Dinickel(II) Complexes of Bis(N-heterocyclic carbene) Ligands Containing [$Ni_2(\mu$-OH)] Cores as Highly Efficient Catalysts for the Coupling of Aryl Chlorides

Yongbo Zhou,[†] Zhenxing Xi,[†] Wanzhi Chen,*[,†,‡] 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

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[Ni_2(3,5-bis(*N*-methylimidazolylidenylmethyl)pyrazolate)$_2$](PF_6)$_2$ (**1**), [$Ni_2(\mu$-OH)(3,5-bis(*N*-pycolylimidazolylidenylmethyl)pyrazolate)](PF_6)$_2$ (**2**), and [$Ni_2(\mu$-OH)(3,5-bis(*N*-pyridylimidazolylidenylmethyl)pyrazolate)](PF_6)$_2$ (**3**) have been prepared from the corresponding imidazolium salts via *in situ* generated silver-carbene complexes. The complexes and imidazolium salts were characterized by elemental analyses and NMR spectroscopy. The structures of **1**−**3** were identified by X-ray diffraction analysis. In complex **1**, two nickel(II) ions are sandwiched by two 3,5-bis(*N*-methylimidazolylidenylmethyl)pyrazolates behaving as anionic tetradentate ligands. Complexes **2** and **3** contain $Ni_2(\mu$-OH) cores with two nickel centers bridged by anionic hexadentate imidazolylidene ligands. Complexes **2** and **3** show excellent catalytic activities in Suzuki−Miyaura and Kumada−Corriu coupling reactions of various aryl chlorides. The cross-coupling reactions of deactivated aryl chlorides with arylboronic acids and Grignard reagents have been accomplished in excellent yields at low catalyst loadings.

Introduction

Metal-catalyzed cross-coupling reactions represent the most useful approach to access biaryls and heterocycles via organic halides with a variety of organometallics.[1] Many transition metals such as chromium,[2] iron,[3] cobalt,[4] manganese,[3b,5] ruthenium,[6] nickel,[7] and palladium[8] have been found to be active for coupling reactions. Pd-catalyzed cross-coupling reactions involving aryl halides have achieved great success and have found versatile applications in the pharmaceutical, fungicide, and materials industries. Nickel as a much cheaper metal and the most promising alternative to Pd is receiving increasing attention. However, nickel catalysts are usually believed to be less catalytically active than corresponding palladium systems. Actually, only a few nickel catalysts have been found to be more effective than their corresponding palladium systems.[9] Because of the low cost of nickel catalysts, the development of new nickel catalysts with catalytic efficiency close to palladium or even higher would be of practical importance for the pharmaceutical industry. The employment of well-defined bimetallic complexes as catalysts would be a possible way to increase the catalytic activity since a binuclear complex containing two metals in close proximity would exhibit a bimetallic cooperative effect[10] and, thus, can be used to activate inert chemical bonds, which is difficult by mononuclear metal com-

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

[†] Zhejiang University.

[‡] Liaocheng University.

(1) (a) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 2004. (b) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (c) Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651.

(2) (a) Xia, G.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 2554. (b) Lee, S.; Fuchs, P. L. *J. Am. Chem. Soc.* **2002**, *124*, 13978.

(3) (a) Furstner, A.; Leitner, A.; Mendez, M.; Krause, H. *J. Am. Chem. Soc.* **2004**, *124*, 13856. (b) Cahiez, G.; Moyeux, A.; Buendia, J.; Duplais, C. *J. Am. Chem. Soc.* **2007**, *129*, 13788. (c) Christiane, C. K.; Benoît, B.; Sandro, P.; Nadine, G.; Paul, K. *Chem. Commun.* **2007**, 1954. (d) Hatakeyama, T.; Nakamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 9844. (e) Chowdhury, R. R.; Crane, A. K.; Fowler, C.; Kwong, P.; Kozak, C. M. *Chem. Commun.* **2008**, 94.

(4) (a) Gomes, P.; Gosmini, C.; Perichon, J. *Org. Lett.* **2003**, *5*, 1043. (b) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2006**, *128*, 1886. (c) Grutters, M. M. P.; Muller, C.; Vogt, D. *J. Am. Chem. Soc.* **2006**, *128*, 7414. (d) Affo, W.; Ohmiya, H.; Fujioka, T.; Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K.; Imamura, Y.; Mizuta, T.; Miyoshi, K. *J. Am. Chem. Soc.* **2006**, *128*, 8068. (e) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860.

(5) Kang, S. K.; Kim, J. S.; Choi, S. C. *J. Org. Chem.* **1997**, *62*, 4208.

(6) (a) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (b) Pastine, S. J.; Gribkov, D. V.; Sames, D. *J. Am. Chem. Soc.* **2006**, *128*, 14220. (c) Ueno, S.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2007**, *129*, 6098. (d) Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Rigo, P. *Organometallics* **2000**, *19*, 3664.

(7) (a) Takahashi, T.; Kanno, K. I. In *Moden Organonickel Chemistry*; Tamaru, Y., Ed.; Wiley-VCH: Weinheim, 2005. (b) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (c) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1340. (d) Gonzalez-Bobes, F.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 5360. (e) Tobisu, M.; Shimasaki, T.; Chatani, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4866. (f) Saito, S.; Oh-tani, S.; Miyaura, N. *J. Org. Chem.* **1997**, *62*, 8024. (g) Inada, K.; Miyaura, N. *Tetrahedron* **2000**, *56*, 8657. (h) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422.

(8) (a) Negishi, E. I.; de Meijere, A. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, 2002. (b) Littke, A.; Fu, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. (c) Goossen, L. J.; Rodriguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824. (d) Hoshi, T.; Nakazawa, T.; Saitoh, I.; Mori, A.; Suzuki, T.; Sakai, J.-i.; Hagiwara, H. *Org. Lett.* **2008**, *10*, 2063. (e) Suzuki, A. *J. Organomet. Chem.* **2002**, *653*, 83.

(9) (a) Blakey, S. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 6046. (b) Liu, J.; Robins, M. J. *Org. Lett.* **2004**, *6*, 3421.

(10) (a) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W. J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, *260*, 1784. (b) Sola, E.; Bakhmutov, V. I.; Torres, F.; Elduque, A.; Lopez, J. A.; Lahoz, F. J.; Werner, H.; Oro, L. A. *Organometallics* **1998**, *17*, 683. (c) Li, H.; Li, L.; Marks, T. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4937. (d) Szuromi, E.; Shen, H.; Goodall, B. L.; Jordan, R. F. *Organometallics* **2008**, *27*, 402. (e) Guo, N.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 2246. (f) Torres, F.; Sola, E.; Elduque, A.; Martinez, A. P.; Lahoz, F. J.; Oro, L. A. *Chem.−Eur. J.* **2000**, *6*, 2120.

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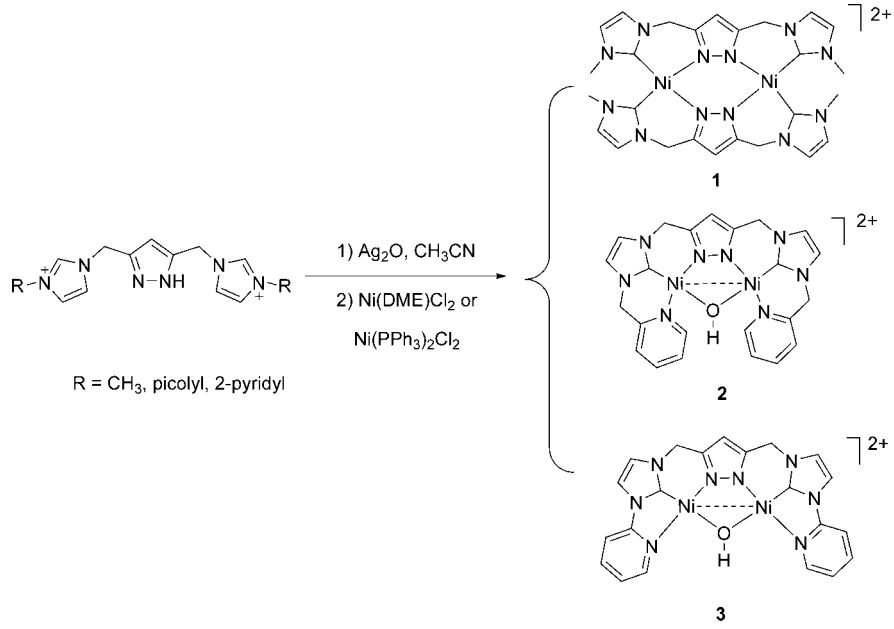
Scheme 1. Synthesis of Complexes 1−3



plexes. For instance, bimetallic catalysts might be suitable for the coupling reactions of aryl chlorides, for which the commonly used catalysts often exhibit low efficiency.[7f−h,8b,e]

Metal complexes of N-heterocyclic carbene (NHC) ligands show enhanced catalytic activities in many C−C coupling reactions that are attributed to the strong σ-donating ability and the unique steric demands of NHCs compared with tertiary phosphines.[11] For the above reason, rationally designed bimetallic nickel complexes supported by NHC ligands would be expected to show enhanced catalytic activity in some organic processes. We have been interested in developing new binuclear metal complexes of multidentate NHC ligands as cooperative catalysts. To explore possible cooperativity in the catalysis, our strategy is to hold two metal centers together with a distance close to a single M−M bond by using the functionalities of the dinucleating and strongly donating multidentate NHC ligands. In our search for bimetallic cooperative catalysts, we found that the pyridine-functionalized bis(NHC) ligands often form mononuclear nickel and palladium complexes,[12] although they are also good catalysts for C−C couplings of a variety of aryl bromides and chlorides, and the dinuclear palladium complexes did not show the expected enhanced catalytic activity.[13] The anionic tetradentate ligand 3,5-bis(*N*-methylimidazolylidenylmethyl)pyrazolate, first reported by us,[14] is potentially useful for the construction of bimetallic complexes with close metal−metal distances since the anionic pyrazolate moiety is a good dinucleating ligand possessing the ability to hold two metals together. We now report the preparation of the dinuclear $[Ni_2(L1)_2](PF_6)_2$ (**1**, L1 = 3,5-bis(*N*-methylimidazolylidenylmethyl)pyrazolate), $[Ni_2(\mu\text{-OH})(L2)](PF_6)_2$ (**2**, L2 = 3,5-bis(*N*-pycolylimidazolylidenylmethyl)pyrazolate), and $[Ni_2(\mu\text{-OH})(L3)](PF_6)_2$ (**3**, L3 = 3,5-bis(*N*-pyridylimidazolylidenylmethyl)pyrazolate) and their structural characterization. As expected, complexes **2** and **3** are highly active Suzuki−Miyaura and Kumada−Corriu coupling catalysts for aryl chlorides under mild conditions due to bimetallic synergetic effects.

Results and Discussion

Synthesis and Spectroscopic Characterization. The ligand precursor 3,5-bis(*N*-methylimidazolylmethyl)pyrazole hexafluorophosphate ($H_3L1\cdot(PF_6)_2$) was first reported by us,[14] and later similar imidazolium salts were described by Waymouth's[15] and Meyer's[16] groups, respectively. 3,5-Bis(*N*-picolylimidazolylmethyl)pyrazole ($H_3L2\cdot(PF_6)_2$) and 3,5-bis(*N*-pyridylimidazolylidenylmethyl)pyrazolate ($H_3L3\cdot(PF_6)_2$) can be easily obtained according to the same procedure from 3,5-bis(chloromethyl)pyrazole and corresponding N-substituted imidazoles in high yields. The formation of $H_3L2\cdot(PF_6)_2$ and $H_3L3\cdot(PF_6)_2$ was characterized by the appearance in their ^1H NMR spectra of the downfield resonances ascribed to acidic pyrazole NH at 13.45 and 13.31 ppm and imidazolium CH groups at 9.34 and 10.17 ppm, respectively.

Nickel-NHC complexes can be prepared from the reaction of imidazolium salts with $Ni(OAc)_2$[17] or the carbene-transfer reaction of a silver-NHC complex with $Ni(DME)Cl_2$ (DME = dimethoxylethane) or $Ni(PPh_3)_2Cl_2$.[18] However, the direct reaction of $H_3L1\cdot PF_6$ and $Ni(OAc)_2$ under the reported conditions did not give the expected complexes. Complexes **1**−**3** were successfully obtained via carbene-transfer reactions (Scheme 1). We have reported that the reaction of 3,5-bis(*N*-methylimidazoliumylmethyl)pyrazole with Ag_2O yielded a tetranuclear silver complex.[14] An acetonitrile solution of the silver compound generated *in situ* was treated with 2 equiv of $Ni(PPh_3)_2Cl_2$ to give a yellow solution of cationic complex **1**. The compound was isolated as a pale yellow, crystalline solid after recrystal-

(11) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Kantchev, E.; O'Brien, C.; Organ, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (c) Kaufhold, O.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4057. (d) Bourissou, D.; Guerret, O.; Gabbai, F, P.; Bertrand, G. *Chem. Rev* **2000**, *100*, 39.

(12) (a) Xi, Z.; Zhang, X.; Chen, W.; Fu, S.; Wang, D. *Organometallics* **2007**, *26*, 6636. (b) Xi, Z.; Liu, B.; Chen, W. *J. Org. Chem.* **2008**, *73*, 3954. (c) Zhang, X.; Xi, Z.; Liu, A.; Chen, W. *Organometallics* **2008**, *27*, 4401. (d) Ye, J.; Chen, W.; Wang, D. *Dalton Trans.* **2008**, 4015.

(13) Ye, J.; Zhang, X.; Chen, W.; Shimada, S. *Organometallics* **2008**, *27*, 4166.

(14) Zhou, Y.; Chen, W. *Organometallics* **2007**, *26*, 2742.

(15) Jeon, S.; Waymouth, R. *Dalton Trans.* **2008**, 437.

(16) Scheele, U.; John, M.; Dechert, S.; Meyer, F. *Eur. J. Inorg. Chem.* **2008**, 373.

(17) (a) Huynh, H. V.; Holtgrewe, C.; Pape, T.; Koh, L. L.; Hahn, E. *Organometallics* **2006**, *25*, 245. (b) Inamoto, K.; Kuroda, J.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T. *Organometallics* **2006**, *25*, 3095.

(18) Wang, X.; Liu, S.; Jin, G. X. *Organometallics* **2004**, *23*, 6002.

lization in acetonitrile. The reaction always forms $[Ni_2(L1)_2](PF_6)_2$ regardless of the Ni:Ag ratio employed. A similar procedure through the reactions of nickel salts and the silver-carbene complexes generated *in situ* from Ag_2O and 3,5-bis(*N*-picolylimidazolylmethyl)pyrazole and 3,5-bis(*N*- pyridylimidazolylmethyl)pyrazole led to dinickel complexes **2** and **3**, respectively. Complexes **1**−**3** are air and moisture stable. The three nickel complexes have been fully characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography.

The absence of acidic NH and CH proton resonances in the ^{1}H NMR spectra of **1**−**3** illustrates that the imidazoliums and pyrazole moieties are deprontonated and the ligands are coordinated to nickel in anionic bis(NHC) forms. The ^{1}H NMR spectrum of complex **1** in DMSO-d_6 shows resonance signals of the imidazolylidene backbone protons at 7.51 and 7.39 ppm as two doublets and pyrazolate protons at 6.70 ppm as a singlet. The resonance signals of the imidazolylidene protons of complex **2** at 7.62 and 7.55 ppm showed downfield shifts relative to those of its parent imidazolium salt $H_3L2(PF_6)_2$ at 7.80 and 7.75 ppm. The corresponding imidazolylidene protons of **3** appeared at 8.35 and 7.69 ppm having downfield shifts from those of the imidazolium at 8.54 and 7.98 ppm. Two kinds of methylene prontons of $H_3L2(PF_6)_2$ appeared at 5.58 ppm as an overlapped multiplet, whereas those of complex **2** containing L2 split into two singlets at 5.62 and 5.37 ppm with equal intensities. The methylene groups of **1** show an AB splitting pattern at 5.74 and 5.55 ppm (^2J = 16 Hz); for comparison the corresponding imidazolium salt was found at 5.41 ppm as a singlet. This illustrates that the rotation of the imidazole ring is prohibited upon complexation. The presence of a hydroxide group in **2** and **3** is characterized by the peaks at 1.90 and 1.67 ppm, respectively. The ^{13}C NMR spectra of complexes **1**−**3** exhibit resonance signals at 152.3, 153.5, and 157.9 ppm ascribed to the carbenic carbon atoms. Usually the ^{13}C chemical shifts of known Ni-NHC complexes appear in the range 149−171 ppm depending on the ancillary ligands.[19] IR spectra of **2** and **3** show broad absorptions at 3441 and 3450 cm^{-1} assignable to hydroxide groups.

Structural Characterization. X-ray crystallography revealed that complex **1** is dimeric in the solid state, residing over a crystallographic inversion center in the middle of two metal ions. The molecular structure of the cation is shown in Figure 1. Each nickel(II) center is four-coordinate, N-bound to two pyrazolate and C-bound to two C2 carbenes of NHC rings. The two nickels are held together by two tetradentate 3,5-bis(*N*-methylimidazolylidenylmethyl)pyrazolate ligands, forming a planar six-membered Ni_2N_4 metallocycle. The nickel centers are in remarkably distorted square-planar coordination geometry as a result of the steric repulsion between the two *cis*-arranged NHC rings and the geometric requirement of sp^3-hybridized methylene. The Ni−C bond distances are normal and well consistent with those of nickel(II)-NHC complexes displaying square-planar geometry ranging from 1.83 to 1.96 Å.[12a,b,19−21] Another structural feature of the complex is that two NHC rings of the same 3,5-bis(*N*-methylimidazolylidenylmethyl)pyrazolate molecule are directed toward the opposite sides of the coordination planes of the two nickel ions. The distance between the two metals is 3.873 Å, excluding any bonding interaction.

The structure of dinickel complex **2** is depicted in Figure 2. The asymmetric unit of the structure consists of one hexadentate 3,5-bis(*N*-picolylimidazolylidenylmethyl)pyrazolate, two independent nickel ions, and one hydroxide. The two nickel centers are bridged by a pyrazolate and a hydroxide, forming a five-membered metallocyclic ring. Two nickels are four-coordinated,

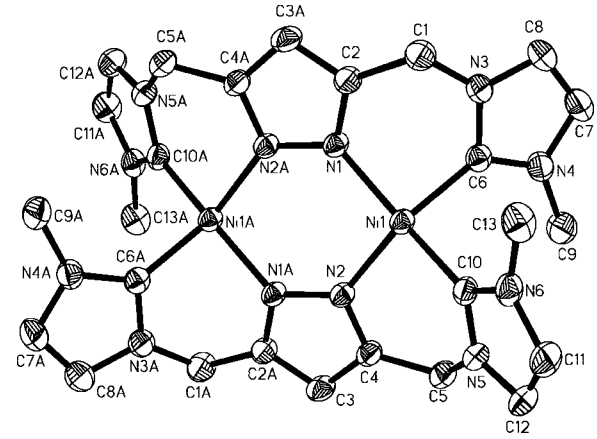


Figure 1. Molecular structure of **1** represented by thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−C(6) 1.874(3), Ni(1)−C(10) 1.875(3), Ni(1)−N(2) 1.922(3), Ni(1)−N(1) 1.922(3), C(6)−Ni(1)−C(10) 88.60(13), C(6)−Ni(1)−N(2) 156.68(12), C(10)−Ni(1)−N(2) 90.05(12), C(6)−Ni(1)−N(1) 90.78(12), C(10)−Ni(1)−N(1) 156.99(12), N(2)−Ni(1)−N(1) 99.32(10). Symmetry codes: #A $-x$, $-y+2$, $-z$.

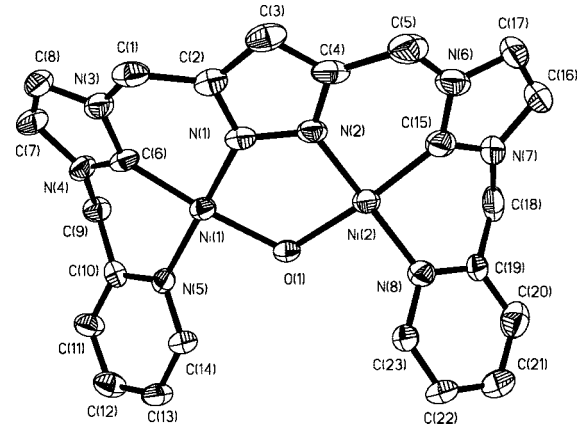


Figure 2. Molecular structure of **2** represented by thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−C(6) 1.832(7), Ni(1)−N(1) 1.853(5), Ni(1)−O(1) 1.877(4), Ni(1)−N(5) 1.922(5), Ni(2)−C(15) 1.822(8), Ni(2)−N(2) 1.848(5), Ni(2)−O(1) 1.888(4), Ni(2)−N(8) 1.900(5), C(6)−Ni(1)−N(1) 89.2(3), C(6)−Ni(1)−O(1) 175.2(2), N(1)−Ni(1)−O(1) 87.3(2), C(6)−Ni(1)−N(5) 91.2(3), N(1)−Ni(1)−N(5) 174.7(2), O(1)−Ni(1)−N(5) 92.63(19), C(15)−Ni(2)−N(2) 89.3(3), C(15)−Ni(2)−O(1) 171.6(3), N(2)−Ni(2)−O(1) 88.1(2), C(15)−Ni(2)−N(8) 91.1(3), N(2)−Ni(2)−N(8) 171.7(2), O(1)−Ni(2)−N(8) 92.6(2).

locating in a $NiCN_2O$ coordination sphere. The geometry about the metal is slightly distorted square planar, as evidenced by the diagonal angles ranging from 171.6(3)° to 175.2(2)°. The two coordination planes are bisected with a dihedral angle of 19.36°, and the cation exhibits a beautiful saddle-shaped conformation. The Ni−C and Ni−N bond distances are comparable to those of complex **1** and other nickel complexes of pyridine-functionalized NHC ligands.[12a,b] The Ni−O bond distances of the nearly symmetric $Ni_2(\mu$-O) unit are consistent with those found in $[\{Ni[C(NtBuCH)_2][O(Me_2SiOSiMe_2)$-$\mu$-$O]\}_2]$ containing asymmetric μ-O bridges.[21] The Ni···Ni distance of 3.255 Å is significantly shorter than that of **1**.

The molecular structure of complex **3** is shown in Figure 3. Similar to **2**, two nickel centers are bound together by a hexadentate 3,5-bis(*N*-pyridylimidazolylidenylmethyl)pyrazolate

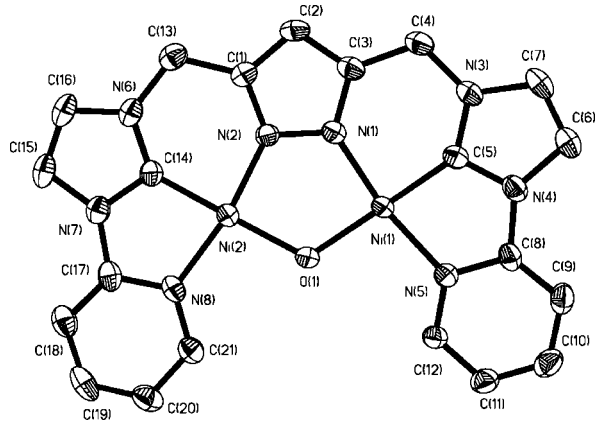


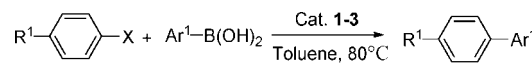
Figure 3. Molecular structure of **3** represented by thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−C(5) 1.807(5), Ni(1)−N(1) 1.845(4), Ni(1)−O(1) 1.878(4), Ni(1)−N(5) 1.928(4), Ni(2)−C(14) 1.810(5), Ni(2)−N(2) 1.850(4), Ni(2)−O(1) 1.872(4), Ni(2)−N(8) 1.929(4), C(5)−Ni(1)−N(1) 88.5(2), C(5)−Ni(1)−O(1) 176.5(2), N(1)−Ni(1)−O(1) 90.72(17), C(5)−Ni(1)−N(5) 81.9(2), N(1)−Ni(1)−N(5) 170.32(19), O(1)−Ni(1)−N(5) 98.95(17), C(14)−Ni(2)−N(2) 88.1(2), C(14)−Ni(2)−O(1) 179.1(2), N(2)−Ni(2)−O(1) 91.30(17), C(14)−Ni(2)−N(8) 98.50(18).

and a hydroxide ion. The most striking structural feature of **3** differing from other two complexes is that all five heterocyclic rings are essentially coplanar with the coordination plane of both metals, as evidenced by the small dihedral angle (0.93°) between the two coordination planes. The Ni···Ni distance in **3** is 3.216 Å, almost equal to that of **2**.

Although a dinickel complex of the N-heterocyclic carbene containing a $Ni_2(\mu\text{-}O)_2$ core has been recently reported,[21] the nickel hydroxide complex of an NHC ligand has not been known so far. We note that the Ni···Ni distances in complexes **2** and **3** are shorter than the sum of the nickel(II) atomic van der Waals radii, 3.3 Å, at which point the chemical interaction may be considered to be insignificant.[22a] The metal−metal contacts are consistent with those of related multinuclear nickel(II) complexes[10d,22b] and some nickel(II) clusters.[22c−e] The dinickel complexes with a five-membered $Ni_2(\mu\text{-N-N})(\mu\text{-OH})$ ring show close contacts between the two metal centers due to the functionality of the ligands, and such short M−M distance may allow bimetallic cooperative catalysis.

Catalytic Suzuki−Miyaura Coupling Reactions. Nickel(II) complexes of N-heterocyclic carbenes are convenient catalyst precursors of C−C coupling reactions since the real active species could be *in situ* generated in the presence of bases or reactants. In the Suzuki−Miyaura reaction, Ni(II) may be reduced to Ni(0) by arylboronic acid via a Pd(II)-related mechanism.[23a] Although a number of nickel complexes of NHC ligands have been reported to be active catalysts for olefin polymerization,[18,23b−e] C−C coupling,[17b,19d,24] and C−N coupling reactions,[25] the bimetallic nickel-NHC complexes have been rarely studied. Under the typical reaction conditions commonly applied for nickel-catalyzed Suzuki reactions,[24] the coupling of aryl halides bearing electron-withdrawing and electron-donating substituents was studied. The results are shown in Table 1. To begin our study complexes **1**−**3** alone were tested as catalysts for Suzuki−Miyaura coupling at 80 °C in toluene under an atmosphere of nitrogen. The results show that complexes **2** and **3** are effective for the reaction of 4-bromophe-

Table 1. Suzuki−Miyaura Cross-Coupling Reactions Catalyzed by Nickel Complexes 1−3[a]



entry	cat. (mol %)	PPh_3 (mol %)	R^1	X	Ar^1	time (h)	yield (%)
1	**3** (1)		COMe	Br	Ph	12	88
2	**2** (1)		COMe	Br	Ph	12	87
3	**1** (1)		COMe	Br	Ph	12	21
4	**3** (1)		Me	Br	Ph	12	52
5	**2** (1)		Me	Br	Ph	12	44
6	**3** (1.5)		Me	Br	Ph	12	59
7	**3** (1.5)		COMe	Cl	Ph	12	41
8	**3** (1.5)		Me	Cl	Ph	12	20
9	**3** (1.5)		OMe	Cl	Ph	12	11
10	**3** (0.04)	1	Me	Br	Ph	3	>99
11	**2** (0.04)	1	Me	Br	Ph	3	>99
12	**3** (0.2)	1	COMe	Cl	Ph	3	>99
13	**2** (0.2)	1	COMe	Cl	Ph	3	>99
14	**3** (0.2)	1	Me	Cl	Ph	3	98
15	**2** (0.2)	1	Me	Cl	Ph	3	96
16	**3** (0.2)	1	Me	Cl	Ph	0.5	17
17	**3** (0.2)	1	Me	Cl	Ph	1	68
18	**3** (0.2)	1	Me	Cl	Ph	2	96
19	**3** (0.2)	1	H	Cl	*p*-tolyl	3	99
20	**2** (0.2)	1	H	Cl	*p*-tolyl	3	98
21	**3** (0.2)	1	Me	Cl	4-(trifluoromethyl) phenyl	3	92
22	**2** (0.2)	1	Me	Cl	4-(trifluoromethyl) phenyl	3	91
23	**3** (0.2)	1	Me	Cl	naphthalen-1-yl	3	82
24	**2** (0.2)	1	Me	Cl	naphthalen-1-yl	3	79

[a] Reaction conditions: aryl halides 1.0 mmol, arylboronic acid 1.2 mmol, $K_3PO_4 \cdot 3H_2O$ 2.4 mmol, toluene 3 mL, 80 °C.

(19) (a) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *575*, 80. (b) Liu, Q. X.; Xu, F. B.; Li, Q. S.; Song, H. B.; Zhang, Z. Z. *Organometallics* **2004**, *23*, 610. (c) Liao, C. Y.; Chan, K. T.; Chang, Y. C.; Chen, C. Y.; Tu, C. Y.; Hu, C. H.; Lee, H. M. *Organometallics* **2007**, *26*, 5826. (d) Chiu, P. L.; Lai, C. L.; Chang, C. F.; Hu, C. H.; Lee, H. M. *Organometallics* **2005**, *24*, 6169.

(20) (a) Schneider, S.; Julius, G.; Loschen, C.; Raubenheimer, H.; Frenking, G.; Herrrmann, W. *Dalton Trans.* **2006**, 1226. (b) Douthwaite, R. E.; Haussinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584. (c) Schaub, T.; Backes, M.; Radius, U. *Chem. Commun.* **2007**, 2037. (d) Huynh, H. V.; Wong, L. R.; Ng, P. S. *Organometallics* **2008**, *27*, 2231. (e) Dible, B.; Sigman, M.; Arif, A. *Inorg. Chem.* **2005**, *44*, 3774. (f) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422. (g) Huynh, H. V.; Holtgrewe, C.; Pape, T.; Koh, L. L.; Hahn, E. *Organometallics* **2006**, *25*, 245. (h) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, *24*, 5925.

(21) Caddick, S.; Cloke, F.; Hitchcock, P.; Lewis, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824.

(22) (a) Soldatov, D. V.; Henegouwen, A. T.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A. *Inorg. Chem.* **2001**, *40*, 1626. (b) Röder, J. C.; Meyer, F.; Pritzkow, H. *Chem. Commun.* **2001**, 2176. (c) Luo, F.; Zheng, J.-m.; Kurmoo, M. *Inorg. Chem.* **2007**, *46*, 8448. (d) Efthymiou, C. G.; Raptopoulou, C. P.; Terzis, A.; Boča, R.; Korabic, M.; Mrozinski, J.; Perlepes, S. P.; Bakalbassis, E. G. *Eur. J. Inorg. Chem.* **2006**, 2236. (e) Chaboussant, G.; Basle, R.; Güdel, H.-U.; Ochsenbei, S.; Parki, A.; Parson, S.; Rajarama, G.; Siebe, A.; Smit, A. A.; Timco, G. A.; Winpenny, R. E. P. *Dalton Trans.* **2004**, 2758.

(23) (a) Moreno-Manas, M.; Perez, M.; Pleixats, R. *J. Org. Chem.* **1996**, *61*, 2346. (b) McGuinness, D. S.; Mueller, W.; Wasserscheid, P.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. *Organometallics* **2002**, *21*, 175. (c) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, *24*, 5925. (d) Campora, J.; Ortiz de la Tabla, L.; Palma, P.; Alvarez, E.; Lahoz, F.; Mereiter, K. *Organometallics* **2006**, *25*, 3314. (e) Buchowicz, W.; Koziol, A.; Jerzykiewicz, L.; Lis, T.; Pasynkiewicz, S.; Pecherzewska, A.; Pietrzykowski, A. *J. Mol. Catal. A* **2006**, *257*, 118.

(24) (a) Robins, M.; Liu, J. *Org. Lett.* **2005**, *7*, 1149. (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.

(25) (a) Gradel, B.; Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* **2001**, *42*, 5689. (b) Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029. (c) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y. *Org. Lett.* **2003**, *5*, 2311. (d) Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K. *J. Org. Chem.* **2007**, *72*, 5069.

nylethanone (Table 1, entries 1 and 2), giving the desired product in good yields, whereas complex **1** showed comparatively lower catalytic activity. Complexes **2** and **3** could also catalyze the Suzuki coupling reactions of aryl chlorides bearing either electron-withdrawing or electron-donating groups, although the coupled products were obtained in low yields (Table 1, entries 7−9). Unfortunately, complex **1** is totally ineffective for unactivated aryl bromides and aryl chlorides under the same conditions.

It has been found that PPh_3 can significantly enhance the catalytic activities of nickel(II)-NHC complexes in Suzuki coupling reactions.[19d,26] The same enhancement effect of PPh_3 was also found for the present nickel complexes. To our delight, in the presence of 1 mol % PPh_3 the deactivated *p*-tolyl bromide could be converted to biphenyl quantitatively within 3 h even at a very much lower catalyst loading of 0.04 mol % of **2** and **3** (Table 1, entries 10 and 11). A turnover number (TON) of 2500 was achieved, which is among the highest for known nickel catalysts for Suzuki−Miyaura reactions of aryl bromides.[17b,19d,24] With the assistance of PPh_3, both **2** and **3** exhibit good activities for the reactions of unactivated aryl chlorides and different arylboronic acids (Table 1, entries 12−24). However, even when the catalyst loading was increased to 0.2 mol % in the case of complex **1**, it is still inactive in the presence of phosphines for unactivated aryl bromide and aryl chloride. These data illustrate that **1** is not suitable for Suzuki coupling. This is probably because complex **1** is coordinately saturated, and the dissociation of NHC and pyrazolate to generate vacant coordination sites for reactants is difficult. For complexes **2** and **3**, the dissociation of the pyridine moiety is comparatively easy, and simultaneously the bridging hydroxide can also be easily broken or lost to produce multiple coordination sites. As a consequence, nickel complexes may generate two catalytically active metal centers.

Because **2** and **3** show similar catalytic activities for aryl bromides and chlorides, we studied only the coupling reactions of aryl chlorides with **3** in detail. Aryl chlorides are usually more difficultly coupled than aryl bromides and iodides; thus a catalyst loading of 0.2−0.8 mol % was used. The coupling reactions of a variety of deactivated and activated aryl chlorides were performed at 80 °C in the presence of PPh_3, and the biphenyls were obtained in excellent yields (Table 2, entries 1−5). Ortho-substituted aryl chlorides such as *o*-tolyl chlorides, 2-chloronaphthylene, and 2-chlorobenzonitrile can be also coupled, giving the corresponding products (Table 2, entries 6−10). Especially, *o*-phenylbenzonitrile and 2-(*p*-tolyl)benzonitrile could be afforded quantitatively when 0.4 mol % of nickel complex was employed within 5 h (Table 2, entries 9 and 10). The latter compound is an important intermediate for the synthesis of many drugs such as iosartan, valsartan, and candesartan.[27] Similarly to *o*-phenylbenzonitrile, the couplings of *m*-chlorobenzonitrile and *p*-chlorobenzonitrile with *p*-tolylboronic acid also gave the expected products in excellent yields (Table 2, entries 11 and 12). In the cases of aryl dichlorides and heteroaryl dichlorides, double coupling reactions occurred when a higher loading of complex **3** at 80 °C was used, affording terphenyls and diarylpyridine in more than 95% yields (Table 2, entries 14−20).

(26) (a) Inada, K.; Miyaura, N. *Tetrahedron* **2000**, *56*, 8657. (b) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447.

(27) (a) Goubet, D.; Meric, P.; Dormoy, J. R.; Moreau, P. *J. Org. Chem.* **1999**, *64*, 4516. (b) Kageyama, H.; Miyazaki, T.; Kimura, Y. *Synlett* **1994**, 371. (c) Miller, J. A.; Farrell, R. P. *Tetrahedron Lett.* **1998**, *39*, 6441. (d) Walla, P.; Kappe, C. O. *Chem. Commun.* **2004**, 564.

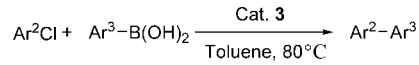
Many efforts have been made in the development of new catalysts that are capable of activation of aryl chlorides due to the lower cost and greater availability of these substrates compared with their bromide or iodide counterparts. However, the known coupling reactions of aryl chlorides often require palladium catalysts in relatively high catalyst loadings in order to achieve practically acceptable yields and reaction rates. Therefore the advantages associated with the use of aryl chlorides may be reduced by the high cost of the catalyst systems. Nickel is preferable to palladium due to its much lower cost. Ni-based catalysts using either Ni(0) or Ni(II) precursors have also been successfully used for the Suzuki reaction of aryl chlorides.[26,28] Normally, 3 mol % or higher loadings of nickel complexes are required to achieve satisfactory yields especially for the reactions of unactivated aryl chlorides. Obviously, the catalytic activities of the present dinickel catalysts are among the highest for the Suzuki couplings of aryl chlorides.

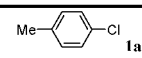
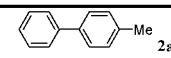
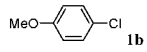
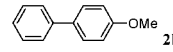
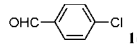
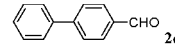
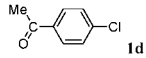
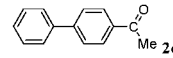
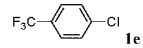
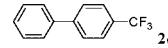
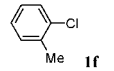
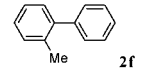
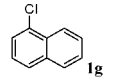
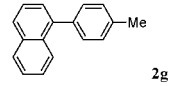
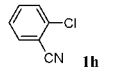
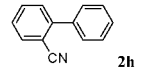
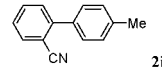
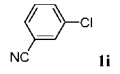
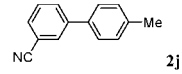
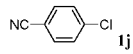
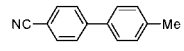
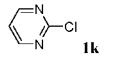
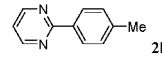
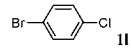
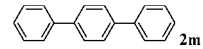
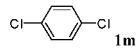
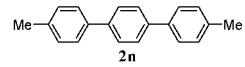
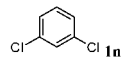
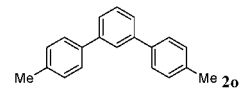
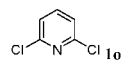
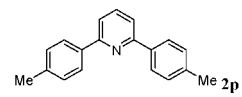
Catalytic Kumada−Corriu Coupling Reactions. On the basis of our experience with nickel-NHC-catalyzed Kumada reactions,[12b] transmetalation is normally more facile than in Suzuki couplings over the same catalyst. We focused our initial efforts on the cross-coupling of Grignard reagents with aryl chlorides at room temperature. The catalytic efficiency of **1**−**3** was screened, and the effect of catalyst loading was examined using neutral chlorobenzene as the substrate. On the basis of our recent success with nickel-NHC complexes in Kumada coupling of aryl chlorides with organomagnesium reagents, we employed a similar condition to examine the reactivities of complexes **1**−**3**.[12b] The results are summarized in Table 3. The listed yields in Table 3 refer to products isolated by column chromatography. Again, we found that complex **1** showed much lower activity compared to those of **2** and **3**. When 0.1−1.0 mol % of **1** was employed, the coupling of chlorobenzene and *p*-tolylmagnesium chloride at room temperature afforded 4-methylbiphenyl in 28−75% yields (Table 3, entries 1−5). Under the same conditions, **2** and **3** are much more efficient than **1** (Table 3, entries 6−15). At room temperature, the same products could be obtained in quantitative yields in the presence of 0.5 mol % or higher loading of **2** and **3**. Even when the catalyst loading of **3** was lowered to 0.1 mol %, the desired product can still be achieved in good yield.

As found for Suzuki reactions discussed above, the results shown in Table 3 illustrate that complex **3** is also more active than **2** in their catalyzed Kumada reactions; thus we used **3** to evaluate the scope of the reaction. As shown in Table 3, a range of biaryls were obtained in up to 99% yields (Table 3, entries 16−33). The catalyst is also applied to the coupling reactions of heteroaryl chlorides such as 2-chloropyridine and 2-chloropyrimidine to give the corresponding products in quantitative yields (Table 3, entries 26 and 27). For 2-chlorotoluene bearing an ortho-positioned methyl group the yield was not influenced remarkably (Table 3, entry 19). Notably, the catalyst is suitable for chlorobenzene derivatives having a nitrile group that is generally not compatible with Grignard reagents. 2-Chlorobenzonitrile can be successfully coupled with *p*-tolylmagnesium bromide to give 2-tolylbenzonitrile, which is an important intermediate of a few antihypertensive drugs (Table 3, entry 20). This procedure provides a more convenient approach for the preparation of sartanbiphenyl derivatives compared to the Suzuki reactions discussed above using the same catalysts, since Grignard reagents are cheaper than organoboronic acids.

Similar to *p*-tolylmagnesium bromide, the coupling reactions of *o*-tolylmagnesium bromide, naphthalen-1-ylmagnesium bro-

Table 2. Suzuki Cross-Coupling Reactions of Aryl or Heteroaryl Chlorides Catalyzed by Nickel Complex 3

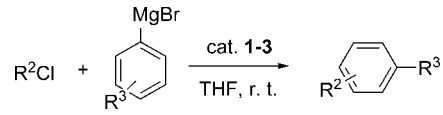


entry	Cat. (mol %)	Ar^2Cl	Ar^3	Product	Time (h)	Yield (%)
1	0.2	 **1a**	Ph	 **2a**	3	98
2	0.2	 **1b**	Ph	 **2b**	3	98
3	0.2	 **1c**	Ph	 **2c**	3	98
4	0.2	 **1d**	Ph	 **2d**	3	>99
5	0.2	 **1e**	Ph	 **2e**	3	>99
6	0.2	 **1f**	Ph	 **2f**	3	98
7	0.2	 **1g**	*p*-tolyl	 **2g**	3	86
8	0.2	 **1h**	Ph	 **2h**	3	83
9	0.4	**1h**	Ph	**2h**	5	>99
10	0.4	**1h**	*p*-tolyl	 **2i**	5	>99
11	0.2	 **1i**	*p*-tolyl	 **2j**	3	98
12	0.2	 **1j**	*p*-tolyl	 **2k**	3	99
13	0.2	 **1k**	*p*-tolyl	 **2l**	3	98
14	0.4	 **1l**	Ph	 **2m**	5	97 [b]
15	0.4	 **1m**	Ph	**2m**	5	78 [b]
16	0.8	**1m**	Ph	**2m**	8	96 [b]
17	0.8	**1m**	*p*-tolyl	 **2n**	8	97 [b]
18	0.8	 **1n**	*p*-tolyl	 **2o**	8	95 [b]
19	0.8	**1n**	*p*-tolyl	**2o**	8	97 [b]
20	0.4	 **1o**	*p*-tolyl	 **2p**	8	>99 [b]

[a] Reaction conditions: aryl halide 1.0 mmol, phenylboronic acid 1.2 mmol, $K_3PO_4 \cdot 3H_2O$ 2.4 mmol, $PPh_3/Ni = 5$, toluene 3 mL, 80 °C. [b] Aryl halide 1.0 mmol, phenylboronic acid 2.4 mmol, $K_3PO_4 \cdot 3H_2O$ 4.8 mmol, toluene 5 mL.

mide, and various activated and deactivated aryl chlorides also occurred at room temperature in good to excellent yields. In the couplings of aryl Grignard reagents with aryl or heteroaryl dihalides, the complete conversion of halides was achieved when

Table 3. Cross-Coupling of Aryl Chlorides with Grignard Reagents Catalyzed by Nickel Complexes 1−3 at Room Temperature



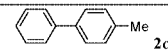
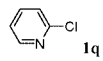
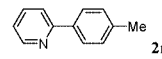
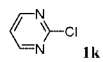
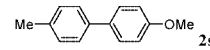
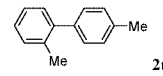
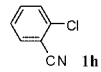
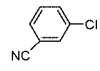
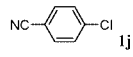
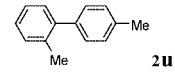
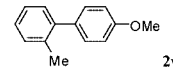
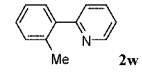
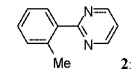
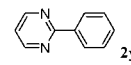
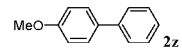
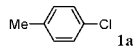
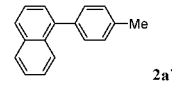
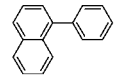
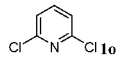
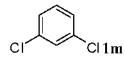
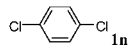
entry	cat. (mol %)	R^2Cl	R^3	product	yield (%)
1	1 (1.0)	 **1p**	*p*-methyl	 **2q**	75
2	1 (0.5)	**1p**	*p*-methyl	**2q**	67
3	1 (0.3)	**1p**	*p*-methyl	**2q**	58
4	1 (0.2)	**1p**	*p*-methyl	**2q**	38
5	1 (0.1)	**1p**	*p*-methyl	**2q**	28
6	2 (1)	**1p**	*p*-methyl	**2q**	>99
7	2 (0.5)	**1p**	*p*-methyl	**2q**	98
8	2 (0.3)	**1p**	*p*-methyl	**2q**	90
9	2 (0.2)	**1p**	*p*-methyl	**2q**	88
10	2 (0.1)	**1p**	*p*-methyl	**2q**	67
11	3 (1)	**1p**	*p*-methyl	**2q**	>99
12	3 (0.5)	**1p**	*p*-methyl	**2q**	>99
13	3 (0.3)	**1p**	*p*-methyl	**2q**	92
14	3 (0.2)	**1p**	*p*-methyl	**2q**	91
15	3 (0.1)	**1p**	*p*-methyl	**2q**	77
16	3 (0.5)	 **1q**	*p*-methyl	 **2r**	>99
17	3 (0.5)	 **1k**	*p*-methyl	**2l**	>99
18	3 (0.5)	**1b**	*p*-methyl	 **2s**	95
19	3 (0.5)	**1f**	*p*-methyl	 **2t**	97
20	3 (0.5)	 **1h**	*p*-methyl	**2i**	95
21	3 (0.5)	 **1i**	*p*-methyl	**2j**	98
22	3 (0.5)	 **1j**	*p*-methyl	**2k**	97
23	3 (0.5)	 **1p**	*o*-methyl	**2f**	>99
24	3 (0.5)	**1a**	*o*-methyl	 **2u**	85
25	3 (0.5)	**1b**	*o*-methyl	 **2v**	72
26	3 (0.5)	**1q**	*o*-methyl	 **2w**	>99
27	3 (0.5)	**1k**	*o*-methyl	 **2x**	>99

Table 3. Continued

entry	cat. (mol %)	R^2Cl	R^3	product	yield (%)
28	3 (0.5)	**1k**	H	 **2y**	99
29	3 (0.5)	**1b**	H	 **2z**	91
30	3 (0.5)	 **1a**	H	**2q**	97
31	3 (0.5)	 **1f**	H	**2f**	90
32	3 (0.5)	**1a**	naphthalen-1-yl	 **2a'**	78
33	3 (0.5)	**1p**	naphthalen-1-yl	 **2b'**	85
34	3 (1)	 **1o**	*p*-methyl	**2p**	99 [b]
35	3 (1)	 **1m**	*p*-methyl	**2o**	97 [b]
36	3 (1)	 **1n**	*p*-methyl	**2n**	98 [b]

[a] Reaction conditions: aryl chloride 1.0 mmol, Grignard reagent 1.2 mmol, THF 3 mL, room temperature, 12 h, under N_2. [b] Aryl chloride 1.0 mmol, Grignard reagent 2.4 mmol.

2.4 equiv of the magnesium reagent and 1.0 mol % of catalyst were employed without the need of elevated temperature, and excellent yields of terphenyls were obtained (Table 3, entries 28−30).

In fact, Suzuki, Stille, and Negishi reactions have been more popularly studied since their superior functional group tolerance to Kumada reactions. Although boronic acids, stannanes, and organozinc are usually derived from Grignard reagents or organolithium compounds, Kumada coupling offers a more direct approach to the synthesis of biaryls when the substrates tolerate the background reactivity of a Grignard reagent. For this reason, the coupling reaction using Grignard reagents still remains an attractive route to biaryls. In order to allow tolerance of organomagnesium reagents to nitro, ester, and nitrile groups, the maintenance of the reaction temperature below 25 °C was needed.[29] However, many procedures require higher temperature to activate C−X especially in the case of the C−Cl bond.[30] The Kumada coupling reactions catalyzed by nickel-NHC complexes or *in situ* generated catalysts from Ni/imidazolium systems have also been explored.[31] Compared with the known mononuclear nickel catalysts of NHC ligands, the nickel complexes **2** and **3** showed the highest catalytic activity at room temperature.

In summary, we have successfully prepared and structurally characterized a few novel dinuclear nickel complexes of bis(N-heterocyclic carbene) ligands. The formation of the stable nickelacycles is due to the dinucleating ability of the pyrazolate moiety, the strong donating ability of carbenes, and the chelating functionalities of the hexadentate ligands. These complexes provided suitable models for the study of bimetallic cooperative catalysis. As expected, the complexes prove highly effective for Suzuki−Miyaura and Kumada−Corriu couplings of a range of aryl halides including unactivated aryl chlorides. Complexes **2** and **3** show by far the best catalytic activities yet reported in the coupling reactions of aryl chlorides with boronic acids and organomagnesium reagents. We tentatively assume that the high catalytic activity may arise from the bimetallic cooperativity of the binickel complexes. The potential of these nickel complexes in other organic transformation is under investigation.

Experimental Section

All the chemicals were obtained from commercial suppliers and used without further purification. 2-(Imidazolylmethyl)-pyridine,[19d] 2-(imidazolyl)pyridine,[32] $Ni(DME)Cl_2$ (DME = 1,2-dimethoxyethane),[33a] $Ni(PPh_3)_2Cl_2$,[33b] and $H_3L1\cdot(PF_6)_2$[14] were prepared according to the known procedure. Elemental analyses were performed on a Flash EA1112 instrument. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance-400 (400 MHz)

(28) (a) Saitoh, A.; Oh-tani, S.; Miyaura, N. *Tetrahedron.* **1998**, *58*, 13079. (b) Zhang, Z. Y.; Hu, Q. S. *J. Am. Chem. Soc.* **2004**, *126*, 3058. (c) Zhang, Z. Y.; Hu, Q. S. *J. Org. Chem.* **2006**, *71*, 2167.

(29) Martin, R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3844.

(30) (a) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889. (b) Ackermann, L.; Gschrei, C. J.; Althammer, A.; Riederer, M. *Chem. Commun.* **2006**, 1419.

(31) (a) Böhm, V. P. W.; Weskamp, T.; Gstöttmayr, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602. (b) Wolf, J.; Labande, A.; Daran, J. C.; Poli, R. *J. Organomet. Chem.* **2006**, *691*, 433. (c) Wolf, J.; Labande, A.; Netella, M.; Daran, J. C.; Poli, R. *J. Mol. Catal. A* **2006**, *259*, 205. (d) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422. (e) Schneider, S. K.; Rentzsch, C. F.; Krüger, A.; Raubenheimer, H. G.; Herrmann, W. A. *J. Mol. Catal. A* **2007**, *265*, 50. (f) Kiyofumi, I.; Jun-ichi, K.; Takao, S.; Kou, K. *Synthesis* **2007**, 2853.

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

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

Table 4. Summary of the Crystallographic Data for 1−3

	$[Ni_2(L1)_2](PF_6)_2$, **1**	$[Ni_2(L2)(OH)](PF_6)_2$, **2**	$[Ni_2(L3)(OH)](PF_6)_2 \cdot CH_3CN$, **3**
formula	$C_{30}H_{36}F_{12}N_{14}Ni_2P_2$	$C_{23}H_{20}F_{12}N_8Ni_2\ OP_2$	$C_{23}H_{21}F_{12}N_9Ni_2OP_2$
fw	1000.09	833.81	846.85
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	7.775(6)	15.508(2)	8.0204(10)
b, Å	11.533(8)	7.7234(16)	13.7196(15)
c, Å	12.120(9)	32.033(3)	14.9468(18)
α, deg	75.005(9)		109.605(9)
β, deg	73.448(8)	114.543(4)	96.7640(10)
γ, deg	84.909(8)		101.033(10)
V, Å3	1006.1(12)	3490.1(9)	1491.0(3)
Z	1	4	2,
D_{calcd}, Mg/m^3	1.651	1.587	1.886
reflns collected	5295	16 180	7744
indep reflns (R_{int})	3488 (0.0208)	6133 (0.0634)	5183 (0.0222)
goodness-of-fit on F^2	0.985	0.926	1.040
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0381, 0.0974	0.0629, 0.1537	0.0518, 0.1357

spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta = 0$ ppm, and coupling constants (*J*) are expressed in Hz.

Synthesis of $[H_3L2](PF_6)_2$. A solution of 3,5-bis(chloromethyl)pyrazole (0.50 g, 3.0 mmol) and 2-(imidazolylmethyl)pyridine (1.05 g, 6.6 mmol) in acetone was refluxed for 5 days. The resulting white solid was filtered and then dissolved in 10 mL of water. Subsequent addition of NH_4PF_6 (1.63 g, 10.0 mmol) to the aqueous solution afforded a white precipitate, which was collected by filtration, washed with water, and dried. Yield: 1.09 g (52%). Anal. Calcd for $C_{23}H_{24}F_{12}N_8P_2$: C, 39.33; H, 3.44; N, 15.95. Found: C, 39.57; H, 3.60; N, 16.08. ^{1}H NMR (400 MHz, DMSO-d_6): 13.45 (s, 1H, NH), 9.34 (s, 2H, NCHN), 8.54 (d, $J = 4.8$, 2H, 6-py), 7.90 (t, $J = 7.6$, 2H, 4-py), 7.80, 7.75 (both s, each 2H, $CH_{imdazole}$), 7.49 (d, $J = 7.2$ Hz, 2H, 3-py), 7.41 (2d, $J = 4.8$, 7.2 Hz, 2H, 5-py), 6.48 (s, 1H, $CH_{pyrazole}$), 5.58 (m, 8H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): 153.8 (Ni-C), 153.7, 149.9, 147.2, 137.9, 137.8, 137.6, 137.3, 128.2, 124.1, 124.0, 123.9, 123.8, 123.7, 122.9, 122.7, 105.5, 53.4, 48.8.

Synthesis of $[H_3L3](PF_6)_2$. A solution of 3,5-bis(chloromethyl)pyrazole (330 mg, 2 mmol) and 2-(imidazolyl)pyridine (638 mg, 4.4 mmol) in acetone was refluxed for 5 days. The resulting white solid was filtered and then dissolved in 10 mL of water. Subsequent addition of NH_4PF_6 (978 mg, 6 mmol) to the aqueous solution afforded a white precipitate, which was collected by filtration, washed with water, and dried. Yield: 688 mg, 51%. Anal. Calcd for $C_{21}H_{20}F_{12}N_8P_2$: C, 37.40; H, 2.99; N, 16.62. Found: C, 37.65; H, 3.10; N, 16.90. ^{1}H NMR (400 MHz, d_6-DMSO): δ 13.31 (s, 1H, NH), 10.17 (s, 2H, NCHN), 8.67 (d, $J = 4.8$ Hz, 2H, 6-py), 8.54 (s, 2H, $CH_{imidazole}$), 8.24 (t, $J = 7.2$ Hz, 2H, 4-py), 8.04 (d, $J = 8.0$ Hz, 2H, 3-py), 7.98 (s, 2H, $CH_{imidazole}$), 7.67 (2d, $J = 4.8$, 7.2 Hz, 2H, 5-py), 6.62 (s, $CH_{pyrazole}$), 5.60 (s, 4H, CH_2). ^{13}C NMR (100 MHz, d_6-DMSO): δ 149.7, 146.7, 141.1, 139.1, 135.7, 125.9, 124.1, 120.1, 114.7, 105.8, 56.8.

Synthesis of $[Ni_2(L1)_2](PF_6)_2$, 1. A solution of $[H_3L1](PF_6)_2$ (0.11 g, 0.2 mmol) in 10 mL of CH_3CN was treated with Ag_2O (92 mg, 0.4 mmol). The mixture was allowed to react at room temperature for 36 h and then filtered to remove a small amount of unreacted Ag_2O. The filtrate was treated with $Ni(PPh_3)_2Cl_2$ (0.13 g, 0.2 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: 43 mg, 43%. Anal. Calcd for $C_{26}H_{30}F_{12}N_{12}P_2Ni_2$: C, 34.02; H, 3.29; N, 18.31. Found: 34.03; H, 3.63; N, 18.61. ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.51 (d, $J = 1.2$ Hz, 4H, $CH_{imidazole}$), 7.39 (d, $J = 1.2$ Hz, 4H, $CH_{imidazole}$), 6.70 (s, 2H, $CH_{pyrazole}$), 5.74 (d, $J = 16$ Hz, 4H, CH_2), 5.55 (d, $J = 16$ Hz, 4H, CH_2), 3.27 (s, 12H, NCH_3) ppm. ^{13}C NMR (100 MHz, d_6-DMSO): δ 152.3 (Ni-*C*), 147.2, 125.7, 121.9, 104.4, 46.5, 36.2.

Synthesis of $[Ni_2(L2)(OH)](PF_6)_2$, 2. A solution of $[H_3L2](PF_6)_2$ (141 mg, 0.2 mmol) in 10 mL of CH_3CN was treated with Ag_2O (184 mg, 0.8 mmol). The mixture was allowed to react at room temperature for 36 h and then filtered to remove a small amount of unreacted Ag_2O. The filtrate was treated with $Ni(DME)Cl_2$ (87 mg, 0.4 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. The yellow solid was washed by ethanol three times and resolved in CH_3CN. Addition of 20 mL of diethyl ether again gave the yellow solid. Yield: 103 mg, 62%. Anal. Calcd for $C_{23}H_{22}F_{12}N_8Ni_2OP_2$: C, 33.13; H, 2.66; N, 13.44. Found: C, 33.24; H, 2.73; N, 13.46. ^{1}H NMR (400 MHz, DMSO-d_6): 9.03 (d, $J = 5.6$, 2H, 6-py), 8.11 (t, $J = 7.6$ Hz, 2H, 4-py), 7.71 (d, $J = 7.6$ Hz, 2H, 3-py), 7.62 (d, $J = 2.0$, 2H, $CH_{imdazole}$), 7.59 (t, $J = 6.4$ Hz, 2H, 5-py), 7.55 (d, $J = 2.0$ Hz, 2H, $CH_{imdazole}$), 6.36 (s, 1H), 5.62 (s, 4H, CH_2), 5.37 (s, 4H, CH_2), 1.90 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.5 (Ni-*C*), 152.0, 149.7, 145.4, 140.7, 125.4, 125.3, 123.1, 102.4, 52.4, 46.6.

Synthesis of $[Ni_2(L3)(OH)](PF_6)_2 \cdot CH_3CN$, 3. The compound was obtained as a yellow solid using the same procedure as for **2** by using $[H_3L3](PF_6)_2$ (134 mg, 0.2 mmol), Ag_2O (184 mg, 0.8 mmol), and $Ni(DME)Cl_2$ (87 mg, 0.4 mmol). Yield: 90 mg, 56%. Anal. Calcd for $C_{21}H_{18}F_{12}N_8Ni_2OP_2$: C, 31.30; H, 2.25; N, 13.91. Found: C, 31.37; H, 2.43; N, 14.13. ^{1}H NMR (400 MHz, DMSO-d_6): 8.35 (s, 2H, $CH_{imidazole}$), 8.35 (m, 4H, 6-py + 4-py), 7.98 (d, $J = 8.0$ Hz, 2H, 3-py), 7.69 (s, 2H, $CH_{imidazole}$), 7.56 (t, $J = 6.4$ Hz, 2H, 5-py), 6.38 (s, 1H, $CH_{pyrazole}$), 5.45 (s, 4H, CH_2), 1.67 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.9 (Ni-*C*), 150.2, 150.1, 144.9, 144.0, 124.2, 123.3, 118.5, 111.8, 103.3, 47.8.

X-ray Diffraction Analysis. Single-crystal X-ray diffraction data for the complexes were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) by using an $\omega-2\theta$ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software.[34] All structures were solved by direct methods and refined against F^2 by full-matrix least-squares techniques.[35] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. Disordered solvent could not be modeled successfully and was removed from the reflection data of **2** with SQUEEZE[36] (solvent accessible void volume 776.1

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

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

(36) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 1998.

Å^3). Details of the X-ray experiments and crystal data are summarized in Table 1.

General Procedure for the Suzuki Cross-Coupling Reaction. In a Schlenk tube, a mixture of aryl halides (1.0 mmol), phenylboronic acid (1.2−2.4 mmol), $K_3PO_4 \cdot 3H_2O$ (2.4−4.8 mmol), and an appropriate amount of catalyst **1**−**3** (0.2−0.8 mol %) with or without 1−5 equiv of triphenylphosphine in 3−5 mL of toluene was stirred at 80 °C for an appropriate duration of time (1−8 h) under nitrogen. The solution was allowed to cool. A 1:1 mixture of ethyl acetate/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL portion of ethyl acetate, and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give a crude product, which was purified by column chromatography on sillca gel to afford the desired product.

General Procedure for the Kumada Cross-Coupling Reaction. A Schlenk tube was charged with nickel complexes **1**−**3** (0.001−0.01 mmol), anhydrous THF (3 mL), and aryl chloride (1.0 mmol). To the solution was added a solution of Grignard reagent (1.2−2.4 mL, 1.0 M in THF) at room temperature with stirring. After it was stirred for 12 h, the reaction was ceased by addition of water. The mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried by $MgSO_4$. The filtrate was concentrated by rotary evaporation, and the crude product was purified by column chromatography on sillca gel to afford the desired product.

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Supporting Information Available: Structural parameters for **1**−**3** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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