A new aspect of nickel-catalyzed Grignard cross-coupling reactions: selective synthesis, structure, and catalytic behavior of a T-shape three-coordinate nickel(I) chloride bearing a bulky NHC ligand†

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Novel T-shape three-coordinate nickel(I) chlorides bearing an *N*-heterocyclic carbene ligand, NiCl(IPr)$_2$ (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene), were isolated by a reaction of Ni(0)(NHC)$_2$ with aryl chlorides. This Ni(I) complex was shown to act as a catalyst in a cross-coupling reaction of aryl halides with phenylmagnesium chloride.

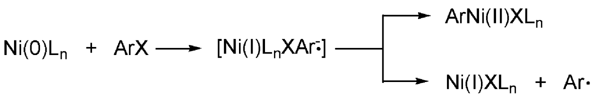
Oxidative addition of aryl halide to zerovalent nickel complexes is an important reaction involved in significant cross-coupling reactions, such as Suzuki–Miyaura and Kumada–Corriu reactions, α-arylation, *N*-arylation, and Heck reactions.[1] Kochi *et al.* have previously investigated oxidative addition of aryl halides to Ni(PEt)$_4$ in detail.[2] One electron transfer from nickel(0) to aryl halide affords the production of nickel(I)-aryl-halide-anion radicals, which are converted to ArNi(II)XL$_n$ or Ni(I)XL$_n$ and an aryl radical (Scheme 1). However, there is a paucity of literature describing the corresponding nickel(I) halides: only nickel(I) chlorides having two or three triphenylphosphine ligands have been presented.[3] A recent study proposed Ni(I)-catalyzed Negishi cross-coupling reaction of alkyl halide.[4] Delocalization of the unpaired electron in the terpyridine ligand was found to be the key to the stabilization of the catalytic active species, illustrating the importance of the Ni(I) chemistry in the catalytic cross-coupling reactions.

Conversely, high catalytic activity has often been achieved when bulky supporting ligands, such as PCy$_3$, P^tBu_3, IPr and SIPr, were used in these reactions.[5] In our recent studies, nickel complexes bearing bulky *N*-heterocyclic carbene (NHC) ligand, 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr), were shown to perform efficient catalytic cross-coupling reactions of haloarenes.[6] Although several nickel(II) oxidative addition products have been isolated using moderate-size ligands,[7] it remains unclear how an aryl halide adds to nickel(0) species bearing bulky ligands and what the key intermediate is in the catalytic reactions. Consequently this prompted us to determine the nickel oxidative adducts bearing a bulky ligand, IPr, and to examine the catalytic activity of the isolated adducts.

A novel, monovalent, 15-electron 3-coordinate nickel chloride, [NiCl(IPr)$_2$] (**2**), was selectively generated from the reaction of a nickel(0) complex, Ni(IPr)$_2$ (**1**), with *p*-chlorotoluene at room temperature (Scheme 2). This result strongly suggests that the product selectivity reported by Kochi can be controlled by the two bulky carbene ligands in **1**. Apparently, these two carbene ligands hamper the formation of oxidative addition adducts, probably due to steric hindrance between the aryl moiety and two IPr ligands. The use of aryl chlorides, such as 4-chloroanisole, 4-chlorobenzophenone and 2-chlorobenzaldehyde, afforded the production of **2** (similar yields) and arenes derived from an aryl radical in THF. The expected biaryl product as a result of radical coupling, 4,4′-dimethylbiphenyl, was detected in the ^{1}H NMR and GC-MS spectrum for the crude mixture as shown in Electronic Supplementary Information (ESI†). Further reaction of **2** with chloroarenes did not yield [NiCl$_2$(IPr)$_2$] (**4**),[6b] but, when dissolved in CDCl$_3$, **4** was generated quantitatively. Complex **2** was quite unstable in air, smoothly changing color from yellow to pale red. Complex **2** was isolated by recrystallization at −30 °C under an N$_2$ atmosphere from hexane–THF (3/1) solution (34% yield).‡

The dissolution of crystals of **2** in C$_6$D$_6$ led to the formation of a dimeric complex **3**[8] and free IPr with **2**, detected in the ^{1}H NMR (Scheme 2). However, with excess free IPr added to the solution, **3** was not detected, indicating the existence of an equilibrium between **2** and **3** + 2IPr. We confirmed this equilibrium by addition of IPr to isolated **3** giving a mixture containing **2** and free IPr (see ESI†).

The complex **2** is paramagnetic, $S = 1/2$ and $g = 2.18$ as demonstrated by magnetic susceptibility measurements and the presence of broad ^{1}H resonances in the NMR spectrum. Single crystals of **2** were obtained from the solution of either hexane or THF–hexane and the structure was determined by X-ray diffraction studies.§ As shown in Fig. 1, both structures showed rare, planar, 3-coordinate T-shape Ni(I) structures (the sum of the angles around Ni is 360.0(3)). One hexane or two THF molecules are included in each cell; however, the solvent was not located in the coordination sphere of nickel. Neither Cl···H hydrogen bonding[10] nor Ni···H anagostic interactions[11] were observed at the methyl groups of the NHC ligand. Although some 3-coordinate nickel(I) complexes bearing diphosphine and diketiminate ligands have been



Scheme 1 Reaction of Ni(0)L$_n$ with haloarenes.[2]

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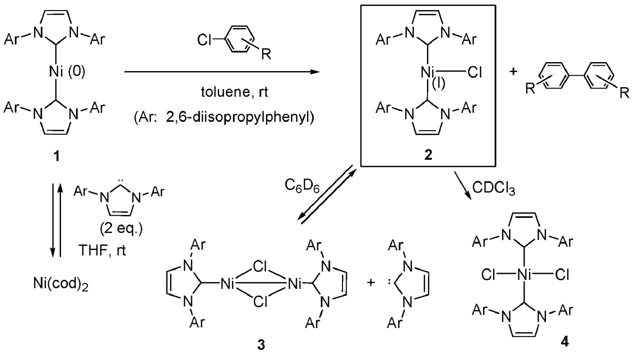
† Electronic supplementary information (ESI) available: Experimental details. CCDC 737686–737687. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b924716e



Scheme 2

structurally determined,[9] this is the first example of a monovalent 3-coordinate nickel complex bearing an NHC ligand.

The SOMO orbital was calculated by a DFT method (GAUSSIAN03, B3LYP/6-31G(d,p)) using the 3-D coordinates in the crystals (see ESI†). Most of the unpaired electron is located in the non-bonding $d_{x^2-y^2}$, whereas only 0.3% is distributed in the halogen–nickel σ^* and carbene π^* plane. This result indicates that the stability of **2** is derived from localization of the unpaired electron at the nickel atom and is in sharp contrast to the Ni(I) terpyridine catalyst, in which the unpaired electron is delocalized in the terpyridine ligand.[4]

In the homogeneous catalytic reactions using the nickel–IPr system, the amount of IPr required for *in situ*-generated nickel catalysts has troubled chemists, because the catalyst activity and/or selectivity of the reactions strongly depend on it.[5a] We added one or two equiv. of IPr to a solution of Ni(cod)$_2$ at room temperature and then added 4-chlorotoluene to the mixture. As a result, when one equiv. of IPr was added, the compound **2** was not generated in abundance but an oxidative addition product and a small amount of **3** were formed. In contrast, when two equiv. of IPr were added, the complex **2** was primarily afforded and isolated with a yield of 39% by recrystallization. These results, the selective formation of nickel(I) complex **2** from **1** (or Ni(cod)$_2$ and two equiv. of IPr) and an aryl halide, may allow the identification of a real active catalyst in the Ni(I)–Ni(III) cycle. Thus, the cross-coupling reaction of aryl halides, 4-bromoanisole and 4-bromobiphenyl, and phenylmagnesium chloride using **2** (1 mol%) as a catalyst was performed. Strikingly, in the presence of free IPr (5 equiv.), 4-methoxybiphenyl and *p*-terphenyl were formed almost quantitatively (93% and 89%, respectively, after silica gel column chromatography) at ambient temperature in 18 h (Scheme 3). The catalytic reactions proceeded in a similar manner to the reactions using **4**, suggesting that **2** is an intermediate in the catalytic reaction using **4** as a precatalyst.[6b] This is a rare example demonstrating the Ni(I)-catalyzed cross-coupling reaction using aryl halides as the coupling reagents.[12]

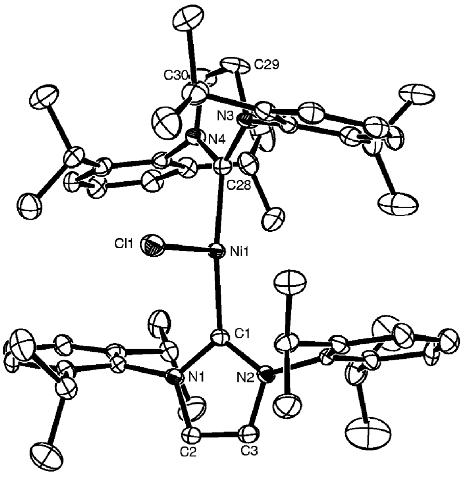
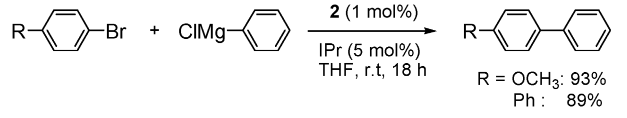


Fig. 1 ORTEP drawing of Ni(I)Cl(IPr)$_2$ (**2**) (50% probability of thermal ellipsoids). All hydrogen atoms and the solvents inside the cell are omitted for clarity.



Scheme 3 Kumada–Corriu cross-coupling reactions mediated by **2**.

In summary, a novel T-shape three-coordinate nickel(I) chloride bearing the IPr ligand was selectively formed and isolated by the reactions of Ni(IPr)$_2$ with chloroarenes. We showed that Ni(I) chloride can act as an efficient catalyst in the catalytic cross-coupling reactions of aryl halides. Further studies on mechanism and possible applications are in progress.

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Notes and references

‡ Experimental details for **2**: To a 20 mL Schlenk tube, Ni(IPr)$_2$ (167 mg, 0.20 mmol), 4-chlorotoluene (26.0 μL, 0.22 mmol), and toluene (3.0 mL) were added at room temperature. After stirring the mixture for 5 h, the solvent was removed under reduced pressure. The residual solid was recrystallized from hexane–THF (3/1) solution at −30 °C, yielding crystals of **2** (60 mg, 34%). ^{1}H NMR (400 MHz, benzene-d_6) $\delta = -3.5, 2.8, 8.3, 8.7$. Other analyses including elemental analysis were unsuccessful unfortunately, because the compound was so unstable even in the solid state that rapid decomposition occurred in air. Direct EI-MS measurement of **2** resulted in no appearance of the MS peaks. The purity of the compound was confirmed by ^{1}H NMR spectroscopy and X-ray diffraction studies using different crystals.

§ Crystal data for **2-THF** and **2-hexane**. **2-THF**·2THF: C62H88ClN4NiO2, Fw = 1015.52, monoclinic, space group $P2_1/n$, $a = 12.197(3)$, $b = 21.922(5)$, $c = 21.563(5)$ Å, $\beta = 91.719(2)°$, $V = 5763(2)$ Å^3, $Z = 4$, $D_c = 1.170$ Mg m^{-3}, $F(000) = 2196$, $T = 123(2)$ K, μ(Mo-Ka) = 0.428 mm^{-1}, 45 886 reflections measured, 13 005 independent ($R_{\text{int}} = 0.088$). The final refinement converged to $R_1 = 0.0754$ for $I > 2(I)$, w$R_2 = 0.1840$ for all data. **2-hexane**·hexane: C60H86ClN4Ni, Fw = 957.52, orthorhombic, space group $P2_12_12_1$, $a = 12.976(4)$, $b = 20.197(7)$, $c = 21.226(7)$ Å, $V = 5563(3)$ Å^3, $Z = 4$, $D_c = 1.143$ Mg m^{-3}, $F(000) = 2076$, $T = 123(2)$ K, μ(Mo-Ka) = 0.436 mm^{-1}, 45 580 reflections measured, 12669 independent ($R_{\text{int}} = 0.090$). The final refinement converged to $R_1 = 0.0691$ for $I > 2(I)$, w$R_2 = 0.1825$ for all data.

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