(bipy) (**3a**) (Scheme 3). The complex **3a** was successfully isolated upon recrystallization in 24% yield. Similarly, 4,4'-dimethyldiphenylamine also gave the analogous complex **3b** in 12% yield upon recrystallization (Scheme 3). Interestingly, although indole did not provide its amination product with **2a**, the transmetallation product **3c** was obtained

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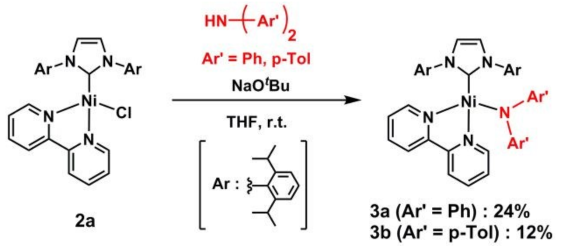
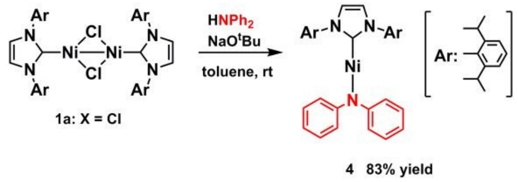
in low yield, 5% and thus was not fully characterised, although the structure was successfully determined by X-ray crystallography.

One of the most remarkable results in this study is that the two-coordinate Ni(I) amide complex Ni(IPr)(NPh_2) (**4**), which may be one of the true active species in amination, was successfully isolated (83% upon recrystallization) and characterized. Compound **4** was obtained from the rapid reaction of **1a** with diphenylamine in the presence of sodium *tert*-butoxide at room temperature (Scheme 4). Compound **4** was stable under an inert atmosphere in solution. The similar monoamino Ni(I) complexes have also been previously reported.[16]



Scheme 3. Stoichiometric reaction of **2a** with diarylamines.



Scheme 4. Stoichiometric reaction of **1a** with diphenylamine.

The paramagnetic complexes **3** and **4** were characterised by ^{1}H NMR, UV-Vis, SQUID, and elemental analysis. Finally, the structures were confirmed by X-ray crystallography. SQUID for **3a** and **3b** showed similar magnetic susceptibilities to those of **2a** and **2b**: $\chi_{mol}T$ = 0.70 and 0.73 at 100 K, respectively, corresponding to S = 1/2. The crystal structures of **3a** and **4** were determined by X-ray crystallography (Figure 2). Nickel, nitrogen, and carbene carbon atoms are arranged in a tetrahedral position in **3a**, which is similar to **2a** and **2b**. In compound **4**: the angle of the three atoms was almost linear with an angle of 169.11(11)°, whereas that of bis(trimethylsilyl)amido Ni(I) was 163.2(2)° in previous reports.[16]

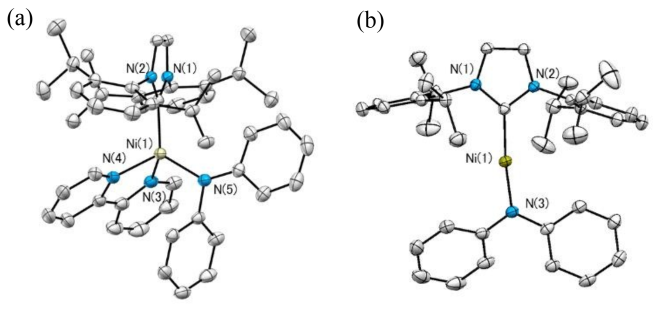


Figure 2. ORTEP drawings of complexes (a) **3a** and (b) **4** with 50% thermal ellipsoids. Hydrogen atoms and solvent molecules (toluene in the crystals of **4**) were omitted for clarity.

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Reactions of the intermediates. Isolation of Ni(I) amido complexes **3a** and **4** prompted us to conduct stoichiometric reactions of them with 4-bromobenzophenone at room temperature. Addition of aryl bromide to a THF solution of **3a** or **4** immediately changed colour and the ^{1}H NMR spectra of the crude mixtures showed the efficient generation of a cross-coupling product, 4-*N*,*N*-diphenylaminobenzophenone (Scheme 5). In particular, the diamagnetic complex **1b**, which is one of the starting compounds in this catalysis, was clearly detected in the crude product mixture by ^{1}H NMR spectroscopy (See ESI). The triarylamine product was isolated after silica gel column chromatography in 72 and 70% yields from **3a** and **4**, respectively. Additionally, the complex **3a** was revealed to be active in the catalytic amination of 4-bromobenzophenone to yield the desired product in 47% yield, strongly suggesting that complex **3a** exists in the catalytic cycle (Scheme 6). We considered that complex **3a** can exist at the resting state, and elimination of Bipy forms **4** as the active species. That is, the equilibria of elimination and coordination of the Bipy ligand between **3** and **4**, and **2** and **1** occurs in activation and stabilization of these Ni(I) complexes. However, because ligand elimination equilibrium between **2** with Bipy and **1** cannot be observed, as noted above, we have to demonstrate whether elimination of this generally robust chelating ligand occurs from **2a** or **2b** even at room temperature.[17] Interestingly, as a result, it can be rapidly released from **2b** at room temperature in the presence of another ligand. The UV-visible spectrum was monitored during the addition of 2,2'-biquinoline (Biq) to a THF solution of **2b** (Scheme 7). Because Biq can coordinate more strongly than Bipy does, due to its rigid structure derived from expanded π-conjugation, Biq could irreversibly replace Bipy on the Ni(I) complex. Therefore, we added Biq to complex **2b** and observed UV spectral changes in the solution at room temperature. Since UV absorption of the complexes varied greatly by substituting the ligand, the spectral changes were clearly observed. As expected, the substitution of Bipy ligand in **2b** with Biq occurred immediately, resulting in a colour change from dark purple to dark blue. The spectra of the resulting solution containing **2b** and Biq agreed well with the isolated Biq complex **5** (Figure 3). Thus, complexes **2** and **3** are considered to have elimination equilibria in solution to form catalytically active complexes and free Bipy in situ. Such facile elimination of Bipy is thought to be rare.[17] Unfortunately, because the exchange reaction was too rapid to monitor the time-dependent ratio of these compounds, there was no experimental evidence that Bipy was dissociatively eliminated. However, the low dissociation energy barrier when **3a** is fragmented to form **4** and Bipy is supported by DFT calculation (ΔE_0 = +11.33 and ΔG_0 = -4.67 kcal/mol at 298 K) (See ESI). In contrast, ligand exchange for the NHC ligand was much slower than for Bipy when free IMes was added to a solution of **2b**. This is also supported by a previous study where a slower

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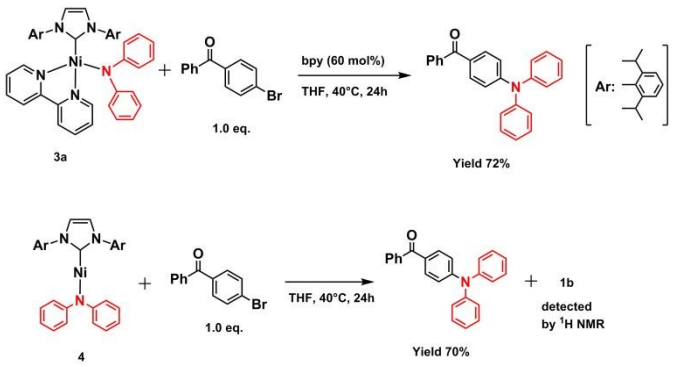
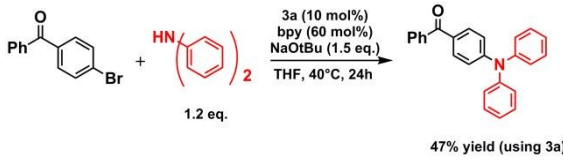
ligand exchange occurs for IPr in mononuclear Ni(I) bisIPr complexes than with triphenylphosphine.[6a]



Scheme 5. Stoichiometric reaction of **3a** and **4** with 4-bromobenzophenone.



Scheme 6. Catalytic reaction of diphenylamine with 4-bromobenzophenone using **3a** as catalyst.

Scheme 7. Ligand exchange reactions of **2b** with 2,2'-biquinoline (Biq) at room temperature.

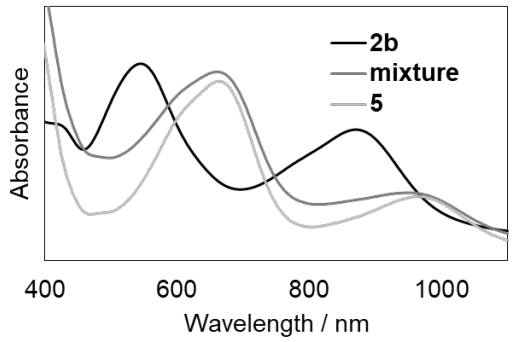


Figure 3. UV spectra for compound **2b** before (black) and after addition of Biq (gray), and for isolated Biq complex **5** (pale gray).

Next, we attempted to detect the intermediate of the reaction of **1b** with amine in the presence or absence of base. However, detection of such intermediate compounds was unsuccessful using NMR and EPR spectroscopy under any conditions. In our previous study, a pyridine molecule coordinated to a IPr-Ni(I) chloride to form a three-coordinate complex, Ni(IPr)(Cl)(pyridine), was thermally stable in the solid state and observed in the ^{1}H NMR spectrum as an equilibrium mixture with **1a** in C_6D_6.[13] Therefore, we suppose that due to the weak coordination ability of diphenylamine onto the Ni(I) centre, the corresponding three-coordinate complex, Ni(IPr)(Br)(diphenylamine), is less stable than the dinuclear Ni(I) bromide.

Detection of oxidative addition intermediate by EPR. Getting mechanistic insights into the oxidative addition of aryl halide to the Ni(I) centre is a most interesting and challenging target. This is because a Ni(III) intermediate has never been directly observed in previous mechanistic studies of catalytic cycles, although some reports have shown the structures of Ni(III) complexes and their reductive elimination processes.[3] Unfortunately, several attempts to isolate the intermediate complex at −30°C was unsuccessful, as this compound was thermally unstable at higher temperatures, leading to fast decomposition into a mixture composed of **1b** and triarylamine in a few minutes at around 20°C. The ^{1}H NMR spectrum of the mixture after heating to room temperature showed only the existence of these expected side products (see ESI). Therefore, we attempted direct observation of the Ni(III) intermediate using EPR spectroscopy at low temperature. After addition of 1 equiv of 4-bromoanisole to the two-coordinate Ni(I) complex **4** in ether at −40°C, removal of the solvent under reduced pressure gave a dark green crystalline solid. Then, the residue was dissolved in THF in a sample tube and rapidly immersed into liquid N_2 just before the EPR measurement. As shown in Figure 4, signals due to new compounds appeared in the EPR spectrum of the reaction mixture. In contrast, no obvious signals were detected when the crystalline solid of starting complex **4** was used as the sample. Whittlesey et al. reported that an unquenched orbital angular momentum can be a reason why there are no signals in the X- and Q-band when the EPR spectrum of the two-coordinate bis-NHC Ni(I) complex were measured, even though the *S* value of the complex was 1/2.[18] The observed signals suggested presence of a mixture of Ni(I) and Ni(III) complexes, where the spin quantum number S = 1/2, based on computer simulations and DFT calculations (see ESI). The Ni(III) intermediate is likely formed after oxidative addition of 4-bromoanisole to Ni(I) amide. Additionally, some three-coordinated Ni(I) amide complex was also possible to exist as one of the products detected in the EPR spectrum. The signals due to one of the compounds, which could be a Ni(III) intermediate, were assigned as rhombic distortion with g_x = 2.125, g_y = 2.104 and g_z = 2.009, whereas the others were rhombic with g_x = 2.555, g_y = 2.308 and g_z = 2.094. There are several examples of well-defined Ni(III) complexes having square planar or square pyramidal geometry around the nickel centre in literatures, showing average *g* values of ca. 2.13-2.17,[19] which are close to the value of g_{av} = 2.08 for the proposed Ni(III) intermediate. The integral ratio of the signals from these Ni(I) and Ni(III) complexes was calculated to be ca. 3 : 2.[20] An alternative pathway can also be proposed from the Ni(I) complexes where disproportionation into diamagnetic Ni(0) and Ni(II) complexes occurs as demonstrated in literatures.[8] Cárdenas, et al. recently proposed an alternative radical oxidative addition pathway on the basis of DFT evidence, in which two molecules of Ni(I) react

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with one alkyl halide to form Ni(II) alkyl and Ni(II) halide, independently.[21] However, because we cannot find the corresponding Ni(0) and/or Ni(II) IPr complexes in the reaction mixture of 4-bromoanisole with **4a** or **3a**, as noted above, these possibilities are unlikely, at least under these conditions.

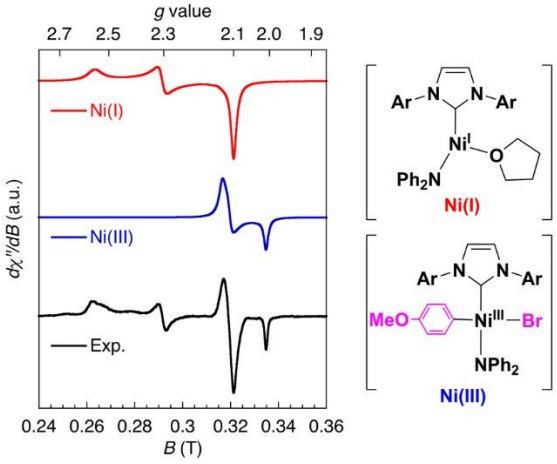

Figure 4. X-band EPR spectrum for the reaction mixture of **4** with 1 equiv of 4-bromoanisole (THF glass, at −178°C) (black), which can be reproduced by computer simulation of the proposed compounds: mononuclear Ni(I) intermediate (red, rhombic: g_x = 2.555, g_y = 2.308 and g_z = 2.094) and Ni(III) product (blue, rhombic: g_x = 2.125, g_y = 2.104 and g_z = 2.009).

Proposed catalytic cycle. Based on the above aspects, we proposed a possible catalytic cycle for Ni(I)-catalysed Buchwald-Hartwig amination of an aryl halide (Figure 5). From two-coordinate mononuclear Ni(I) chloride, transmetallation occurs with an amine and a base. Proton abstraction from the amine can proceed before and/or after coordination to the Ni centre with the base. Because amide complex **4** has a monomeric structure, active mononickel intermediates are favourable throughout this catalytic cycle. Complex **4** reacts with the aryl halide to form the Ni(III) oxidative addition product, which can easily eliminate triarylamine, resulting in a reduction to the starting Ni(I) halide. Reversible coordination of Bipy to two-coordinate Ni(IPr)X and Ni(IPr)NAr_2 (**4**) forms stabilised tetrahedral 17e Ni(I) complexes as resting states, and thermal elimination of these complexes can regenerate the active intermediates. The existence of the resting states can decrease the concentration of these highly active intermediates to avoid catalyst deactivation pathways at the late stage of the reaction. Transmetallation of Ni(I) species involved in the catalytic cross-coupling cycle has also been proposed as a mechanism of Ni(I)-catalysed cross-coupling reactions in literature.[9] However, the other possible pathway, via oxidative addition on Ni(I) halide and subsequent transmetallation, may still be possible and should be studied in the future.

Strong evidence in the literature indicates that the Ni(0)/Ni(II) cycle is dominant even when Ni(I) phosphine complexes are used.[8] There is no direct evidence, but we believe that the electron-donating ability of the ligand may alter the catalytic cycle. NHC ligands are generally stronger σ-donors than phosphorus ligands, resulting in the stabilization of higher-valent metal centers such as Ni(I) and Ni(III), and acting as catalysts without disproportionation to Ni(0) and Ni(II) species.

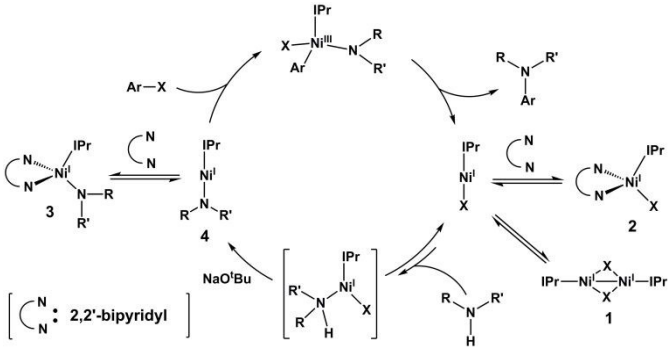

Figure 5. Proposed reaction mechanism of Ni(I)-catalysed Buchwald-Hartwig amination of aryl halides.

Conclusions

In summary, we have uncovered one of the catalytic cycles involved in the Buchwald-Hartwig amination of aryl bromides mediated by Ni(I) NHC complexes. Although a catalytic system between Ni(I) and Ni(III) has been discussed as a possible pathway in many previous reports, experimental studies determining such intermediate key compounds have been poorly defined. Our findings in this study showed that mononuclear Ni(I) and Ni(III) NHC complexes are experimentally and theoretically possible as intermediates in the catalytic cross-coupling reaction. A bidentate ligand, 2,2'-bipyridyl, can stabilize Ni(I) NHC complexes, which efficiently mediate amination of aryl bromides with several amines attempted. Several stoichiometric chemical reactions revealed the presence of a two-coordinate 13e IPr-Ni(I) intermediate. The Ni(III) intermediate was thermally unstable, but its existence was strongly suggested by EPR measurements, followed by the thermal formation of cross-coupling product and diamagnetic dinuclear Ni(I) halide complex. 2,2'-Bipyridyl was able to behave as a hemi-labile ligand to the Ni(I) centre, leading the highly reactive intermediates to stable resting states. Alternatively, the NHC ligand appears to bind to the nickel centre in a stable manner, conserving the mononuclear Ni(I) intermediates to some extent. We are now in the process of studying further this unusual and highly active catalytic process by conducting thorough experiments and discussions which include kinetic analysis.

Experimental

Experimental details

General. All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and glovebox (MBraun UniLab) as otherwise noted. THF, toluene, hexane, benzene-d_6 were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Volatile organic reagents used for

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coupling reactions were distilled just before use. Other reagents were used as received. Bis(4-methoxyphenyl)amine,[22a] N-(p-tolyl)-[1,1'-biphenyl]-4-amine,[22b] 4-fluoro-N-phenylaniline,[22a] N-(p-tolyl)naphthalen-1-amine,[22c] and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr)[22d] were prepared according to the literature methods. Nickel dimers : $[Ni(IPr)(\mu\text{-}X)]_2$ (X = Cl, Br) (**1a**, **1b**) were prepared according to the literature methods.[12] Column chromatography of organic products was carried out using slica gel (Kanto Kagaku, silica gel 60N (spherical, neutral)). The ^1H NMR spectra were taken with a Bruker Avance-III400 Y plus 400 MHz spectrometer at room temperature. Chemical shifts (δ) were recorded in ppm from the solvent signal. The magnetic properties of the materials were investigated using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. The elemental analysis was carried out with YANACO CHN Corder JM-11, AUTO-SAMPLER, using aluminum pan, where the samples were held in a glovebox. The UV-Vis measurements were taken with a PerkinElmer Lambda 35 UV/Vis Spectrometer using either a 10 mm quartz cell. The X-band EPR spectra were collected with a Bruker EMX Plus spectrometer equipped with a continuous flow N_2 cryostat. EPR simulation was conducted using a PHI program.[23]

[NiCl(bpy)(IPr)] (2a). In a glovebox, $[Ni(IPr)(\mu\text{-}Cl)]_2$ (**1a**) (30 mg, 0.030 mmol), 2,2'-bipyridyl (bpy) (9.5 mg, 0.061 mmol), and THF (1.0 mL) were added to a 5 mL screw-capped tube. After the compounds were dissolved, hexane (1.5 mL) was slowly added to the solution and cooled to -30°C. Dark purple crystals of **2a** were obtained, after removal of the liquid and washing with small amount of cold hexane (60 mg, 0.094 mmol, 95% yield). ^1H NMR (C_6D_6): δ 0.81~1.59 (bs), 6.17 (bs), 6.77 (bs). Elemental analysis calcd (%) for $C_{37}H_{44}ClN_4Ni$: C, 69.55; H, 6.94; N, 8.77; found: C, 69.18; H, 6.97; N, 8.44.

[NiBr(bpy)(IPr)] (2b). In a glovebox, $[Ni(IPr)(\mu\text{-}Br)]_2$ (**1b**) (110 mg, 0.104 mmol), 2,2'-bipyridyl (bpy) (40.7 mg, 0.261 mmol), and THF (15 mL) were added to a 25 mL screw-capped tube. After the compounds were dissolved, hexane (23 mL) was slowly added to the solution and cooled to -30°C. Dark purple crystals of **2b** were obtained, after removal of the liquid and washing with cold hexane (132 mg, 0.193 mmol, 93% yield). ^1H NMR (C_6D_6): δ 1.39 (bs), 6.32 (bs), 6.77 (bs). Elemental analysis calcd (%) for $C_{37}H_{44}BrN_4Ni{\cdot}2THF{\cdot}1bpy$: C, 67.15; H, 6.97; N, 8.54; found: C, 67.25; H, 7.18; N, 8.45.

[NiBr(biq)(IPr)] (5). In a glovebox, $[Ni(IPr)(\mu\text{-}Br)]_2$ (**1b**) (80 mg, 0.076 mmol), 2,2'-biquinoline (biq) (42.8 mg, 0.167 mmol, 2.2 eq.), and THF (1.0 mL) were added to a 5 mL screw-capped tube. After the compounds were dissolved, hexane (2.0 mL) was slowly added to the solution and cooled to -30°C. Dark blue crystals of **5** were obtained, after removal of the liquid and washing with small amount of cold hexane (95.1 mg, 80% yield). ^1H NMR (C_6D_6): δ 14.34 (bs), 11.54 (bs), 6.55 (bs), 5.99 (bs), 1.72 (bs), -0.25 (bs). Elemental analysis calcd (%) for $C_{45}H_{48}BrN_4Ni$: C, 68.98; H, 6.18; N, 7.15; found: C, 68.24; H, 6.32; N, 6.95.

General procedure for amination reaction of 4-bromobenzophenone with aromatic amines. In a glovebox, a 20 mL Schlenk tube was charged with **2a** (31.9 mg, 0.05 mmol), 2,2'-bipyridyl (15.6 mg, 0.10 mmol), aromatic amine (0.60 mmol), NaO^tBu (71.1 mg, 0.75 mmol), 4-bromobenzophenone (130.6 mg, 0.50 mmol), and THF (0.2 mL). The reaction mixture was stirred at 40-80°C for 24-48 h. After addition of water, the organic layer was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine and dried by Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with flash column chromatography eluted with dichloromethane/hexane (1/3) to obtain corresponding triarylamines.

Stoichiometric reaction of Ni(I) complex 2a with diarylamines. In a glovebox, complex **2a** (100 mg, 0.16 mmol), diarylamine (0.16 mmol), NaO^tBu (34.0 mg, 0.35 mmol) and THF (2 mL) were placed in a 20 mL Schlenk tube. The suspension was stirred for 1 hour at room temperature to give a dark purple solution. The volatiles were removed in vacuo, the residual solid was extracted with THF and evaporated to dryness. The residue was washed with hexane to give **3a** or **3b** as a black solid.

Complex **3a**. The title compound was isolated as a black solid in 24% yield. ^1H NMR (C_6D_6): δ 0.81-1.59 (bs), 6.17 (bs), 6.77 (bs). Elemental analysis calcd (%) for $C_{49}H_{54}N_5Ni{\cdot}0.5Et_2O$: C, 75.74; H, 7.35; N, 8.66; found: C, 75.74; H, 7.38; N, 8.85.

Complex **3b**. The title compound was isolated as a black solid in 12% yield. Elemental analysis calcd (%) for $C_{51}H_{58}N_5Ni{\cdot}0.8THF$: C, 75.90; H, 7.58; N, 8.15. Found: C, 76.30; H, 7.44; N, 7.78.

Stoichiometric reaction of Ni(I) complex 1a with diarylamines. In a glovebox, complex **1a** (50.0 mg, 0.052 mmol), diarylamine (35.1 mg, 0.207 mmol), NaO^tBu (24.0 mg, 0.249 mmol) and toluene (2 mL) were placed in a 20 mL Schlenk tube. The suspension was stirred for 10 minutes at room temperature to give a dark blue solution. The volatiles were removed in vacuo, the residual solid was extracted with toluene and evaporated to dryness. The residue was washed with hexane to give **4** as a purple solid (53.2 mg, 83 %). ^1H NMR (C_6D_6): δ 0.81-1.59 (bs), 6.17 (bs), 6.77 (bs). Elemental analysis calcd. (%) for $C_{39}H_{46}N_3Ni/Et_2O$: C, 74.89; H, 8.19; N, 6.09; found: C, 74.63; H, 8.24; N, 6.54.

Stoichiometric reaction of Ni(I) amide complexes (3a, 4) with 4-bromobenzophene.

*Using complex **3a** as a substrate*

In a glovebox, a 20 mL Schlenk tube was charged with **3** (50 mg, 0.065 mmol), bpy (51 mg, 0.33 mmol), 4-bromobenzophenone (17 mg, 0.065 mmol), and THF (1.0 mL). The reaction mixture was stirred at 40°C for 24 h. After addition of water, the organic layer was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine and dried by Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with flash column chromatography eluted with dichloromethane/hexane (1/3) to obtain the corresponding triarylamine (16.3 mg, 0.047 mmol, 72 % yield).

*Using complex **4** as a substrate*

The experiment was similarly conducted to the above method, using **4** (30 mg, 0.049 mmol), 4-bromobenzophenone (13 mg, 0.049 mmol), and THF (0.2 mL) to obtain the corresponding triarylamine (12.0 mg, 0.034 mmol, 70 % yield).

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Catalytic reaction of diphenylamine with 4-bromobenzophenone using 3a as catalysts. The experiment was similarly conducted to the above catalytic method with **2a**, using **3a** (38.6 mg, 0.050 mmol), 4-bromobenzophenone (130.6 mg, 0.50 mmol), diphenylamine (101.5 mg, 0.60 mmol), bpy (46.9 mg, 0.30 mmol), NaO^{t}Bu (71.1 mg, 0.74 mmol) and THF (0.2 mL) to obtain the corresponding triarylamine (82.8 mg, 0.237 mmol, 47 % yield).

Product details of amines.

(4-(bis(4-methoxyphenyl)amino)phenyl)(phenyl)methanone

This reaction was conducted with bis(4-methoxyphenyl)amine and the reaction condition was 40°C/24 h. The title compound was isolated as a yellow oil in 91% yield. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, *J* = 6.4 Hz, 2H, *Benzoyl*), 7.67 (d, *J* = 9.0 Hz, 2H, *Benzoyl*), 7.53 (t, *J* = 6.4 Hz, 1H, *Benzoyl*), 7.44 (t, *J* = 7.2 Hz, 2H, *Benzoyl*), 7.14 (d, *J* = 9.0 Hz, 4H, *Anisyl*), 6.88-6.84 (m, 6H), 3.81 (s, 6H, -*OMe*). ^{13}C NMR ($CDCl_3$): δ 195.1 (*C*=O), 157.1 (*Anisyl*), 152.8 (*Benzoyl*), 139.3 (*Anisyl*), 138.8 (*Benzoyl*), 132.1 (*Benzoyl*), 131.5 (*Benzoyl*), 129.6 (*Benzoyl*), 128.1 (*Benzoyl*), 127.9 (*Anisyl*), 116.7 (*Benzoyl*), 115.0 (*Anisyl*), 55.5 (-O*Me*). Elemental analysis calcd (%) for $C_{27}H_{23}NO_3$: C, 79.20; H, 5.66; N, 3.42; found: C, 78.96; H, 5.82; N, 3.26.

(4-((4-fluorophenyl)(phenyl)amino)phenyl)(phenyl)methanone

This reaction was conducted with 4-fluoro-N-phenylaniline and the reaction condition was 80°C/48 h. The title compound was isolated as a yellow oil in 91% yield. ^{1}H NMR ($CDCl_3$): δ 7.77 (d, *J* = 7.0 Hz, 2H, *Benzoyl*), 7.72 (d, *J* = 8.8 Hz, 2H, *Benzoyl*), 7.55 (t, *J* = 7.4 Hz, 1H, *Benzoyl*), 7.46 (t, *J* = 6.8 Hz, 2H, *Ph*), 7.33 (t, *J* = 7.9 Hz, 2H, *Ph*), 7.19-7.12 (m, 5H), 7.04 (t, *J* = 8.6 Hz, 2H, *Ph*), 6.98 (d, *J* = 8.8 Hz , 2H, *Benzoyl*). ^{19}F NMR ($CDCl_3$): δ -116.93. ^{13}C NMR ($CDCl_3$): δ 195.1 (*C*=O), 161.1 (*Ph*, $1J_{C\text{-}F}$ = 243.6 Hz), 151.9 (*Benzoyl*), 146.4 (*Ph*), 142.5 (*Ph*, $4J_{C\text{-}F}$ = 3.1 Hz), 138.4 (*Benzoyl*), 132.0 (*Benzoyl*), 131.7 (*Benzoyl*), 129.7 (*Benzoyl*), 129.6 (*Ph*), 129.5 (*Benzoyl*), 128.1 (*Benzoyl*), 128.0 (*Ph,* $3J_{C\text{-}F}$ = 8.2 Hz), 125.6 (*Benzoyl*), 124.7 (*Ph*), 119.0 (*Ph*), 116.7 (*Ph*, $2J_{C\text{-}F}$ = 22.5 Hz). Elemental analysis calcd (%) for $C_{25}H_{18}FNO$: C, 81.72; H, 4.94; N, 3.81; found: C, 81.70; H, 5.01; N, 3.78.

(4-(naphthalen-1-yl(phenyl)amino)phenyl)(phenyl)methanone

This reaction was conducted with N-phenylnaphthalen-1-amine and the reaction condition was 80°C/48 h. The title compound was isolated as a yellow oil in 79% yield. ^{1}H NMR ($CDCl_3$): δ 7.90 (t, *J* = 8.0 Hz, 2H, *Benzoyl*), 7.81 (d, *J* = 8.4 Hz, 1H, *Napthyl*), 7.73 (d, *J* = 7.2 Hz, 2H, *Benzoyl*), 7.67 (d, *J* = 8.7 Hz, 2H, *Benzoyl*), 7.50-7.36 (m, 7H), 7.28-7.21 (m, 4H), 7.06 (t, *J* = 7.0 Hz, 1H, *Benzoyl*), 6.88 (d, *J* = 9.0 Hz , 2H, *Benzoyl*). ^{13}C NMR ($CDCl_3$): δ 195.1 (*C*=O), 152.3 (*Benzoyl*), 146.6 (*Ph*), 142.1 (*Naphthyl*), 138.5 (*Benzoyl*), 135.2 (*Naphthyl*), 132.1 (*Benzoyl*), 131.9 (*Benzoyl*), 131.5 (*Benzoyl*), 130.9 (*Benzoyl*), 129.5 (*Ph*), 129.4 (*Naphthyl*), 128.8 (*Naphthyl*), 128.5(*Ph*), 128.0 (*Naphthyl*), 127.5(*Ph*), 127.4 (*Naphthyl*), 126.8 (*Naphthyl*), 126.4 (*Naphthyl*), 126.3(*Ph*), 124.3 (*Benzoyl*), 124.1 (*Naphthyl*), 123.7 (*Naphthyl*), 117.7 (*Benzoyl*). Elemental analysis calcd (%) for $C_{29}H_{21}NO{\cdot}0.5H_2O$: C, 85.27; H, 5.43; N, 3.43; found: C, 85.20; H, 5.35; N, 3.14.

(4-(naphthalen-1-yl(p-tolyl)amino)phenyl)(phenyl)methanone

This reaction was conducted with N-(p-tolyl)naphthalen-1-amine and the reaction condition was 80°C/48 h. The title compound was isolated as a yellow oil in 72% yield. ^{1}H NMR ($CDCl_3$): δ 7.91 (t, *J* = 7.3 Hz, 2H, *Benzoyl*), 7.82 (d, *J* = 7.7 Hz, 1H, *Naphthyl*), 7.73 (d, *J* = 8.2 Hz, 2H, *tolyl*), 7.65 (d, *J* = 9.5 Hz, 2H, *Benzoyl*), 7.53-7.47 (m, 3H), 7.44-7.37 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 2H, *tolyl*), 7.10 (d, *J* = 8.2 Hz , 2H, *tolyl*), 6.81 (d, *J* = 8.6 Hz, 2H, *Benzoyl*), 2.31 (s, 3H, *tolyl*). ^{13}C NMR ($CDCl_3$): δ 195.4 (*C*=O), 152.7 (*Benzoyl*), 143.9 (*tolyl*), 142.3 (*Naphthyl*), 138.7 (*Benzoyl*), 135.3 (*tolyl*), 134.3 (*Naphthyl*), 132.2 (*Benzoyl*), 131.5 (*Benzoyl*), 131.0 (*Benzoyl*), 130.2 (*Benzoyl*), 129.6 (*tolyl*), 128.6 (*Naphthyl*), 128.4 (*Naphthyl*), 128.1 (*tolyl*), 127.4 (*Naphthyl*), 127.3 (*Naphthyl*), 126.8 (*Naphthyl*), 126.4 (*Naphthyl*), 124.8 (*Benzoyl*), 123.9 (*tolyl*), 117.1 (*Benzoyl*), 20.9 (-*C*H$_3$). Elemental analysis calcd (%) for $C_{30}H_{23}NO{\cdot}0.3H_2O$: C, 85.89; H, 5.69; N, 3.34; found: C, 86.00; H, 5.55; N, 3.32.

(4-((3-fluorophenyl)amino)phenyl)(phenyl)methanone

This reaction was conducted with aniline and the reaction condition was 60°C/48 h. The title compound was isolated as a pale yellow solid in 94% yield. ^{1}H NMR ($CDCl_3$): δ 7.78 (m, 4H), 7.56 (t, *J* = 7.5 Hz, 1H, *Benzoyl*), 7.48 (t, *J* = 7.4 Hz, 2H *Benzoyl*), 7.27 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 2H, *Benzoyl*), 6.93 (m, 2H), 6.74 (m, 1H) 6.22 (brs, 1H, -N*H*). ^{19}F NMR ($CDCl_3$): δ -111.54. ^{13}C NMR ($CDCl_3$): δ 195.2 (*C*=O), 164.8 (*Ph*, $1J_{C\text{-}F}$ = 243.7 Hz), 147.0 (*Benzoyl*), 142.8 (*Ph*, $3J_{C\text{-}F}$ = 10.7 Hz), 138.5 (*Benzoyl*), 132.6 (*Benzoyl*), 131.8 (*Benzoyl*), 130.7 (*Ph*, $3J_{C\text{-}F}$ = 9.7 Hz), 129.6 (*Benzoyl*), 128.2 (*Benzoyl*), 115.3 (*Benzoyl*), 115.2 (*Ph*, $4J_{C\text{-}F}$ = 2.8 Hz), 109.6 (*Ph*, $2J_{C\text{-}F}$ = 24.4 Hz), 106.8 (*Ph*, $2J_{C\text{-}F}$ = 21.1 Hz). Elemental analysis calcd (%) for $C_{19}H_{14}FNO$: C, 78.33; H, 4.84; N, 4.81; found: C, 78.08; H, 4.81; N, 4.75.

Computational details

All the calculations were performed using the GAUSSIAN 09 package.[24] The geometry optimization was performed using the functionals of B3LYP, B3LYP-D3BJ, and BP86 without symmetry restriction. The standard 6-31G(d) or 6-31G(d,p) basis sets for all atomes were employed. Furthermore, the nature of stationary points was checked by the vibrational frequency analysis at the same level. The dissociaton energy of **3a** complex to **4** with bpy was corrected for zero point energy (ZPE) and basis set superposition error (BSSE). The relative Gibbs free energies were estimated at the condition of 298.15 K and 1 atm. All the computation was carried out using the computer facilities at Research Institute for Information Technology, Kyushu University.

X-ray crystallography

Single crystals of **2a-2b**, **3a-3c**, **4** and **5** for X-ray diffraction were grown at −30°C from the toluene/hexane (for **4**) and the THF/hexane (for the other compounds) solutions. All the data were obtained at 123 K using a Rigaku Saturn CCD diffractometer with a confocal mirror and graphite-monochromated Mo Kα radiation (*λ* = 0.71070 Å). Data reduction of the measured reflections was performed using the software package CrystalStructure.[25] The structures were solved by direct methods (SIR2008)[26] and refined by full-matrix least-squares fitting based on F^2, using the program SHELXL 97-2, PC version.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located at ideal positions and included in the refinement, but were restricted to riding on the atom to which they were bonded. CCDC 1878020-1878026 contains the supplementary crystallographic data for this paper. A copy of the data can be

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Conflicts of interest

The authors declare no conflict of interest.

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Author Contributions

These authors contributed equally: YF made Ni complexes. TI conducted experiments for catalysis and its mechanistic study. TI also managed the whole study with KM. YY conducted theoretical calculations. RI conducted EPR measurements. SK did SQUID measurements. YK measured ESI-TOF MS and did elemental analysis.

Notes and references

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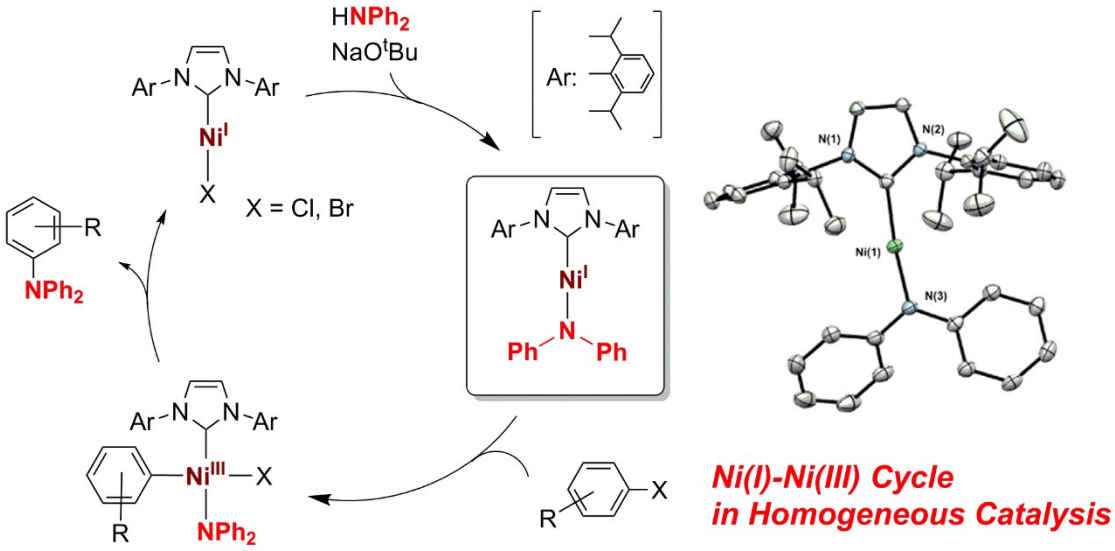
Ni(I)-Ni(III) Cycle in Buchwald-Hartwig Amination of Aryl Bromide Mediated by NHC-ligated Ni(I) Complexes

Takahiro Inatomi,[a] Yukino Fukahori,[a] Yuji Yamada,[a] Ryuta Ishikawa,[a] Shinji Kanegawa,[b] Yuji Koga[a] and Kouki Matsubara*[a]

NHC-ligated Ni(I) intermediates in Buchwald-Hartwig amination of aryl halides were isolated and determined. The presence of Ni(III) intermediate was also indicated at low temperature.



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