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[CNN]-Pincer Nickel(II) Complexes of N-Heterocyclic Carbene (NHC): Synthesis and Catalysis to Kumada Reaction of Unactivated C-Cl Bonds

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Yunqiang Sun, Xiaoyan Li and Hongjian Sun*

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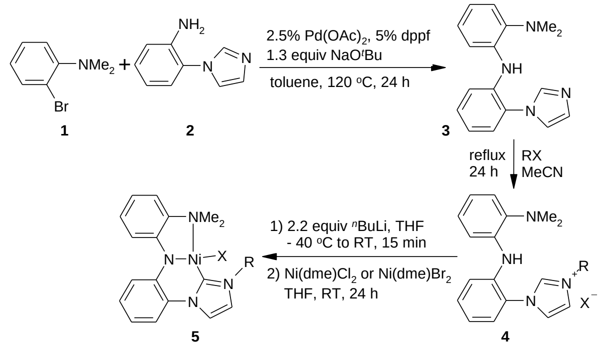
Three novel [CNN]-pincer nickel(II) complexes with NHC-amine arms were synthesized by three steps. Complex 5b was proven to be an efficient catalyst for the Kumada coupling of aryl chlorides or aryl dichlorides under mild conditions.

Since the seminal reports by Shaw[1] and van Koten[2] in the late 1970s, pincer complexes have been intensively developed because of their high stability, activity and variability. Their applications have been discovered in the fields of organic synthesis, catalysis, sensors and supramolecular chemistry.[3] Pincer ligands could be typically abbreviated as [EYE]-type where Y stands for a central donor (Y = C, N, etc.) and E represents the donors such as amines ($-NR_2$), phosphines ($-PR_2$), phosphites ($-P(OR)_2$), ethers (-OR), thioethers (-SR), selenoethers (-SeR) and even NHCs.[4] Symmetrical [EYE]-type pincer ligands with two identical E-donors were intensively investigated because of their easily synthesized and readily variable properties.[5] By comparison, the study on the pincer ligands with two different E-donors (abbreviated as [EYE']-type) attracted increased attentions owing to the unique properties provided by two different E-donors. Therefore, [EYE']-pincer metal complex may have some surprising cooperating effects and unexpected reactivity.[6] However, the research on unsymmetric [EYE']-pincer complexes is less than that on symmetric [EYE]-pincer complexes because of their relatively laborious synthesis.

NHCs have been widely used in organometallic chemistry and catalysis over the last two decades.[7] Compared to the well-known phosphine ligands, the NHCs were considered to be better ligands because they bind metal centre more strongly. In addition, the NHCs can be easily modified by the introduction of various substituents on the heterocycle.[8] Amine was also a very important ligands for formation of pincer complexes. NHCs based [CCC][9] or [CNC][10] pincer complexes and amines based [NNN][11] or [NCN][12] pincer complexes with two identical donor atoms have been well studied. Some of them were demonstrated to be excellent pre-catalysts for the catalytic reactions, such as C,C-cross coupling reactions,[13] hydroamination,[14] hydrogenation[15] and so on. However, there were few examples of NHC-amines pincer ligands, especially for the coordination complex of nickel.[16] This triggered our interest for the synthesis of [CNN]-pincer ligands with two different kinds of donor and the preparation of novel [CNN]-pincer nickel complexes.

In this paper, we reported the preparation and characterization of novel [CNN]-pincer nickel complexes with NHCs and amines as donors. These complexes could efficiently catalyze the Kumada coupling reaction of unreactive C-Cl bonds.

Scheme1: Synthesis of the [CNN]-ligands **4a - 4c**.



	4a (92%)	**4b** (78%)	**4c** (90%)
	5a (80%)	**5b** (87%)	**5c** (80%)
R	^{n}Bu	^{i}Pr	Bn
X	Br	Br	Cl

The precursor **3** of the [CNN]-pincer ligands was synthesized through a Pd-catalyzed C,N-coupling of *N*,*N*-dimethylaminobromobenzene with 2-(imidazol-1-yl)phenylamine in moderate yield.[17] Treatment of **3** with RX under reflux afforded the unsymmetric pincer ligands **4a - 4c**. After the lithiation of **4a - 4c**,

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, People's Republic of China. E-mail: hjsun@sdu.edu.cn.

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$Ni(dme)Cl_2$ or $Ni(dme)Br_2$ (dme: dimethoxyethane) was added to give rise to the [CNN]-pincer Ni(II) complexes **5a - 5c** in the yields of 80 - 87%.

Complexes **5a - 5c** were very air stable both in the solid state and in solution. In the ^{1}H NMR spectra of ligands **4a - 4c**, the NHC protons displayed at 10.49, 10.58 and 10.81 ppm while amine protons (PhN*H*Ph) were registered at 6.56, 6.52 and 6.64 ppm. After the Ni-N coordination, the singlet of two methyl groups ($–NMe_2$) in **4a - 4c** were split into two peaks in complexes **5a - 5c** because the free rotation of C_{ph}-N_{Me} bond was blocked and the two methyl groups have different chemical environments.

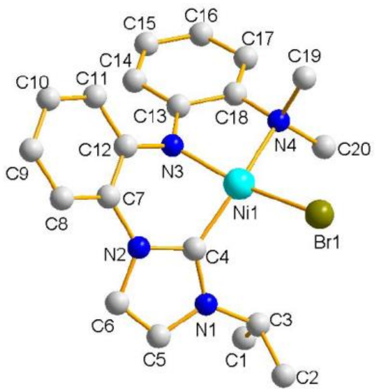
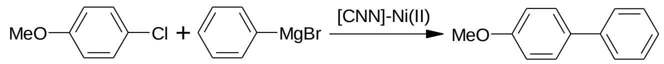


Figure 1. X-ray structure of complex **5b** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): N3−Ni1 1.847(5), N4−Ni1 2.013(6), C4−Ni1 1.881(7), Br1−Ni1 2.327(1); N3-Ni1-C4 88.2(3), N3-Ni1-N4 85.6(2), C4-Ni1-N4 161.2(3), N3-Ni1-Br1 161.0(2), C4-Ni1-Br1 95.8(2), N4-Ni1-Br1 95.9(2).

5b as green crystals could be obtained through solvent evaporation from Et_2O. The structure of **5b** was confirmed by X-ray crystallographic analysis (Figure 1). With the coordination of one C_{NHC} atom, one chlorine atom and two amino N atoms, the central nickel atom has a distorted square-planar configuration consisting of one five-membered and one six-membered chelate ring. Compared to the similar [NNN]-pincer nickel complex,[17] complex **5b** has a slightly longer Ni-N (amide) distance (N4-Ni1 = 2.013 Å (**5b**) *vs* 1.982 Å[17]) and shorter Ni-N (amine) distance (N3−Ni1 = 1.847 Å (**5b**) *vs* 1.8907 Å[17]). On the other side, **5b** showed a slightly shorter Ni-C_{NHC} distance (C4−Ni1 = 1.881 Å (**5b**) *vs* 1.905 Å[18]).

With the three novel pincer complexes **5a - 5c**, we initially evaluated their catalytic activity for the cross-coupling reaction of 1-chloro-4-methoxybenzene with phenyl magnesium bromide in THF as a probe reaction. With a loading of 1 mol %, complex **5b** showed the highest catalytic activity (Table 1, entries 1 - 3) among these three complexes. It seemed that the influence of R group on the catalytic activity of the complexes was obvious, excessive steric hindrance resulted in the increase of catalytic activity of the catalyst. A catalyst loading of 2 mol % was also necessary to complete the reaction (Table 1, entry 4). Compared to the reported NHCs based [CNC][10f] and amines based [NNN][11d] symmetric pincer Ni(II) complexes, the [CNN]-pincer Ni(II) complexes were more efficient. THF was the best reaction media compared with toluene, Et_2O and DME (Table 1, entries 5 - 7).

Table 1. Kumada cross-coupling of 1-chloro-4-methoxybenzene with phenyl magnesium bromide catalyzed by nickel catalyst[a]

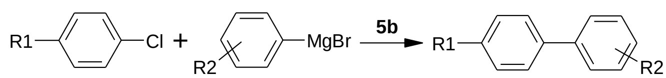


Entry	Catalyst (mol%)	Solvent	Yield (%)[b]
1	**5a** (1)	THF	37
2	**5b** (1)	THF	76
3	**5c** (1)	THF	45
4	**5b** (2)	THF	93
5	**5b** (2)	Toluene	43
6	**5b** (2)	Et_2O	51
7	**5b** (2)	DME	36

[a] 25 °C, 24 hrs, 0.5 mmol *p*-$MeOC_6H_4Cl$, 0.75 mmol C_6H_5MgBr. [b] Isolated yields.

Under the optimized condition, we examined the substrate scope using **5b** (2 mol %) as a catalyst in THF at 25 °C for 24 hrs. Interestingly, activated aryl chlorides with electron-withdrawing group ($-CF_3$) gave relatively lower yields (Table 2, entries 10 - 11) compared to the unactivated aryl chlorides including *p*-MeC_6H_4Cl and *p*-$MeOC_6H_4Cl$ (Table 2, entries 4, 6 and 7). When sterically hindered Grignard reagent, such as *o*-MeC_6H_4MgBr, was used as the nucleophilic species, only lower yields were obtained (Table 2, entries 2, 5 and 8) than those of less hindered reagents *p*-MeC_6H_4MgBr and *p*-$MeOC_6H_4MgBr$ (Table 2, entries 1, 3, 6 and 9).

Table 2. Kumada cross-coupling reaction of aryl chlorides with Grignard reagents catalyzed by **5b**[a].

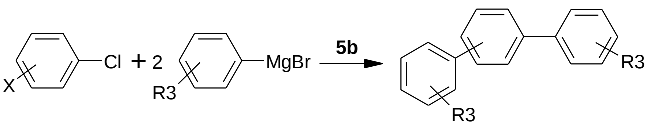


Entry	R1	R2	Yield (%)[b]
1	H	*p*-Me	92
2	H	*o*-Me	86
3	H	*p*-OMe	96
4	Me	H	91
5	Me	*o*-Me	83
6	Me	*p*-OMe	95
7	OMe	H	93
8	OMe	*o*-Me	83
9	OMe	*p*-Me	89
10	CF_3	H	84
11	CF_3	*p*-OMe	87

[a] 25 °C, 24 hrs, 2 mol % **5b**, 0.5 mmol aryl chloride, 0.75 mmol Grignard reagent. [b] Isolated yields.

Complex **5b** also showed good catalytic activity for the "one-pot" double coupling of aryl dichlorides with Grignard reagents though this kind of coupling could be more challenging. Because aryl dichlorides have two reaction sites, 2.5 equiv of the Grignard reagent and a catalyst loading of 3 mol % were used. From Table 3 it could be seen that due to the potential steric hindrance effect, only moderate yields were obtained for *o*-dichlorobenzene as substrates (Table 3, entries 1 - 3), whereas *m*- and *p*-dichlorobenzene could be converted to the corresponding terphenyls in good yields (Table 3, entries 4 - 10).

Table 3. Kumada cross-coupling reaction of aryl dichlorides with Grignard reagents catalyzed by **5b**[a].



Entry	X	R3	Yield (%)[b]
1	*o*-Cl	H	72
2	*o*-Cl	*p*-Me	65
3	*m*-Cl	H	92
4	*m*-Cl	*p*-Me	89
5	*m*-Cl	*p*-OMe	93
6	*p*-Cl	H	94
7	*p*-Cl	*p*-Me	89
8	*p*-Cl	*o*-Me	85

[a] 25 ^{o}C, 24 hrs, 3 mol % **5b**, 0.5 mmol aryl dichloride, 1.25 mmol Grignard reagent. [b] Isolated yield.

In summary, three [CNN]-pincer nickel(II) complexes (**5a - 5c**) with NHC and amine as donors were designed and fully characterized. X-ray crystallography shows that the NHC and amine coordinate to the nickel centre in a pincer fashion to form the five- and six-membered rings. With a catalyst loading of 2 mol %, Complex **5b** displayed high activity and was able to efficiently catalyze the cross-coupling of aryl chlorides or dichlorides with aryl Grignard reagents under mild conditions.

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