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Monovalent Nickel Complex Bearing a Bulky *N*-Heterocyclic Carbene Catalyzes Buchwald–Hartwig Amination of Aryl Halides under Mild Conditions

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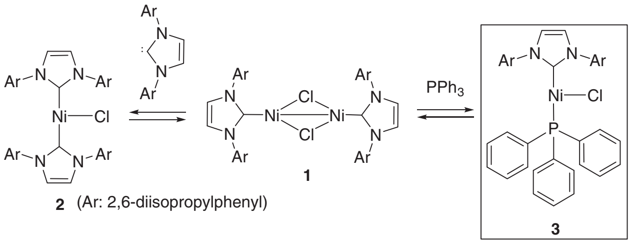
Monovalent nickel complex bearing a bulky *N*-heterocyclic carbene (NHC) and triphenylphosphine was synthesized and demonstrated to catalyze the Buchwald–Hartwig amination of aryl halides with diarylamines to form triarylamines under mild conditions.

Catalytic *N*-arylation of amine is an attractive and useful synthetic process to produce arylamines efficiently under rather mild conditions.[1] In order to make triarylamines from poorly nucleophilic diarylamines particularly, several studies using Pd,[2] Ni,[3] and Cu[4] catalysts have been reported recently. Such chemicals are known to have electronic, photoelectronic, and magnetic properties, and benefit as a wide spectrum of new materials, such as organic light-emitting diodes, photovoltaic cells, nonlinear optics, and organic photoconductors.[5,6] Most reports for the nickel- or palladium-catalyzed reactions have shown that zero- and divalent species are the key intermediates in the catalytic cycles. However, in several cross-coupling reactions, such as the Kumada–Tamao–Corriu cross coupling,[7] and Negishi coupling reactions,[8] radical catalysis has been proposed via the formation of monovalent species as the intermediates which make the reactions faster than those with zero- and divalent species. As for the Buchwald–Hartwig amination, Gao et al. proposed similar catalytic cycles with magnesium amide and nickel complexes,[3] however the evidence is still unsatisfying.

Previously we showed that a monovalent nickel NHC complex was isolated and used as a catalyst for the Kumada–Tamao–Corriu cross coupling for the first time.[9] Louie et al. also reported nickel(I) NHC complexes, which were active for Suzuki and Kumada–Tamao–Corriu cross-coupling reactions.[10] However, the activities of the catalysts were not very high, probably because the steric hindrance derived from two bulky carbene ligands restricts the access of substrates. Now, we prepared a new NHC/phosphine mixed complex of monovalent nickel, which catalyzed the Buchwald–Hartwig amination of aryl halides under ambient conditions.

Our previous report also showed the existence of an equilibrium (Scheme 1), indicating the labile nature of one of the NHC ligands in **2**. This prompted us to introduce a phosphine ligand to dinickel(I) dichloride **1** instead of NHC.[11] The monovalent nickel complex **3** bearing NHC/phosphine ligand formed quantitatively in the presence of 2 equiv of PPh_3 (Scheme 1), as expected. The compound **3** could be isolated in 66% yield by recrystallization from THF/hexane solution at $-30\,°C$.[12] Dissolving the crystals in benzene-d_6 generated the mixture of **1** and **3** again, suggesting that a similar equilibrium to **2** exists in solution. Addition of 2 equiv of PPh_3 to the mixture again formed only **3**. As the compound **2** reacts with chloroform to form diamagnetic nickel dichloride, $[NiCl_2(IPr)_2]$ (IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), the compound **3** also reacts smoothly at ambient temperature to form the analogous nickel(II) dichloride, $[NiCl_2(PPh_3)(IPr)]$.[13] The easy radical abstraction of chlorine suggested the radical nature of **3**.



Scheme 1.

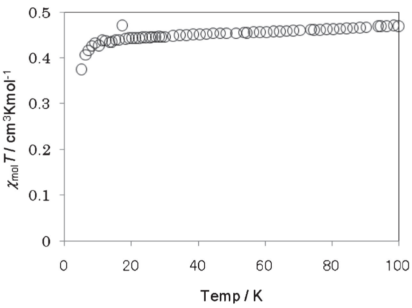


Figure 1. $\chi_{mol}T$ vs. T plot for **3**, obtained from SQUID measurement.

The compound **3** is paramagnetic, demonstrated by a magnetic susceptibility measurement; the value of $\chi_{mol}T$ is $0.37\,cm^3\,K\,mol^{-1}$ at 5 K (Figure 1). This indicates that the spin quantum number, S, is 1/2. The structure was finally determined by single-crystal X-ray diffraction[14] as shown in Figure 2 in combination with elemental analysis. Notably the nickel atom takes a planar Y-shape three-coordinate conformation, where the sum of the three angles around Ni(1) is 359.6(1)°, in contrast to **2** taking T-shape coordination. The T- or Y-shape of the three-coordinate nickel species has sometimes been discussed in reports,[15] probably due to not steric reasons but to some electronic influence arising from the ligands.[16] In our case, we discussed that difference of the electronic properties in NHC and PPh_3 ligands may also lead to such shape differences. Each bond distance between Ni(1) and Cl(1), P(1), or C(1) is in the range of normal single bond length, 2.179(9), 2.20(1), or 1.930(3), respectively. Similar results have been shown in the structure of

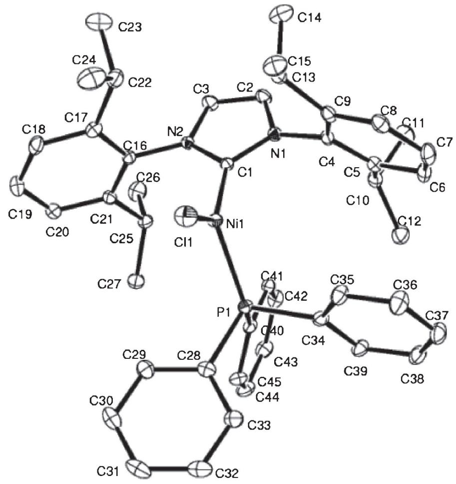
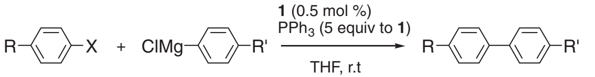


Figure 2. ORTEP drawing of [Ni^{I}Cl(IPr)(PPh$_3$)] (**3**) (50% probability of thermal ellipsoids). All hydrogen atoms are omitted for clarity. Representative bond distances and angles are as follows: Ni(1)–Cl(1) = 2.179(9), Ni(1)–P(1) = 2.20(1), Ni(1)–C(1) = 1.930(3), C(2)–C(3) = 1.346(4) Å; Cl(1)–Ni(1)–P(1) = 113.31(4), Cl(1)–Ni(1)–C(1) = 134.2(1), P(1)–Ni(1)–C(1) = 112.1(1)°.

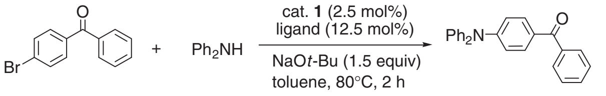
2 previously, suggesting that most of the unpaired electron does not exist in the ligands but in the independent d orbital of nickel.[9]

At first we examined Kumada–Tamao–Corriu cross-coupling reactions of aryl halides in the presence of the monovalent nickel complex. Because the solution of **3** forms a mixture of **1**, **3**, and free phosphine, we added 5 equiv of PPh$_3$ to the solution of **1** before the reactions. As expected, the complex showed good performance toward the coupling reaction as shown in eq 1. For example, only 1.0 mol % of **3** (**1** (0.5 mol %) + 5 equiv PPh$_3$) provided 4-methoxybiphenyl and *p*-terphenyl in 98 and 92% yields in 3 h, whereas 1.0 mol % of **2** (**1** (0.5 mol %) + 5 equiv IPr) gave these compounds in 93 and 89% yields in longer time, 18 h.



(1)

R, R', X	yield / %
OMe, H, Br	98
Ph, H, Br	92
H, Me, Br	86
H, Me, Cl	69

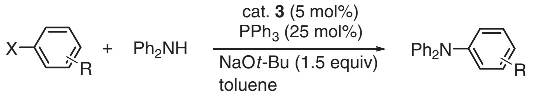


(2)

ligand	yield / %
IPr	61
-	80
PPh$_3$	99

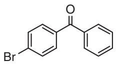
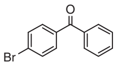
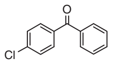
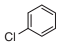
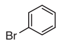
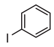
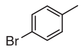
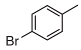
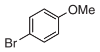
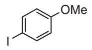
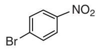
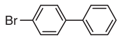
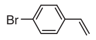
We also examined the Buchwald–Hartwig amination of aryl halides with diphenylamine, since triarylamine was generated efficiently in the reaction of diphenylamine with bromobenzene in the presence of a similar nickel complex, [Ni^{II}Cl$_2$(IPr)(PPh$_3$)], previously.[17] At first, we examined amination reactions at 80 °C for 2 h using some catalyst systems (eq 2). Significantly, the reaction yields increased in the following order: **1** with IPr (12.5 mol %, 2.5 equiv to nickel) (61% isolated yield) < **1** without ligand (80%) < **1** with PPh$_3$ (12.5 mol %) (99%), suggesting that the in situ formation of **3** is the important process to stabilize and/or to activate the catalyst system. It is of interest that the reaction was not affected by the presence of excess phosphine ligand, suggesting that coordination of the substrates to coordinatively unsaturated nickel species might not be the rate-determining step in the catalytic cycle.

The catalyst activity of the system using **3** and PPh$_3$ is comparable to that using **1** and PPh$_3$, but sometimes better than using **1**. Thus, in the presence of **3**, PPh$_3$ (25 mol %, 5 equiv to nickel), and base, we added several aryl halides to diphenylamine (eq 3).[18] At first, the reaction of activated 4-bromobenzophenone resulted in the formation of the coupling product efficiently at 40 °C as a surprise to us (Table 1, Entry 1). Even at room temperature, the reactions of 4-bromobenzophenone, 4-bromotoluene, 4-iodoanisole, and *p*-bromonitrobenzene proceeded to form the triarylamine derivatives in 40–70% yields (Entries 2, 7, 10, and 11). The reactions of bromides and iodides at 70 °C gave the amination products in good yields (Entries 5, 6, 8, 9, and 12). Using chlorobenzene or 4-bromostyrene as a reactant provided the desired product in moderate yield, 41 or 43% (Entry 4 or 13). The yield from 4-bromostyrene did not improve even in longer reaction time. We assumed that the catalyst could be decomposed or deactivated with the olefinic substrate, because the yield only increased when we added 10 mol % of the nickel catalyst.



(3)

Table 1. Buchwald–Hartwig amination of aryl halides mediated by **3**[a]

Entry	Aryl halides	Temp/°C	Time/h	Yield/%[b]
1		40	24	97
2		25	72	68
3		70	72	96
4		70	24	41
5		70	24	74
6		70	24	77
7		25	72	43
8		70	24	60
9		70	48	66
10		25	72	52
11		25	72	49
12		70	72	75
13		70	72	43

[a] The reaction was carried out with diphenylamine (1.2 equiv) and NaO*t*-Bu. [b] Isolated yields were determined after silica gel column chromatography.

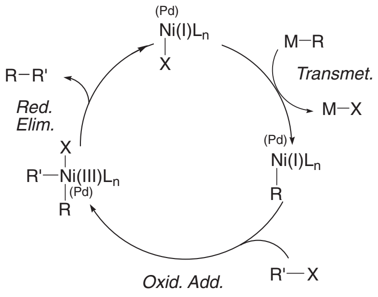


Figure 3. Proposed mechanism of the cross-coupling reactions.

Several reports describe the mechanism of the "radical" catalysis in nickel and palladium chemistries: transmetallation occurs to exchange halogen ligand of Ni(I) (or Pd(I)) halide and subsequent oxidative addition of aryl halide forms Ni(III) (or Pd(III)) species, easily giving a coupling product (Figure 3).[3,7,8] We also considered that the formation of nickel(I) phenyl or amide species could be the initial reaction in the Kumada–Tamao–Corriu coupling or Hartwig–Buchwald amination, respectively, that was inferred from preliminary experimental results.[19] Detailed mechanistic study for the reactions are now in progress.

In summary, we successfully isolated and structurally determined the phosphorus-substituted NHC complex of monovalent nickel from dinickel(I) halide. The complex has a unique three-coordinate Y-shape structure in the solid state and a suitable nature for catalysis in solution, making the unsaturated site easily with liberation of phosphine ligand, that may be attributed to the radical nature of the nickel(I) center. As expected, the complex has high catalyst activities toward the Kumada–Tamao–Corriu cross coupling and Buchwald–Hartwig amination of aryl halides. Strikingly, amination of aryl halide with diphenylamine proceeded to form triphenylamine derivatives even at low temperatures, that has never been reported previously to the best of our knowledge.

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12 Procedure for **3**: In a glovebox, [Ni(μ-Cl)(IPr)]$_2$ (**1**) (0.03 mmol, 29.0 mg), PPh$_3$ (0.06 mmol, 15.7 mg), and THF (0.5 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. Yellow prismatic crystals of **3** were obtained, after removal of the liquid and washing with small amount of hexane (28.1 mg, 66% yield). Anal. Calcd for $C_{45}H_{51}N_2PClNi$: C, 72.55; H, 6.90; N, 3.76%. Found: 72.47; H, 6.95; N, 3.93%. Details are shown in the Supporting Information, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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