Dalton
Transactions

COMMUNICATION

Cite this: *Dalton Trans.*, 2014, **43**, 9410

Received 13th February 2014,
Accepted 17th April 2014

DOI: 10.1039/c4dt00461b

www.rsc.org/dalton

[CNN]-pincer nickel(II) complexes of N-heterocyclic carbene (NHC): synthesis and catalysis of the Kumada reaction of unactivated C–Cl bonds†

Yunqiang Sun, Xiaoyan Li and Hongjian Sun*

Three novel [CNN]-pincer nickel(II) complexes with NHC-amine arms were synthesized in 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 attention owing to the unique properties provided by two different E-donors. Therefore, the [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 the 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 ligand for formation of pincer complexes. NHC based [CCC][9] or [CNC][10] pincer complexes and amine 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-amine 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 donors 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.

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 yields.[17] Treatment of **3** with RX under reflux afforded the unsymmetric pincer ligands **4a–4c**. After the lithiation of **4a–4c**, $Ni(dme)Cl_2$ 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% (Scheme 1).

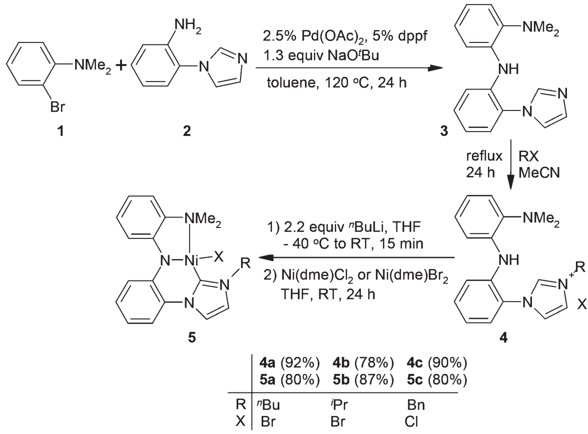
Complexes **5a–5c** were very air stable both in the solid state and in solution. In the ^1H NMR spectra of ligands **4a–4c**, the NHC protons appeared at 10.49, 10.58 and 10.81 ppm while amine protons (PhN*H*Ph) were registered at 6.56, 6.52 and 6.64 ppm. After the Ni–N coordination, the singlet of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

5b as green crystals could be obtained through solvent evaporation from Et_2O. The structure of **5b** was confirmed by X-ray crystallographic analysis (Fig. 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

---

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

† Electronic supplementary information (ESI) available: Detailed experimental procedures, characterization data of products and the crystallographic data for **5b**. CCDC 981371. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00461b



Scheme 1 Synthesis of the [CNN]-ligands **4a–4c**.

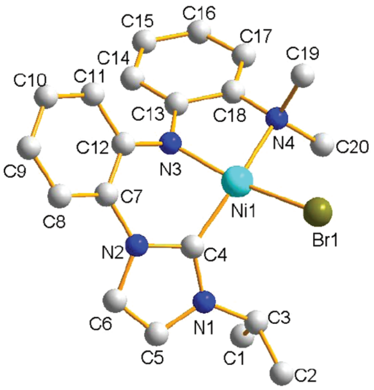
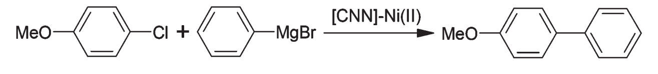


Fig. 1 X-ray structure of complex **5b** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): N3–Ni1 1.847(5), N4–Ni1 2.013(6), C4–Ni1 1.881(7), Br1–Ni1 2.327(1); N3–Ni1–C4 88.2(3), N3–Ni1–N4 85.6(2), C4–Ni1–N4 161.2(3), N3–Ni1–Br1 161.0(2),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

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 hand, **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 the R group on the catalytic activity of the complexes was obvious; excessive steric hindrance resulted in the increase of the 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 NHC based [CNC][10f] and amine based [NNN][11d] symmetric pincer Ni(II) complexes, the [CNN]-pincer Ni(II) complexes were more efficient. THF was the best reaction medium compared with toluene, Et$_2$O and DME (Table 1, entries 5–7).

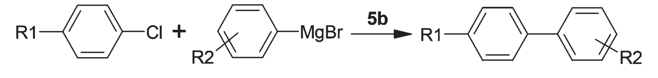
Table 1 Kumada cross-coupling of 1-chloro-4-methoxybenzene with phenyl magnesium bromide catalyzed by a nickel catalyst[a]



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$_2$O	51
7	**5b** (2)	DME	36

[a] 25 °C, 24 h, 0.5 mmol *p*-MeOC$_6$H$_4$Cl, 0.75 mmol C$_6$H$_5$MgBr. [b] Isolated yields.

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 h, 2 mol% **5b**, 0.5 mmol aryl chloride, and 0.75 mmol Grignard reagent. [b] Isolated yields.

Under the optimized conditions, we examined the substrate scope using **5b** (2 mol%) as a catalyst in THF at 25 °C for 24 h. Interestingly, activated aryl chlorides with an electron-withdrawing group (–CF$_3$) gave relatively lower yields (Table 2, entries 10 and 11) compared to the unactivated aryl chlorides including *p*-MeC$_6$H$_4$Cl and *p*-MeOC$_6$H$_4$Cl (Table 2, entries 4, 6 and 7). When a sterically hindered Grignard reagent, such as *o*-MeC$_6$H$_4$MgBr, was used as the nucleophilic species, only lower yields were obtained (Table 2, entries 2, 5 and 8) than those with less hindered reagents *p*-MeC$_6$H$_4$MgBr and *p*-MeOC$_6$H$_4$MgBr (Table 2, entries 1, 3, 6 and 9).

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 the substrate (Table 3, entries 1 and 2), whereas *m*- and *p*-dichlorobenzene could be

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 °C, 24 h, 3 mol% **5b**, 0.5 mmol aryl dichloride, and 1.25 mmol Grignard reagent. [b] Isolated yields.

converted to the corresponding terphenyls in good yields (Table 3, entries 3–8).

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.

We gratefully acknowledge the support by NSF China no. 21072113 and Shandong ZR2010BZ002.

Notes and references

1 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020.

2 G. van Koten, K. Timmer, J. G. Noltes and A. L. Spek, *J. Chem. Soc., Chem. Commun.*, 1978, 250.

3 (*a*) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759; (*b*) D. Benito-Garagorri and K. Kirchner, *Acc. Chem. Res.*, 2008, **41**, 201; (*c*) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750.

4 (*a*) G. van Koten and D. Milstein, *Organometallic Pincer Chemistry*, Wiley, 2013; (*b*) J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761.

5 (*a*) R. Langer, G. Leitus, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2011, **50**, 2120; (*b*) M. Albrecht and M. M. Lindner, *Dalton Trans.*, 2011, **40**, 8733; (*c*) J. Aydin, K. S. Kumar, M. J. Sayah, O. A. Wallner and K. J. Szabó, *J. Org. Chem.*, 2007, **72**, 4689.

6 (*a*) J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *J. Am. Chem. Soc.*, 2005, **127**, 10840; (*b*) C. Gunanathan and D. Milstein, *Acc. Chem. Res.*, 2011, **44**, 588; (*c*) M. Yang, Y. Liu, J. Gong and M. Song, *Organometallics*, 2011, **30**, 3793; (*d*) J. Niu, X. Hao, J. Gong and M. Song, *Dalton Trans.*, 2011, **40**, 5135; (*e*) N. Liu, L. Wang and Z. Wang, *Chem. Commun.*, 2011, **47**, 1598; (*f*) X. Zhang and Z. Wang, *J. Org. Chem.*, 2012, **77**, 3658.

7 (*a*) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (*b*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (*c*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*d*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768; (*e*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (*f*) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677; (*g*) M. J. Iglesias, A. Prieto and M. C. Nicasio, *Org. Lett.*, 2012, **14**, 4318; (*h*) T. Hatakeyama, S. Hashimoto, K. Ishizuka and M. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 11949; (*i*) R. Jothibasu, K. Huang and H. V. Huynh, *Organometallics*, 2010, **29**, 3746.

8 (*a*) J. Berding, J. A. van Paridon, V. H. S. van Rixel and E. Bouwman, *Eur. J. Inorg. Chem.*, 2011, 2450; (*b*) C. Valente, S. Calimsiz, K. H. Hoi, D. Mallik, M. Sayah and M. G. Organ, *Angew. Chem., Int. Ed.*, 2012, **51**, 3314.

9 (*a*) A. J. Huckaba, B. Cao, T. K. Hollis, H. U. Valle, J. T. Kelly, N. I. Hammer, A. G. Oliver and C. E. Webster, *Dalton Trans.*, 2013, **42**, 8820; (*b*) A. R. Chianese, S. E. Shaner, J. A. Tendler, D. M. Pudalov, D. Y. Shopov, D. Kim, S. L. Rogers and A. Mo, *Organometallics*, 2012, **31**, 7359.

10 (*a*) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239; (*b*) K. Inamoto, J. Kuroda, K. Hiroya, Y. Noda, M. Watanabe and T. Sakamoto, *Organometallics*, 2006, **25**, 3095; (*c*) W. Wei, Y. Qin, M. Luo, P. Xia and M. Wong, *Organometallics*, 2008, **27**, 2268; (*d*) M. Hernández-Juárez, M. Vaquero, E. Álvarez, V. Salazar and A. Suárez, *Dalton Trans.*, 2013, **42**, 351; (*e*) M. Xu, X. Li, Z. Sun and T. Tu, *Chem. Commun.*, 2013, **49**, 11539; (*f*) K. Inamoto, J. Kuroda, T. Sakamoto and K. Hiroya, *Synthesis*, 2007, 2853.

11 (*a*) O. Vechorkin and X. Hu, *Angew. Chem., Int. Ed.*, 2009, **48**, 2937; (*b*) O. Vechorkin, Z. Csok, R. Scopelliti and X. Hu, *Chem. – Eur. J.*, 2009, **15**, 3889; (*c*) P. Ren, O. Vechorkin, K. von Allmen, R. Scopelliti and X. Hu, *J. Am. Chem. Soc.*, 2011, **133**, 7084; (*d*) O. Vechorkin, V. Proust and X. Hu, *J. Am. Chem. Soc.*, 2009, **131**, 9756; (*e*) J. Breitenfeld, O. Vechorkin, C. Corminboeuf, R. Scopelliti and X. Hu, *Organometallics*, 2010, **29**, 3686.

12 (*a*) P. Steenwinkel, R. A. Gossage and G. van Koten, *Chem. – Eur. J.*, 1998, **4**, 759; (*b*) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750; (*c*) J. S. Fossey and C. J. Richards, *Organometallics*, 2004, **23**, 367; (*d*) S. Gosiewska, S. M. Herreras, M. Lutz, A. L. Spek, R. W. A. Havenith, G. P. M. van Klink, G. van Koten and R. J. M. K. Gebbink, *Organometallics*, 2008, **27**, 2549.

13 (*a*) J. Kuroda, K. Inamoto, K. Hiroya and T. Doi, *Eur. J. Org. Chem.*, 2009, 2251; (*b*) K. Inamoto, J. Kurod, E. Kwon, K. Hiroy and T. Doi, *J. Organomet. Chem.*, 2009, **694**, 389; (*c*) S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller and

R. H. Crabtree, *Organometallics*, 2001, **20**, 5485; (*d*) K. Inamoto, J. Kuroda, K. Hiroya, Y. Noda, M. Watanabe and T. Sakamoto, *Organometallics*, 2006, **25**, 3095; (*e*) O. Vechorkin, D. Barmaz, V. Proust and X. Hu, *J. Am. Chem. Soc.*, 2009, **131**, 12078.

14 (*a*) J. Cho, T. K. Hollis, T. R. Helgerta and E. J. Valente, *Chem. Commun.*, 2008, 5001; (*b*) T. R. Helgert, T. K. Hollis and E. J. Valente, *Organometallics*, 2012, **31**, 3002.

15 (*a*) W. Zuo and P. Braunstein, *Organometallics*, 2012, **31**, 2606; (*b*) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon and D. Milstein, *Nat. Chem.*, 2011, **3**, 609.

16 (*a*) C. Zhang and Z. Wang, *Organometallics*, 2009, **28**, 6507; (*b*) M. Boronat, A. Corma, C. González-Arellano, M. Iglesias and F. Sánchez, *Organometallics*, 2010, **29**, 134; (*c*) E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon and D. Milstein, *Organometallics*, 2011, **30**, 3826; (*d*) Y. Sun, C. Koehler, R. Tan, V. T. Annibale and D. Song, *Chem. Commun.*, 2011, **47**, 8349; (*e*) W. Guo and Z. Wang, *J. Org. Chem.*, 2013, **78**, 1054.

17 Z. Csok, O. Vechorkin, S. B. Harkins, R. Scopelliti and X. Hu, *J. Am. Chem. Soc.*, 2008, **130**, 8156.

18 A. Liu, X. Zhang and W. Chen, *Organometallics*, 2009, **28**, 4868.