6636 *Organometallics* **2007,** *26,* 6636–6642

Synthesis and Structural Characterization of Nickel(II) Complexes Supported by Pyridine-Functionalized N-Heterocyclic Carbene Ligands and Their Catalytic Acitivities for Suzuki Coupling

Zhenxing Xi,[†] Xiaoming Zhang,[†] Wanzhi Chen,*,[†] Shizhou Fu,[‡] and Daqi Wang[‡]

Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou 310028, People's Republic of China, and School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, People's Republic of China

Received August 5, 2007

The imidazolium salts bis(*N*-pyridylimidazoliumyl)methane hexafluorophosphate ($[H_2L1](PF_6)_2$) and bis(*N*-picolyl)benzimidazoliumyl)methane hexafluorophosphate ($[H_2L2](PF_6)_2$) as the precursors of potentially tetradentate NHC ligands were synthesized in 63–98% yields. Their reactions with Ag_2O afforded silver−NHC complexes $[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3$ (**1**) and $[Ag_4(L2)_2(CH_3CN)_2](PF_6)_4$ (**2**), respectively. Further reactions of these silver complexes as carbene transfer reagents yielded square-planar nickel(II) complexes $[NiL1](PF_6)_2$ (**3**) and $[NiL2](PF_6)_2$ (**4**), respectively. These silver and nickel complexes have been fully characterized by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis. Both **3** and **4** catalyzed Suzuki-type cross-coupling of aryl chlorides and bromides containing electron-withdrawing and electron-donating substituents. Complex **3** is a more active catalyst under mild conditions.

Introduction

Recently, N-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry and catalysis.[1] The strong σ-donating ability of these N-heterocyclic carbenes leads to the formation of many stable metal−carbene complexes, which are good catalysts in numerous organic transformations, especially C−C[2] and C−N[3] coupling reactions. In addition, the metal−NHC complexes are also promising candidates for metal−organic materials.[4] The imidazolylidenes are readily accessible through deprotonation of *N,N′*-disubstituted imidazolium salts, and their corresponding metal complexes exhibit enhanced reactivity compared to analogous phosphine complexes. They provide a powerful complement to phosphine/arsine ligands for a wide array of reactions from olefin metathesis to cross-coupling reactions.

The construction of carbon−carbon bonds via transition metal-catalyzed cross-coupling reactions is one of the most important organic processes. Although several metals have proven to be active, palladium is the most efficient one and shows remarkable catalytic activities in various C−C coupling reactions. Thus palladium-catalyzed cross-coupling reactions between Ar−M (M = SnR_3,[5] $B(OR)_2$,[6] BiR_2,[7] or MgX[8]) and Ar−X (X = halogen, sulfonate, or triflate) for the synthesis of biaryl derivatives have been widely investigated. These reactions provide a convenient and practical approach for various aromatic compounds.

---

* Corresponding author. Tel & fax: (+)86-571-88273314. E-mail: chenwzz@zju.edu.cn.

[†] Zhejiang University.

[‡] Liaocheng University.

(1) (a) Bourisou, D.; Guerret, O.; Gabbaı, F. P.; Bertrand, G. *Chem. Rev* **2000**, *100*, 39. (b) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617–618*, 17. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (d) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (e) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951.

(2) (a) Yang, C.; Nolan, S. P. *Organometallics* **2002**, *21*, 1020. (b) Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991. (c) Yang, C.; Nolan, S. P. *J. Org. Chem.* **2002**, *67*, 591. (d) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194. (e) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470. (f) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804. (g) Ray, L.; Shaikh, M. M.; Ghosh, P. *Organometallics* **2007**, *26*, 958. (h) Karimi, B.; Enders, D. *Org. Lett.* **2006**, *8*, 1237. (i) Wang, R.; Twamley, B.; Shreeve, J. M. J. *Org. Chem.* **2006**, *71*, 426. (j) Bedford, R. B.; Betham, M.; Bruce, D. W.; Danopoulos, A. A.; Frost, R. M.; Hird, M. *J. Org. Chem.* **2006**, *71*, 1104. (k) Frey, G. D.; Schutz, J.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2005**, *24*, 4416.

(3) (a) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307. (b) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423. (c) Grasa, G. A.; Viciu, M. S.; Huang, J.; Nolan, S. P. *J. Org. Chem.* **2001**, *66*, 7729. (d) Viciu, M. S.; Kelly, R. A., III; Stevens, E. D.; Naud, F.; Studer, M.; Nolan, S. P. *Org. Lett.* **2003**, *5*, 1479. (e) Viciu, M. S.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 2229. (f) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (g) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (h) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125.

(4) (a) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496. (b) Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Chou, Y. L.; Zhang, Z.-Z. *Organometallics* **2003**, *22*, 309. (c) Lee, C. K.; Lee, K. M.; Lin, I. J. B. *Organometallics* **2002**, *21*, 10.

(5) (a) Gallagher, W. P.; Maleczka, R. E., Jr. *J. Org. Chem.* **2005**, *70*, 841. (b) Lin, J. H.; Liang, Y.; Wang, D. P.; Liu, W. J.; Xie, Y. X.; Yin, D. L. *J. Org. Chem.* **2005**, *70*, 2832. (c) Elzein, E.; Palle, V.; Wu, Y.; Maa, T.; Zeng, D.; Zablocki, J. *J. Med. Chem.* **2004**, *47*, 4766. (d) Romo, D.; Choi, N. S.; Li, S.; Buchler, I.; Shi, Z.; Liu, J. O. *J. Am. Chem. Soc.* **2004**, *126*, 10582. (e) Liu, J.; Kadnikova, E. N.; Liu, Y.; McGehee, M. D.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9486. (f) Ricci, A.; Angelucci, F.; Bassetti, M.; Sterzo, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 1060.

(6) (a) Taylor, R. H.; Felpin, F. X. *Org. Lett.* **2007**, *9*, 2911. (b) Li, S.; Lin, Y.; Cao, J.; Zhang, S. *J. Org. Chem.* **2007**, *72*, 4067. (c) Fang, Y. Q.; Karisch, R.; Lautens, M. *J. Org. Chem.* **2007**, *72*, 1341. (d) Buszek, K. R.; Brown, N. *Org. Lett.* **2007**, *9*, 707. (e) Prediger, P.; Moro, A. V.; Nogueira, C. W.; Savegnago, L.; Menezes, P. H.; Rocha, J. B. T.; Zeni, G. *J. Org. Chem.* **2006**, *71*, 3786. (f) Raghavanpillai, A.; Burton, D. J. *J. Org. Chem.* **2006**, *71*, 194. (g) Chang, Y. C.; Lee, J. C.; Hong, F. E. *Organometallics* **2005**, *24*, 5686.

(7) Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *24*, 5025.

(8) (a) Martin, R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3844. (b) Hartwig, J. F.; Roy, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 8704. (c) Yang, L. M.; Huang, L. F.; Luh, T. Y. *Org. Lett.* **2004**, *6*, 1461. (d) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884.

10.1021/om700796g CCC: $37.00

Nickel is preferable to palladium because it is much cheaper and easier to remove from products. Much effort has been devoted to the synthesis and structural characterization of nickel complexes containing NHC ligands.[9] Although nickel−NHC complexes have also shown catalytic activities, in contrast to the large number of reports on palladium catalysts, the nickel−NHC complexes for C−C coupling reactions have not been well studied.[10] In addition, most of the so far reported nickel catalysts use nickel(0) such as $Ni(COD)_2$ as catalyst precursor, which is expensive and very air-sensitive.[11] The active nickel(0) may also be generated in situ by reductions of Ni(II) with reductants such as BuLi and alkoxide-activated sodium hydride.[12] This also brings about handling inconvenience since the reductants are usually also air-sensitive.

Although a large number of transition metal carbene complexes have now been known, very few contain chelating carbenes.[10e,f,13] We have recently reported the synthesis and structures of a family of silver clusters stabilized by pyridine-functionalized bis(*N*-heterocyclic carbene) ligands.[14] These silver aggregates contain short Ag−Ag contacts and show intensely luminescent properties. We have noted that cationic nickel(II) carbene complexes containing hemilabile picolyl imidazolylidene ligands show good catalytic activities for olefin polymerization[13b] and Suzuki coupling of aryl halides with phenyl boronic acid.[10f] As a continuation, here in this paper we describe the synthesis and structural characterization of a few nickel complexes containing pyridine-functionalized bis(*N*-heterocyclic carbene) ligands. These nickel−NHC complexes are highly efficient catalysts for Suzuki coupling reactions of aryl chlorides and bromides under mild conditions.

Experimental Section

All the chemicals were obtained from commercial suppliers and used without further purification. 2-(Imidazolyl)pyridine,[15] $Ni(DME)Cl_2$ (DME = 1,2-dimethoxyethane),[16a] and $Ni(PPh_3)_2Cl_2$[16b] were prepared according to known procedures. Elemental analyses were performed on a Flash EA1112 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from TMS at $\delta = 0$ ppm, and coupling constants (J) are expressed in Hz.

Synthesis of $[H_2L1](PF_6)_2$. A solution of 2-(imidazolyl)pyridine (0.725 g, 5.0 mmol) in 5 mL of dibromomethane was refluxed overnight. The resulting white solid was filtered and then dissolved in 10 mL of water. Subsequent addition of NH_4PF_6 (1.0 g, 6 mmol) to the aqueous solution afforded a white precipitate, which was collected by filtration and dried. Yield: 1.45 g, 98%. Anal. Calcd for $C_{17}H_{16}N_6P_2F_{12}$: C, 34.36; H, 2.71; N, 14.14. Found: C, 33.95; H, 2.60; N, 13.90. ^{1}H NMR (dmso-*d*$_6$): 10.37 (s, NC*H*N, 2H), 8.71 (d, J = 4.8 Hz, *o*-C_5H_4N, 2H), 8.64 (s, NCHC*H*N, 2H), 8.26 (m, NC*H*CHN + *p*-C_5H_4N, 4H), 8.05 (d, J = 8.4 Hz, *m*-C_5H_4N, 2H), 7.70 (2d, J = 4.8, 7.2 Hz, *m*-C_5H_4N, 2H), 6.83 (s, NC*H*$_2$N, 2H). ^{13}C NMR (dmso-*d*$_6$): 149.9, 146.5, 141.3, 137.5 (N*C*HN), 126.2, 123.8, 120.2, 59.62.

Synthesis of $[H_2L2](PF_6)_2$. The compound was prepared according to the same procedure as for H_2L1 starting from *N*-pyridylmethylbenzimidazole and CH_2Br_2. Yield: 63%. Anal. Calcd for $C_{27}H_{24}F_{12}N_6P_2$: C, 44.89; H, 3.35; N, 11.63. Found: C, 44.51; H, 3.56; N, 11.79. ^{1}H NMR (dmso-*d*$_6$): 10.50 (s, NC*H*N, 2H), 8.45 (d, J = 4.8 Hz, *o*-C_5H_4N, 2H), 8.34 (d, J = 8.4 Hz, *p*-C_5H_4N, 2H), 8.04 (d, J = 8.4 Hz, *m*-C_5H_4N, 2H), 7.92 (dt, J = 1.6, 7.6 Hz, C_6H_4, 2H), 7.79 (t, J = 7.6 Hz, C_6H_4, 2H), 7.72 (m, *m*-C_5H_4N + C_6H_4, 4H), 7.52 (s, NC*H*$_2$N, 2H), 7.39 (2d, J = 1.6, 7.6 Hz, C_6H_4, 2H), 6.00 (s, NC*H*$_2$Py, 4H). ^{13}C NMR (dmso-*d*$_6$): 152.3, 149.5, 144.8 (N*C*HN), 137.6, 131.2, 130.1, 127.4, 127.3, 123.8, 122.9, 114.2, 113.7, 55.6, 50.1.

Synthesis of $[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3\cdot 2H_2O\cdot 0.5HPF_6$, 1. A solution of H_2L1 (178 mg, 0.3 mmol) in 10 mL of CH_3CN was treated with Ag_2O (464 mg, 2 mmol). The mixture was allowed to react at room temperature for 10 h, then filtered to remove a small amount of unreacted Ag_2O. The filtrate was condensed to ca. 2 mL, and a white solid was isolated after addition of 20 mL of Et_2O. Yield: 185 mg, 81%. Anal. Calcd for $C_{38}H_{34.5}Ag_3N_{14}P_{3.5}F_{21}$ ($[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3\cdot 0.5HPF_6$): C, 30.06; H, 2.29; N, 12.92. Found: C, 30.36; H, 2.44; N, 12.56. ^{1}H NMR (dmso-*d*$_6$): 8.27 (d, J = 1.6 Hz, *o*-C_5H_4N, 4H), 8.14 (s, NC*H*CHN, 4H), 7.97 (d, J = 4.8 Hz, *p*-C_5H_4N, 4H), 7.87 (m, *m*-C_5H_4N + NCHC*H*N, 8H), 7.34 (dt, J = 1.6 Hz, 4.8 Hz, *m*-C_5H_4N, 4H), 6.88 (br, NC*H*$_2$N, 4H), 2.07 (s, C*H*$_3$CN, 6H). ^{13}C NMR (dmso-*d*$_6$): 181.9 (Ag-*C*), 150.1, 148.8, 140.4, 124.6, 123.7, 121.7, 118.4, 115.8, 65.8, 1.5.

Synthesis of $[Ag_4(L2)_2(CH_3CN)_2](PF_6)_4\cdot 2CH_3CN$, 2. A solution of H_2L2 (144 mg, 0.20 mmol) in 10 mL of acetonitrile was treated with Ag_2O (92 mg, 0.40 mmol) at room temperature. After Ag_2O completely disappeared, the solution was filtered and concentrated to ca. 2 mL. Addition of 20 mL of diethyl ether afforded a white solid. Yield: 101 mg, 48%. Anal. Calcd for $C_{64}H_{59}Ag_4F_{24}N_{17}P_4$ ($[Ag_4(L2)_2(CH_3CN)_2](PF_6)_4\cdot 3CH_3CN$): C, 37.00; H, 2.86; N, 11.46. Found: C, 37.10; H, 3.11; N, 11.21. ^{1}H NMR (dmso-*d*$_6$): 8.60 (d, J = 4.4 Hz, *o*-C_5H_4N, 4H), 8.13 (d, J = 7.2 Hz, *p*-C_5H_4N, 4H), 7.98 (d, J = 7.6 Hz, C_6H_4, 8H), 7.81 (d, J = 7.2 Hz, *m*-C_5H_4N, 4H), 7.62 (m, *m*-C_5H_4N + C_6H_4,

---

(9) (a) Malyshev, D. A.; Scott, N. M.; Marion, N.; Stevens, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nolan, S. P. *Organometallics* **2006**, *25*, 4462. (b) Silva, L. C.; Gomes, P. T.; Veiros, L. F.; Pascu, S. I.; Duarte, M. T.; Namorado, S.; Ascenso, R.; Dias, A. R. *Organometallics* **2006**, *25*, 4391. (c) Schaub, T.; Backes, M.; Radius, U. *Organometallics* **2006**, *25*, 4196. (d) Huynh, H. V.; Holtgrewe, C.; Pape, T.; Koh, L. L.; Hahn, E. *Organometallics* **2006**, *25*, 245. (e) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Qi.; Zhang, Y. *Organometallics* **2005**, *24*, 5925. (f) Liu Q.-X.; Xu, F.-B.; Li, Q.-S.; Song, H.-B.; Zhang, Z.-Z. *Organometallics* **2004**, *23*, 610. (g) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490. (h) Hou, H.; Gantzel, P. K.; Kubiak, C. P. *J. Am. Chem. Soc.* **2003**, *125*, 9564.

(10) (a) McGuinness, D. S.; Cavell, K. J. *Organometallics* **1999**, *18*, 1596. (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Hermann, W. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3387. (c) Sato, Y.; Sawaki, R.; Mori, M. *Organometallics* **2001**, *20*, 5510. (d) Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698. (e) Inamoto, K.; Kuroda, J.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T. *Organometallics* **2006**, *25*, 3095. (f) Chiu, P. L.; Lai, C.-L.; Chang, C.-F.; Hu, C.-H.; Lee, H. M. *Organometallics* **2005**, *24*, 6169.

(11) (a) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054. (b) Lipshutz, B. H.; Ueda, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4492. (c) Lipshutz, B. H.; Tasler, S.; Chrisman, W.; Spliethoff, B.; Tesche, B. *J. Org. Chem.* **2003**, *68*, 1177. (d) Tasler, S.; Lipshutz, B. H. *J. Org. Chem.* **2003**, *68*, 1190. (e) Gradel, B.; Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2001**, *42*, 5689. (f) Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029.

(12) (a) Brenner, E.; Fort, Y. *Tetrahedron Lett.* **1998**, *39*, 5359. (b) Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron* **1999**, *55*, 12829. (c) Desmarets, C.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2000**, *41*, 2875. (d) Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2000**, *41*, 2881. (e) Desmarets, C.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2001**, *42*, 247. (f) Desmarets, C.; Schneider, R.; Fort, Y. *Tetrahedron* **2001**, *57*, 7657. (g) Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron* **2002**, *58*, 6913. (h) Desmarets, C.; Schneider, R.; Fort, Y.; Walcarius, A. *J. Chem. Soc., Perkin Trans. 2* **2002**, *1844*. (i) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y. *Org. Lett.* **2003**, *5*, 2311. (j) Tang, Z.-Y.; Hu, Q.-S. *J. Org. Chem.* **2006**, *71*, 2167. (k) Saito, S.; Oh-tani, S.; Miyaura, N. *J. Org. Chem.* **1997**, *62*, 8024.

(13) (a) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841. (b) Lee, C.-C.; Ke, W.-C.; Chan, K.-T.; Lai, C.-L.; Hu, C.-H.; Lee, H. M. *Chem.*−*Eur. J.* **2007**, *13*, 582. (c) Wang, X.; Liu, S.; Jin, G.-X. *Organometallics* **2004**, *23*, 6002. (d) Douthwaite, R. E.; Haussinger, D.; Green, M. L. H.; Silcock, P. J. *Organometallics* **1999**, *18*, 4584.

(14) (a) Zhou, Y.; Chen, W. *Organometallics* **2007**, *26*, 2742. (b) Liu, B.; Chen, W.; Jin, S. *Organometallics* **2007**, *26*, 3660.

(15) Zhang, H.; Cai, Q.; Ma, D. W. *J. Org. Chem.* **2005**, *70*, 5164.

(16) (a) Tyree, S. Y., Jr. *Inorg. Synth.* **1953**, *4*, 104. (b) Venanzi, L. M. *J. Chem. Soc.* **1958**, *719*.

Table 1. Summary of the Crystallographic Data for 1–4

	$[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3 \cdot 2H_2O \cdot 0.5HPF_6$, **1**	$[Ag_4(L2)_2(CH_3CN)_2](PF_6)_4 \cdot 2CH_3CN$, **2**	$[Ni(L1)](PF_6)_2$, **3**	$[Ni(L2)](PF_6)_2 \cdot 0.5HPF_6$, **4**
formula	$C_{38}H_{38.5}Ag_3F_{21}N_{14}O_2P_{3.5}$	$C_{62}H_{56}Ag_4F_{24}N_{16}P_4$	$C_{17}H_{14}F_{12}N_6$ NiP_2	$C_{27}H_{22.5}F_{15}N_6NiP_{2.5}$
fw	1553.83	2036.59	650.99	851.62
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$
a, Å	13.713(3)	12.925(2)	16.612(2)	31.200(6)
b, Å	14.184(3)	50.191(10)	11.5736(16)	12.400(3)
c, Å	16.298(4)	13.278(3)	14.089(2)	17.250(3)
α, deg	93.397(2)			
β, deg	105.256(2)	108.770(3)	124.863(2)	113.370(3)
γ, deg	98.345(3)			
V, Å3	3010.0(12)	8156.0(3)	2222.6(5)	6126.0(2)
Z	2	4	4	8
D_{calcd}, Mg/m^3	1.714	1.659	1.945	1.847
no. of reflns collected	15 452	40 765	5648	15 282
no. of indep reflns (R_{int})	10 331 (0.0223)	14 297 (0.0966)	1956 (0.0221)	5300 (0.1012)
goodness-of-fit on F^2	1.072	0.966	1.014	1.157
R ($I > 2\sigma I$)	0.0866, 0.2392	0.0921, 0.2059	0.0327, 0.0895	0.0999, 0.2128

12H), 7.24 (NC*H*$_2$N, 4H), 5.91 (s, NC*H*$_2$Py, 8H), 2.07 (s, C*H*$_3$CN, 6H). ^{13}C NMR (dmso-d_6): 190.3 (Ag-*C*), 154.4, 151.1, 139.3, 133.9, 133.6, 125.6, 125.5, 124.9, 124.8, 118.4, 113.3, 112.2, 59.1, 57.4, 1.5.

Synthesis of [Ni(L1)](PF$_6$)$_2$, 3. A solution of H_2L1 (178 mg, 0.3 mmol) in 10 mL of CH_3CN was treated with Ag_2O (464 mg, 2 mmol). The mixture was allowed to react at room temperature for 10 h, and then filtered to remove a small amount of unreacted Ag_2O. The filtrate was treated with $Ni(PPh_3)_2Cl_2$ (196 mg, 0.3 mmol). After it was stirred for 10 h at room temperature, the solution was filtered. The filtrate was concentrated to ca. 5 mL. Addition of 20 mL of diethyl ether gave a yellow solid. Yield: 143 mg, 73%. Anal. Calcd for $C_{17}H_{14}F_{12}N_6NiP_2$: C, 31.37; H, 2.17; N, 12.91. Found: C, 31.69; H, 2.28; N, 12.75. ^{1}H NMR (dmso-d_6): 8.88 (d, J = 5.2 Hz, *o*-C_5H_4N, 2H), 8.62 (d, J = 1.2 Hz, NC*H*CHN, 2H), 8.51 (t, J = 7.2 Hz, *p*-C_5H_4N, 2H), 8.29 (d, J = 8.4 Hz, *m*-C_5H_4N, 2H), 8.13 (d, J = 1.2 Hz, NCHC*H*N, 2H), 7.77 (t, J = 7.2 Hz, *m*-C_5H_4N, 2H), 6.68 (s, NC*H*$_2$N, 2H). ^{13}C NMR (dmso-d_6): 158.9 (Ni-*C*), 150.0, 149.6, 144.1, 124.7, 124.2, 119.0, 112.6, 63.9.

Synthesis of [Ni(L2)](PF$_6$)$_2$·0.5HPF$_6$, 4. The compound was obtained as a yellow solid using the same procedure as for **3** by using H_2L2 (72 mg, 0.1 mmol), Ag_2O (46 mg, 0.2 mmol), and $Ni(DME)Cl_2$ (21 mg, 0.1 mmol). Yield: 53 mg, 62%. Anal. Calcd for $C_{27}H_{22}F_{12}N_6NiP_2$ ([Ni(L2)](PF$_6$)$_2$): C, 41.62; H, 2.85; N, 10.79. Found: C, 41.21; H, 3.12; N, 11.25. ^{1}H NMR (dmso-d_6): 8.69 (d, J = 5.2 Hz, *o*-C_5H_4N, 2H), 8.32 (t, J = 7.6 Hz, C_6H_4, 2H), 8.18 (m, *p*-C_5H_4N + *m*-C_5H_4N, 4H), 8.39 (d, J = 8.4 Hz, *m*-C_5H_4N, 2H), 7.71 (m, C_6H_4, 4H), 7.65 (t, J = 6.8 Hz, C_6H_4, 2H), 7.03 (s, NC*H*$_2$N, 2H), 6.19 (s, NC*H*$_2$Py, 4H). ^{13}C NMR (dmso-d_6): 159.0 (Ni-*C*), 153.3, 152.7, 141.8, 133.9, 132.4, 125.9, 125.8, 125.8, 125.7, 125.4, 112.3, 59.7, 49.8.

X-ray Structural Determination. Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo Kα radiation (λ = 0.71073 Å) by using the $\omega-2\theta$ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software.[17] The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTXL package.[18] Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C−H distances of 0.93–0.97 Å and $U_{iso}(H) = -1.2 - 1.5U_{eq}(C)$. Hexafluorphosphate anions and solvent molecules in **1**, **2**, and **4** are severely disordered and are not well modeled. These disorders lead to high *R* values. Hydrogen atoms bound to water molecules were located in the Fourier difference map, and their distances were fixed. Further details of the structural analysis are summarized in Table 1.

Results and Discussion

Synthesis of the Imidazolium Salts and Complexes. The imidazolium salts $[H_2L1]Br_2$ and $[H_2L2]Br_2$ could be easily prepared from the condensation reaction of *N*-pyridylimidazole and *N*-pyridylmethylimidazole with CH_2Br_2. Subsequent addition of NH_4PF_6 to the aqueous solutions of the resulting imidazolium bromides yielded the corresponding hexafluorophosphates $[H_2L1](PF_6)_2$ and $[H_2L2](PF_6)_2$ in high yields. The two imidazolium salts were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as elemental analyses. ^{1}H NMR spectra in DMSO-d_6 show downfield resonance signals at ca. 10.4 ppm assignable to the acidic NCHN protons of the imidazolium rings. Treatment of the multidentate imidazolium salts with Ag_2O in CH_3CN smoothly afforded silver−NHC complexes $[Ag_3(L1)_2(CH_3CN)_2](PF_6)_3$ (**1**) and $[Ag_4(L2)_2(CH_3CN)_2](PF_6)_4$ (**2**) under mild conditions. The carbene transfer reactions of **1** and **2** with $Ni(DME)Cl_2$ afforded nickel(II) complexes $[Ni(L1)](PF_6)_2$ (**3**) and $[Ni(L2)](PF_6)_2$ (**4**), respectively. The synthetic routes for the silver and nickel complexes are illustrated in Scheme 1.

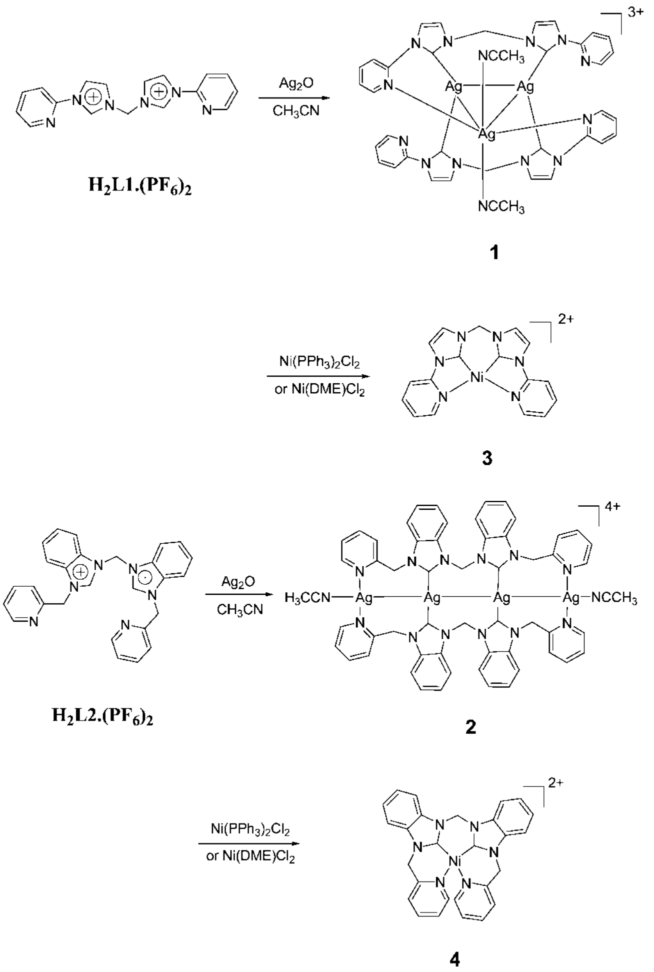
The silver− and nickel−NHC complexes **1–4** were characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectra of complexes **1–4** in DMSO-d_6 show the complete disappearance of acidic 2H-imidazolium protons, which is diagnostic for the loss of the carbonium protons and the formation of metal carbene complexes. The ^{1}H NMR spectrum of **1** gives two doublets at 7.84 and 8.14 ppm, whereas ^{1}H NMR of **3** shows two singlets at 8.13 and 8.62 ppm due to the two imidazolidene backbone protons. ^{13}C NMR spectra of the two silver−NHC complexes exhibit resonance signals as singlets at 181.9 and 190.3 ppm, respectively, assignable to carbenic carbons. These chemical shifts are quite consistent with those of previously reported silver−NHC clusters containing pyridine-functionalized NHC ligands.[14] No Ag−C coupling was observed for both silver compounds. Actually, the majority of Ag−NHC complexes undergo rapid carbene exchange in solution and only a few Ag−NHC complexes give well-resolved

---

(17) *SMART-CCD* Software, version 4.05; Siemens Analytical X-ray Instruments: Madison, WI, 1996.

(18) Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*, Program for X-ray Crystal Structure Refinement; University of Göttingen: Götingen, Germany, 1997.

Scheme 1. Synthesis of the Silver−Carbene and Nickel−Carbene Complexes



J_{AgC}.[19] In the ^{13}C spectra of the nickel complexes, the carbenic carbon resonance signals appear as singlets at 158.9 and 159.0 ppm for **3** and **4**, respectively.

Structural Description. Complexes **1**–**4** were additionally characterized by X-ray crystallography. Crystallographic information is summarized in Table 1. X-ray diffraction analysis showed that complex **1** was a trinuclear silver complex. The molecular structure consists of three independent silver atoms surrounded by two L1 ligands, shown in Figure 1. Each L1 interacts with three silver atoms in a tridentate fashion with one pyridine uncoordinated. In the triangular Ag_3 core, two silver ions are bicoordinated by two carbenic carbon atoms from two different L1 in nearly linear conformation with C−Ag−C angles of 176.5(4)° and 170.5(4)°, respectively, whereas the third one is tetracoordinated by two acetonitrile and two pyridine with the same ligands *trans*-positioned. The four Ag−C bonds are normal, and the bond distances fall in the range 2.099(10)–2.121(10) Å, which are consistent with the reported values of known silver−NHC complexes.[14,19,20] The two imidazolylidene rings bonded to the same silver atom bisect each other with dihedral angles of 32.79° and 39.52° for Ag(1) and Ag(2), respectively. Weak Ag−Ag interactions are observed for the Ag_3 ring, as indicated by the short Ag−Ag contacts of ca. 3.0 Å. These short Ag−Ag separations have also been found in a few silver clusters containing NHC ligands by us and others.[21,22] Although a few triangular Ag_3 clusters supported by NHC ligands have been previously reported,[21] trinuclear complexes containing two kinds of silver ions with quite different coordination geometry are not known.

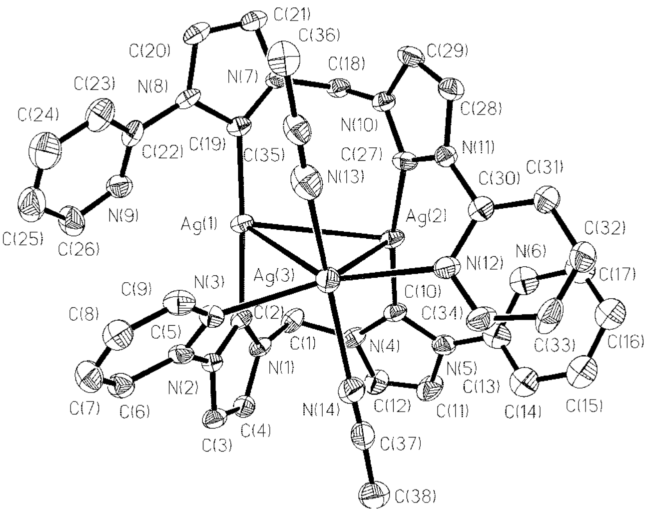


Figure 1. Molecular structure of $[Ag_3(L1)_2(CH_3CN)_2]^{3+}$ (**1**). Selected bond distances (Å) and angles (deg): Ag(1)−Ag(3) 2.966(1), Ag(1)−Ag(2) 3.299(1), Ag(2)−Ag(3) 2.955(1), Ag(1)−C(19) 2.112(10), Ag(1)−C(2) 2.121(10), Ag(2)−C(10) 2.099(11), Ag(2)−C(27) 2.099(10), Ag(3)−N(14) 2.412(13), Ag(3)−N(12) 2.472(10), Ag(3)−N(13) 2.461(17), Ag(3)−N(3) 2.497(9), C(19)−Ag(1)−C(2) 176.5(4), C(10)−Ag(2)−C(27) 170.5(4), N(14)−Ag(3)−N(12) 86.9(3), N(14)−Ag(3)−N(13) 155.9(5), N(12)−Ag(3)−N(13) 87.1(4), N(14)−Ag(3)−N(3) 87.8(4), N(12)−Ag(3)−N(3) 153.4(3), N(13)−Ag(3)−N(3) 87.2(4), Ag(3)−Ag(1)−Ag(2) 55.99(3), Ag(3)−Ag(2)−Ag(1) 56.29(3), Ag(2)−Ag(3)−Ag(1) 67.72(3).

Compound **2** is a tetranuclear silver complex having a zigzag Ag_4 chain and crystallizes in the monoclinic space group $P2_1/c$. A structural drawing of the cation is provided in Figure 2. In the asymmetric unit there are four independent silver atoms. The four silver atoms are held together by two L2 ligands with short Ag−Ag contacts, in which the Ag−Ag bond distances are 3.043(1)–3.121(1) Å. The Ag−Ag distances in **2** are comparable to the reported values in the silver−NHC complexes.[14,21,22] The two internal silver atoms are bicoordinated by two usual carbene carbon atoms in a slightly bent geometry with C−Ag−C angles of 173.0(4)° and 169.2(4)°. The Ag−C bond distances are normal and are found in the range 2.036(11)−2.145(13) Å. The reason for the deviation from linearity is probably due to the restriction imposed by the linking methylene group on the NHC rings and the silver−silver interactions. The two imidazolylidene rings around each silver atom are bisected with the dihedral angles of 71.27° and 78.22° for Ag(1) and Ag(2), respectively. The two terminal silver atoms

---

(19) (a) Lee, K. M.; H. Wang, M. J.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2852. (b) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R. *Organometallics* **2003**, *22*, 4384. (c) Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (d) Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterböck, M.; Ongania, K. H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325. (e) Ku, R. Z.; Huang, J. C.; Cho, J. Y.; Kiang, F. M.; Reddy, K. R.; Chen, Y. C.; Lee, K. J.; Lee, J. H.; Lee, G. H.; Peng, S. M.; Liu, S. T. *Organometallics* **1999**, *18*, 2145. (f) Ramnial, T.; Abernethy, C. D.; Spicer, M. D.; McKenzie, I. D.; Gay, I. D.; Clyburne, J. A. C. *Inorg. Chem.* **2003**, *42*, 1391.

(20) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.

(21) (a) Catalano, V. J.; Malwitz, M. A.; Etogo, A. O. *Inorg. Chem.* **2004**, *43*, 5714. (b) Catalano, V. J.; Malwitz, M. A. *Inorg. Chem.* **2003**, *42*, 5483. (c) Catalano, V. J.; Moore, A. L. *Inorg. Chem.* **2005**, *44*, 6558.

(22) (a) Garrison, J. C.; Simons, R. S.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. *Chem. Commun.* **2001**, *1780*. (b) Garrison, J. C.; Simons, R. S.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2003**, *673*, 1.

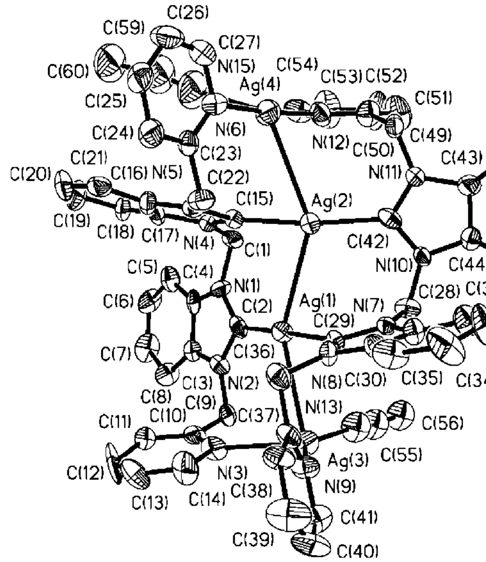


Figure 2. Molecular structure of the cation $[Ag_4(L2)_2]^{4+}$ (**2**). Selected bond distances (Å) and angles (deg): Ag(1)−Ag(2) 3.043(1), Ag(1)−Ag(3) 3.066(1), Ag(2)−Ag(4) 3.121(1), Ag(1)−C(29) 2.102(11), Ag(1)−C(2) 2.145(13), Ag(2)−C(15) 2.036(11), Ag(2)−C(42) 2.067(12), Ag(3)−N(13) 2.233(13), Ag(3)−N(9) 2.249(10), Ag(3)−N(3) 2.405(11), Ag(4)−N(6) 2.205(13), Ag(4)−N(12) 2.231(12), Ag(4)−N(15) 2.524(17), C(29)−Ag(1)−C(2) 173.0(4), C(15)−Ag(2)−C(42) 169.2(4), N(13)−Ag(3)−N(9) 141.5(4), N(13)−Ag(3)−N(3) 121.7(4), N(9)−Ag(3)−N(3) 96.6(4), N(6)−Ag(4)−N(12) 175.5(4), N(6)−Ag(4)−N(15) 86.5(5), N(12)−Ag(4)−N(15) 94.9(5), Ag(2)−Ag(1)−Ag(3) 144.54(4), Ag(1)−Ag(2)−Ag(4) 144.75(4).

are each tricoordinated by a pyridyl nitrogen atom, a carbene carbon atom, and an acetonitrile molecule. The Ag(3) is in a triangular coordination geometry, whereas Ag(4) is T-shaped. A similar Ag_4 complex has been described recently,[14b] in which the NHCs act as bridging ligands and each links unsymmetrically two silver atoms, forming triangular AgAgC rings.

The structure of **3** is shown in Figure 3. The central Ni(II) ion is coordinated by two pyridine and two NHC carbons in a square-planar geometry. The non-hydrogen atoms of the cation are almost perfectly coplanar, as indicated by the small dihedral angles (1.5–3.8°) between the coordination plane defined by NiC_2N_2 and the imidazolylidene and pyridine rings. The C−Ni−C angle (85.01(17)°) is much smaller than that of N−Ni−N (111.16(13)°) due to the geometric constraint of the ligand. The Ni−C and Ni−N bond distances are not unusual when compared to those of the known nickel(II)−NHC complexes.[9]

Nickel complexes **4** have also been characterized by single-crystal X-ray diffraction. Although **4** crystallizes in a different space group than **3**, they have basically the same structures. The structure of **4** is shown in Figure 4. The nickel(II) ion is tetracoordinated by two carbene and two pyridine rings in a square-planar geometry. The ligand is bonded to nickel in a tetradentate fashion. Two NHCs and two pyridine rings are *cis*-positioned around the central nickel(II) center. The Ni−C bond distances are ca. 1.836(8) and 1.848(9) Å, whereas the Ni−N distances are 1.927(7) and 1.928(7) Å, respectively, which are all comparable to those of **3**. The Ni−C bond distances for nickel(II)−NHC complexes are normally found to range from 1.86 to 1.92 Å.[9,10]

Because of the geometric requirement of the substituents, the coordinated pyridine rings and imidazolylidene rings are not coplanar with the central nickel. The dihedral angle between the two *cis*-positioned imidazolylidene rings is 13.01°, whereas the two pyridine rings are nearly perpendicular, with an angle of 86.96°.

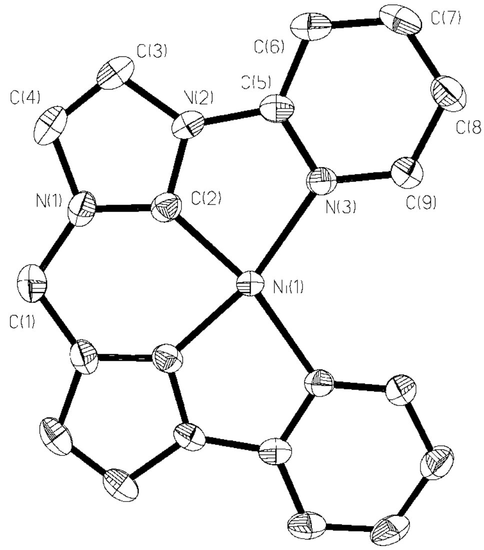


Figure 3. Molecular structure of the cation $[Ni(L1)]^{2+}$ (**3**). Selected bond distances (Å) and angles (deg): Ni(1)−C(2) 1.809(3), Ni(1)−N(3) 1.991(2), C(2)−Ni(1)−C(2)#1 85.01(17), C(2)−Ni(1)−N(3)#1 166.84(11), C(2)−Ni(1)−N(3) 81.94(11), N(3)#1−Ni(1)−N(3) 111.16(13). Symmetry code: #1 $-x+2$, y, $-z+1/2$.

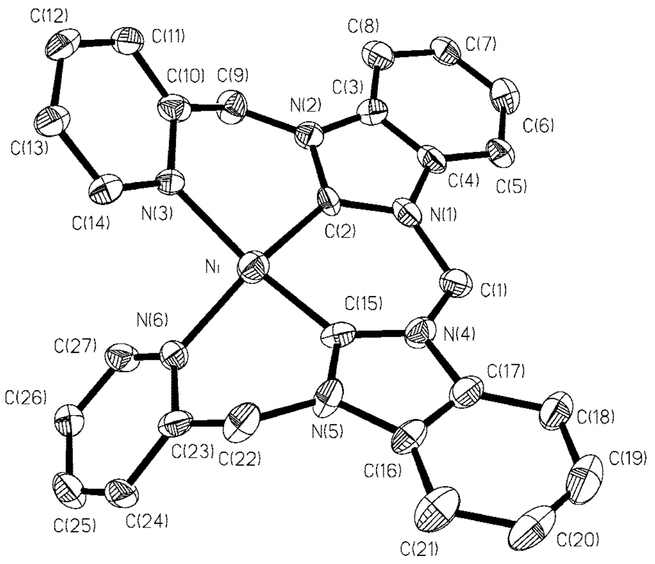
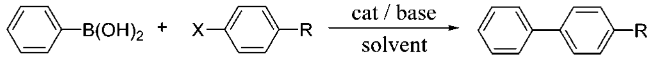


Figure 4. Molecular structure of the cation $[Ni(L2)]^{2+}$ (**4**). Selected bond distances (Å) and angles (deg): Ni−C(15) 1.836(8), Ni−C(2) 1.848(9), Ni−N(6) 1.928(7), Ni−N(3) 1.927(7), C(15)−Ni−C(2) 89.8(4), C(15)−Ni−N(6) 93.8(3), C(2)−Ni−N(6) 157.3(3), C(15)−Ni−N(3) 160.9(3), C(2)−Ni−N(3) 90.7(3), N(6)−Ni−N(3) 93.1(3).

Catalytic Properties. The transition metal-catalyzed Suzuki coupling reaction has been widely employed for the preparation of biaryl derivatives. Great success has been achieved in this field by using Pd−NHC complexes. Recently, Ni−NHC complexes have also shown good acitivities for the coupling of arylboronic acid with aryl or alkyl halides including unactivated aryl chlorides.[23] The nickel-catalyzed Suzuki coupling reactions of aryl chlorides with phenylboronic acid were examined by using **3** and **4** as the catalyst precursors under different

Table 2. Nickel-Catalyzed Coupling of Phenylboronic Acid with Aryl Chlorides and Bromides[a]



entry	cat. (mol %)	ligand (equiv)	R	X	solvent	base	*t* (h)	yield (%)[b]
1	**3** (3)		Me	Cl	toluene	K_3PO_4	24	15
2	**3** (10)		Me	Cl	toluene	K_3PO_4	24	24
3	**3** (3)		Me	Cl	toluene	KF	24	0
4	**3** (10)		Me	Cl	toluene	Cs_2CO_3	24	11[c]
5	**3** (10)		Me	Cl	toluene	NaOBu-*t*	24	10[c]
6	**3** (10)		Me	Cl	toluene	KOBu-*t*	24	9[c]
7	**3** (10)		Me	Cl	toluene	K_2CO_3	24	11[c]
8	**3** (10)		Me	Cl	toluene	K_3PO_4	24	31[c]
9	**3** (3)		Me	Cl	dioxane	K_3PO_4	24	23
10	**3** (3)		Me	Cl	DMSO	K_3PO_4	24	23
11	**3** (3)	PPh_3 (2)	Me	Cl	toluene	K_3PO_4	10	95
12	**3** (3)	IPr.HCl (2)	Me	Cl	toluene	K_3PO_4	24	13
13	**3** (1)	PPh_3 (2)	Me	Cl	toluene	K_3PO_4	10	87
14	**3** (3)	PPh_3 (1)	Me	Cl	toluene	K_3PO_4	10	85
15	**3** (3)	PPh_3 (1)	OMe	Cl	toluene	K_3PO_4	10	81
16	**3** (3)	PPh_3 (1)	CHO	Cl	toluene	K_3PO_4	10	100
17	**3** (3)	PPh_3 (1)	COMe	Cl	toluene	K_3PO_4	10	100
18	**3** (3)	PPh_3 (2)	OMe	Cl	toluene	K_3PO_4	10	90
19	**3** (3)	PPh_3 (2)	CHO	Cl	toluene	K_3PO_4	10	100
20	**3** (3)	PPh_3 (2)	COMe	Cl	toluene	K_3PO_4	10	100
21	**3** (3)	PPh_3 (2)	Me	Cl	dioxane	K_3PO_4	10	65
22	**3** (3)	PPh_3 (2)	OMe	Cl	dioxane	K_3PO_4	10	61
23	**3** (3)	PPh_3 (2)	CHO	Cl	dioxane	K_3PO_4	10	70
24	**3** (3)	PPh_3 (2)	COMe	Cl	dioxane	K_3PO_4	10	76
25	**3** (3)		Me	Br	toluene	K_3PO_4	10	21
26	**3** (3)		OMe	Br	toluene	K_3PO_4	10	15
27	**3** (3)		CHO	Br	toluene	K_3PO_4	10	95
28	**3** (3)		COMe	Br	toluene	K_3PO_4	10	93
29	**3** (3)	PPh_3 (2)	Me	Br	toluene	K_3PO_4	10	100
30	**3** (3)	PPh_3 (2)	OMe	Br	toluene	K_3PO_4	10	95
31	**4** (3)	PPh_3 (2)	Me	Cl	toluene	K_3PO_4	10	77
32	**4** (3)	PPh_3 (2)	OMe	Cl	toluene	K_3PO_4	10	68
33	**4** (3)	PPh_3 (2)	CHO	Cl	toluene	K_3PO_4	10	90
34	**4** (3)	PPh_3 (2)	COMe	Cl	toluene	K_3PO_4	10	93
35	**4** (3)	PPh_3 (2)	Me	Br	toluene	K_3PO_4	10	85
36	**4** (3)	PPh_3 (2)	OMe	Br	toluene	K_3PO_4	10	77
37	**4** (3)		CHO	Br	toluene	K_3PO_4	10	45
38	**4** (3)		COMe	Br	toluene	K_3PO_4	10	54

[a] Reaction conditions: 1 mmol of aryl halide, 1.2 mmol of phenylboronic acid, 2.4 mmol of $K_3PO_4.3H_2O$ as base, 1–10 mol % nickel catalyst **3** or **4**, 3 mL of toluene as solvent under nitrogen atmosphere at 80 °C. [b] Isolated yield. [c] GC yield at 100 °C.

conditions. The results are summarized in Table 2. The nickel complexes themselves are active catalysts for the coupling of phenylboronic acid and various aryl chlorides bearing electron-withdrawing or electron-donating substituents at 80–100 °C, and the yields of the target products are not high. A variety of bases are effective for the coupling reactions of *p*-chlorotoluene and phenylboronic acid at 100 °C, and the yields are normally below 30% for the deactivated chlorotoluene, even when 10% of Ni catalyst **3** was used and the reactions were allowed to react for 24 h (entries 4–8). The results show that among the bases employed K_3PO_4 is the most suitable base, and stronger bases such as KO*t*Bu and Cs_2CO_3 lead to lower yields compared to K_3PO_4 (entries 4 and 6). KF is too weak of a base for the reaction, and only a trace of *p*-methylbiphenyl was observed by gas chromatography. No significant changes were found between dioxane and DMSO.

The nickel complex **3** is more efficient for the coupling reactions of phenyl bromide in the absence of additional ligand (entries 25–28). Even when 3% of catalyst **3** was used, the substituted phenyl bromide bearing either electron-donating or electron-withdrawing groups could be reacted in the presence of K_3PO_4 as base with much shorter reaction time as compared to aryl chlorides. For instance, the reaction of 4-bromobenzoaldehyde and 4-bromoacetophenone proceeded in 95% and 93% isolated yields at 80 °C for 10 h, respectively.

The catalytic activity of the Suzuki coupling reactions can be dramatically improved by adding 1–2 equiv of PPh_3. Three mol % of Ni catalyst **3** together with 2 equiv of PPh_3 in toluene achieved nearly 100% conversion within 10 h at 80 °C even for electron-rich aryl chlorides (entries 11, 18 19, and 20). It was interestingly observed that the employment of 1 equiv of PPh_3 was enough for the generation of the active species for the coupling reactions. For instance, when 3 mol % Ni catalyst **3** and 3% PPh_3 were used at 80 °C within 10 h, 4-methylbiphenyl and 4-methoxylbiphenyl could be afforded in 85% and 81% yields, respectively (entries 14 and 15). Increasing the loading of PPh_3 to 2 equiv slightly improve the yields. The same catalytic system is more active for electron-deficient aryl chlorides. Under the same conditions, 4-chlorobenzaldehyde and 4-chloroacetophenone coupled with phenylboronic acid to form the target products in nearly 100% isolated yield (entries 16 and 17). Compared to toluene, dioxane is a poor solvent for both activated and deactivated aryl chlorides; only modest yields of 61–76% were obtained (entries 21–24).

---

(23) (a) Steiner, G.; Krajete, A.; Kopacka, H.; Ongania, K.-H.; Wurst, K.; Preishuber-Pfluegl, P.; Bildstein, B. *Eur. J. Inorg. Chem.* **2004**, *14*, 2827. (b) Liu, J.; Robins, M. J. *Org. Lett.* **2004**, *6*, 3421. (c) Gonzalez-Bobes, F.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 5360. (d) Saito, B.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 9602.

We also investigated the catalytic activity of **4** in Suzuki coupling reactions under the same conditions. When 3 mol % **4** and 6 mol % PPh_3 were used at 80 °C within 10 h, aryl chlorides with electron-donating groups such as 4-chlorotoluene and 4-chloroanisole gave 77% and 68% isolated yields (entries 31 and 32), and aryl chlorides with electron-withdrawing groups such as 4-chlorobenzaldehyde and 4-chloroacetophenone produced the target product in 90% and 93% isolated yields (entries 33 and 34), respectively. Catalyst **4** is more efficient for aryl bromides than aryl chlorides. Phenyl bromides containing electron-donating groups coupled with phenylboronic acid to give the corresponding product in 77–85% isolated yields (entries 35 and 36). However, without additional PPh_3, electron-deficient phenyl bromides could provide the corresponding biphenyl in only moderate yields (entries 37 and 38). The results above show that **4** is less efficient than **3** in Suzuki coupling reactions.

It is commonly thought that the in situ generated Ni(0) is the real catalytically active species. Phenylboronic acid was believed to act as a reducing reagent. The additional PPh_3 is supposed to stabilize the labile Ni(0) species and thus remarkably enhance the Suzuki coupling reaction. Nickel(II) complexes such as $NiCl_2(dppe)$ and $NiCl_2(PPh_3)_2$ in the presence of an excess of phosphines have shown their catalytic activities in Suzuki cross-coupling reactions of aryl mesylates, tosylates, and halides.[24] To gain insight into the real catalytically active species in the presence of phosphine, attempts have been made to isolate and identify the Ni−NHC−phosphine species. Reaction of PPh_3 and **3** (2:1) in CH_3CN at room temperature for 2 h did not lead to any new complex, and PPh_3 and **3** could be recovered. The same reactions at 80 °C afforded a complicated mixture, evidenced by the NMR spectrum, this mixture being unidentifiable by NMR.

In summary, triangular Ag_3 and linear chain Ag_4 complexes have been synthesized and structurally characterized via the simple deprotonation reaction of the pyridine-functionalized imidazolium salts with Ag_2O. Short silver−silver contacts have been observed. The carbene transfer reactions of these silver complexes with $Ni(DME)Cl_2$ afforded square-planar nickel(II) complexes supported by pyridine-functionalized N-heterocylic carbene ligands. The Ni(II)−NHC/PPh_3 system combined with K_3PO_4 was demonstrated to be efficient and high yielding for the Suzuki coupling reactions of aryl chlorides and bromides. The methodology is applicable to a variety of electron-rich and electron-deficient aryl chlorides. Good to excellent yields were obtained for aryl bromides and aryl chlorides. Further studies are in progress to improve the catalytic activity and to expand the scope of the methodology to other C−C and C−N coupling reactions.

Acknowledgment. The authors thank the National Natural Science Foundation of China (20572096) and Natural Science Fundation of Zhejiang Province (R405066) for financial support.

Supporting Information Available: Structural parameters for **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700796G

---

[24] Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447.