Synthesis and Structures of Nickel Halide Complexes Bearing Mono- and Bis-coordinated N-Heterocyclic Carbene Ligands, Catalyzing Grignard Cross-Coupling Reactions

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Substitution of phosphine ligands in nickel(II) halide complexes by now attractive N-heterocyclic carbene (NHC) ligands is one of the well-known organometallic reactions. New, simple, and easy-to-prepare nickel(II) halides bearing both a phosphine and an NHC ligand, [$NiX_2(PPh_3)(NHC)$], were synthesized by the reaction of [$NiX_2(PPh_3)_2$] (X = Cl and Br) with 1 equiv of a bulky NHC ligand. Rather small NHC ligands did not form NHC/PR_3 mixed complexes. Controlling the amount of the NHC ligand and purification led to successful isolation in good to moderate yields and structural determination of these carbene complexes. Studies on catalytic Grignard cross-coupling reactions using three complexes, the NHC/PPh_3 mixed complex, a "bis"-carbene complex, and [$NiCl_2(PPh_3)_2$], revealed that the monocarbene complex catalyzes reactions with the highest activity, but, in comparison, catalysis does not proceed well using the latter two complexes.

Introduction

The chemistry of nickel complexes now stands at an important position in useful organic catalytic reactions.[1] Although some toxicity of nickel compounds has been pointed out, they are inexpensive in comparison with corresponding palladium and platinum analogues. However, the catalyst activity of nickel compounds is regarded as lower than that of palladium complexes in most attractive catalytic cross-coupling reactions,[2] and a number of useful reactions catalyzed by organonickel reagents have not been developed. Focusing on the versatile nickel catalysts, simple Ni(0) and Ni(II) complexes, such as [Ni(COD)$_2$], [NiX_2(monophosphine)$_2$], and [NiX_2(η^2-bisphosphine)] (X = Cl, Br), have been used in many useful catalytic reactions.[3] Recently, new complexes bearing the N-heterocyclic carbene (NHC) ligand have attracted considerable attention,[4] and these compounds must be more widely exploited as versatile active catalysts in organic synthesis.

For the purpose of constructing a new nickel catalyst inducing many catalytic reactions, five points seem to be significant. They must (i) be prepared facilely, (ii) be thermally and air stable, (iii) easily form a coordinatively unsaturated site, (iv) have electron-donating ligands to stabilize the unsaturated site and to accelerate the oxidative addition process, and (v) have bulky substituents on the ligands to enhance the reductive elimination process. Thus, a simple and easy-to-access nickel complex should have an NHC ligand, which is a typical σ-donor that can substitute classical 2*e*-donor ligands and forms thermally stable metal complexes.[5] This prompted us to develop such novel nickel(II) complexes having NHC ligands and to adopt nickel catalysts for several organic reactions.

The substitution of phosphine ligands in nickel(II) halide complexes by NHC ligands is one of the well-known organometallic reactions. Herrmann et al. showed that a reaction of $NiX_2(PPh_3)_2$ with stable NHC carbene ligands gave nickel(II) complexes bearing two NHC ligands, [$NiX_2(NHC)_2$] (**1** and **2**).[6] However, according to our result, this known preparative procedure afforded new, stable nickel(II) complexes, [$NiX_2(PPh_3)(NHC)$] (**3**), in good to moderate yields only when bulky 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene was used as the carbene ligand. This nickel compound has only one carbene ligand, and one triphenylphosphine ligand remains in the nickel(II) center. Although the analogous palladium monocarbene

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[1] Recent reviews and textbooks for organonickel catalysis: (a) *Modern Organonickel Chemistry*; Tamaru, Y., Ed.; Wiley-VCH: Weinheim, 2005. (b) *Comprehensive Organometallic Chemistry II, Vol. 12*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995. (c) Hassan, J.; Se'vignon, M.; Gozzi, C.; Schulz, E.; Lemaire M. *Chem. Rev.* **2002**, *102*, 1359−1469. (d) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263−303. (e) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340−348.

[2] There are a number of reviews and books for organopalladium catalysis, for example: (a) *Palladium in Organic Synthesis*; Tsuji, J., Ed.; Springer: Berlin, 2005. (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., De Meijere, A., Eds.; Wiley: New York, 2002. (c) *Perspectives in Organopalladium Chemistry for the XXI Century*; Tsuji, J., Ed.; Elsevier Science: Amsterdam, 1999.

[3] Representative examples of nickel-complex-catalyzed cross-coupling reactions: (a) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80, and references therein. (b) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958−1969. (c) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347−3354. (d) Negishi, E.-I.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821−1823. (e) Saito, S.; Sakai, M.; Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 2993−2996. (f) Terao, J.; Watanabe, H.; Ikumi, A.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2002**, *124*, 4222−4223. (g) Terao, J.; Ikumi, A.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2003**, *125*, 5646−5647.

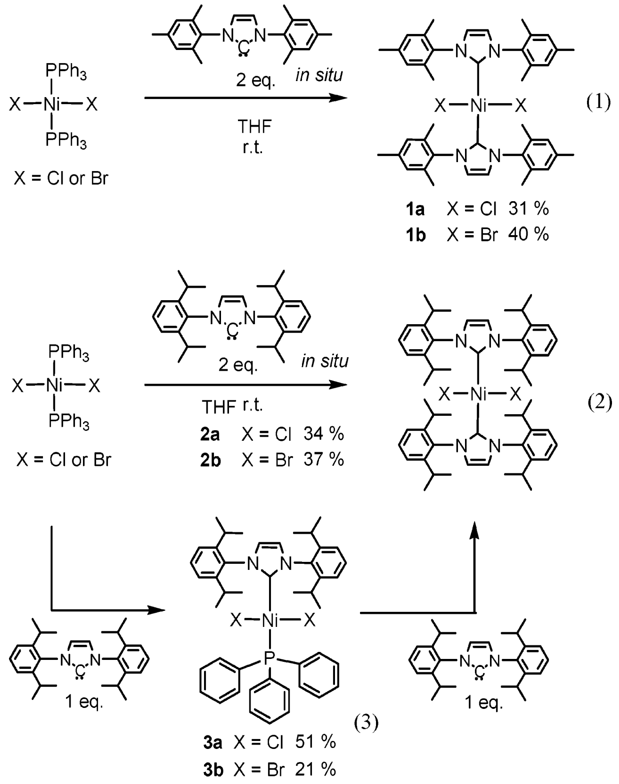
[4] Coupling reactions catalyzed by nickel N-heterocyclic carbene complexes: (a) McGuinness, D. S.; Cavell, K. J. *Organometallics* **1999**, *18*, 1596−1605. (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Hermann, W. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3387−3389. Sato, Y.; Sawaki, R.; Mori, M. *Organometallics* **2001**, *20*, 5510−5512. (c) Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698−3699.

[5] Reviews for the carbenes: (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309. (b) Weskamp, T.; Böhm V. P. W.; Herrmann W. A. *J. Organomet. Chem.* **2000**, *600*, 12−22. (c) Bourissou, D.; Guerret, O.; Gabba, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.

[6] Synthesis of $NiX_2(NHC)_2$: Herrmann, W. A.; Gerstberger, G.; Spiegler, M. *Organometallics* **1997**, *16*, 2209−2212.

10.1021/om0602658 CCC: $33.50

Scheme 1



complexes are well-known,[7] this is the first example of nickel(II) monocarbene monophosphine complexes. We noticed that, as in the well-known ruthenium carbene complexes bearing NHC and PR$_3$ that Grubbs developed,[8] this phosphine ligand could easily be eliminated under ambient reaction conditions to generate a coordinatively unsaturated site on the nickel. The nickel compound **3** showed high activity in catalytic Grignard cross-coupling reactions, whereas [NiCl$_2$(NHC)$_2$] (**2**) and [NiCl$_2$(PPh$_3$)$_2$] showed lower activity under the same conditions.

Results and Discussion

Preparation of Nickel(II) NHC Complexes. The substitution reaction of the phosphine ligands in the nickel complex with the NHC ligands smoothly proceeded in a THF solution at room temperature, as Herrmann reported.[6] We also added the carbene ligands, which were prepared just before use, to the THF solution of nickel materials, [NiX$_2$(PPh$_3$)$_2$] (X = Cl, Br). As shown in Scheme 1 (1) and (2), the reaction of [NiX$_2$(PPh$_3$)$_2$] (X = Cl, Br) with 2 equiv of two carbene ligands (1,3-bis(mesityl)imidazol-2-ylidene, IMes; 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, I^{i}Pr) afforded the nickel(II) bis(carbene) complexes [NiX$_2$L$_2$] (**1a**, X = Cl, L = IMes; **1b**, X = Br, L = IMes; **2a**, X = Cl, L = I^{i}Pr; **2b**, X = Br, L = I^{i}Pr) as expected. These were thermally and air-stable orange crystals, and crystallization in a hexane solution at −30 °C gave hexagonal pillar crystals containing one hexane molecule in the lattice.

In the formation of the complex **1a** or **1b**, even when the quantity of added IMes was smaller than 2 equiv, only **1a** or **1b** was obtained with recovering some amount of the starting material. However, in sharp contrast, employing less than 2 equiv of the I^{i}Pr added to [NiX$_2$(PPh$_3$)$_2$] revealed the detection of unexpected nickel complexes in the crude mixture. These new compounds are nickel(II) monocarbene complexes with one remaining PPh$_3$ ligand, [NiX$_2$(PPh$_3$)(I^{i}Pr)] (**3a**, X = Cl; **3b**, X = Br), as a result of detailed NMR and IR analysis, as shown below. Fortunately, complexes **3a** and **3b** can be isolated by removal of [NiX$_2$(PPh$_3$)$_2$] by extracting the crude mixture with hexane and then sublimation of triphenylphosphine at 80−110 °C under reduced pressure (1×10^{-2} Pa) for 1 h in moderate to good yields (51 and 21%, respectively). Contaminated, small amounts of **2a** and **2b** were finally removed by recrystallization. Complexes **3a** and **3b** are dark purple prismatic crystals and are air-stable in the solid state. These were also thermally stable even above 150 °C. However, in solution, these compounds decomposed upon exposing to air in several minutes at room temperature to form white solids. Although, reportedly, mixed carbene/phosphine palladium complexes slowly induced redistribution of carbene and phosphine ligands to form a bisphosphine complex and a biscarbene complex by ligand exchange in solution,[7a,d] the ligand replacement in the nickel complexes **3a** and **3b** never proceeded to form **2a** and **2b** in THF at room temperature for 1 day.

In addition, more than 1 equiv of I^{i}Pr added to the isolated **3a** and **3b** resulted in quantitative formation of **2a** and **2b**, respectively, which suggested that complexes **3a** and **3b** are intermediates in the formation of **2a** and **2b**. Thus, complexes **3a** and **3b** were obviously obtained by the substitution reaction of [NiX$_2$(PPh$_3$)$_2$] with only one I^{i}Pr ligand. Of interest is that using only I^{i}Pr led to the formation of monocarbene complexes **3a** and **3b**, whereas adding IMes to [NiX$_2$(PPh$_3$)$_2$] did not. In other words, the second substitution by I^{i}Pr in the formation of **2a** or **2b** proceeded more slowly than that by IMes in the formation of **1a** or **1b**. This is probably due to the bulkiness of the I^{i}Pr ligand in comparison with that of IMes; that is, the substituted bulky I^{i}Pr in the complex **3a** or **3b** inhibited the second substitution of triphenylphosphine. Such a mechanism generating intermediary monocarbene complexes was not reported in the synthesis of the biscarbene nickel complexes shown by Herrmann et al.[6]

Characterization of Nickel(II) NHC Complexes. All the complexes **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** were fully characterized on the basis of detailed NMR and IR spectroscopy, and these structures were confirmed by X-ray diffraction studies. The ^{1}H and ^{13}C NMR spectra of **1a** and **1b** and **2a** and **2b** were quite similar to each other. The ^{1}H resonances due to protons at the 4 and 5 positions of the five-membered imidazole ring of **1a** and **1b** appeared at δ 6.62 and 6.63, respectively. Also, the spectra of **2a** and **2b** showed similar signals at δ 6.54 and 6.58, respectively. Coordination of the carbenes to nickel was evidenced by detecting carbene carbons directly bound to nickel in the ^{13}C NMR spectra; the resonances appeared at δ 167.48, 168.92, 168.43, and 170.40 for **1a**, **1b**, **2a**, and **2b**, respectively, which are all in good agreement with other known NHC nickel

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(7) There are several reports including properties of mixed NHC/PR$_3$ palladium complexes, see: (a) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617−618*, 616−628. (b) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *585*, 348−352. (c) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 1591−1593. (d) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilson, D. J.; McKerrecher, D. *Chem. Commun.* **2001**, 1388−1389. (e) Frey, G. D.; Schütz, J.; Herdtweck, E.; Herrmann W. A. *Organometallics* **2005**, *24*, 4416−4426. (f) Bertogg, A.; Camponovo, F.; Togni A. *Eur. J. Inorg. Chem.* **2005**, 347−356.

(8) (a) Sanford, M. S.; Love, J. A.; Grubbs R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554. (b) Sanford, M. S.; Ulman, M.; Grubbs R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749−750. (c) Trnka, T. M.; Grubbs R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.

Table 1. Crystallographic Data for 2a, 2b, and 3a

	2a	**2b**	**3a**
formula/fw	$C_{60}H_{86}Cl_2N_4Ni$/992.94	$C_{60}H_{86}Br_2N_4Ni$/1081.86	$C_{45}H_{37}Cl_2N_2PNi$/766.35
cryst dimens, mm	0.20 × 0.20 × 0.10	0.30 × 0.14 × 0.12	0.50 × 0.40 × 0.30
cryst syst/space group	orthorhombic/$P2_12_12$	orthorhombic/$P2_12_12$	monoclinic/$P2_1/n$
a, Å	13.216(3)	13.250(2)	21.017(5)
b, Å	20.490(2)	20.591(3)	12.687(3)
c, Å	10.877(3)	10.835(4)	31.957(8)
β, deg			97.57(3)
V, Å^3	2945.5(12)	3066.(1)	8447(4)
Z	4	4	8
D_{calc}, g/cm^3	1.120	1.216	1.206
temp, K	293(2)	293(2)	293(2)
radiation (λ, Å)	Mo Kα (0.71069 Å)		
μ_{calc}, cm^{-1}	9.16	17.18	6.54
F(000)	1072	1144	1592
scan type	$\omega-2\theta$	$\omega-2\theta$	ω
θ range, deg	1.83 to 27.50	1.83 to 27.50	1.73 to 27.68
no. of indep reflns	3795 [R(int) = 0.0000]	3809 [R(int) = 0.0000]	19 505 [R(int) = 0.1114]
no. of reflns used ($I > 2\sigma(I)$)	1761	1326	10 155
no. of variables	307	304	919
refinement method	full-matrix least-squares on F^2		
GOF^a on F^2	1.044	0.957	0.998
R_1/wR_2 ($I > 2\sigma(I)$)^b	0.0629/0.1380	0.0622/0.0995	0.0617/0.1559
R_1/wR_2 (all)^c	0.1811/0.1873	0.2604/0.1384	0.1521/0.1901
$\Delta\rho_{max.}$, e Å^{-3}	0.415 and −0.424	0.717 and −0.724	0.724 and −0.560

^{a} GOF = $[\sum w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$. ^{b} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $wR(F_2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

complexes.[9] On the other hand, in the ^{13}C and ^{31}P NMR spectra of **3a** and **3b**, similar characteristic signals indicating the existence of a phosphine ligand in **3** were observed: especially, the ^{13}C doublet signals due to the carbene carbons at δ 165.3 (**3a**) having a large coupling with phosphorus at the *trans* position (137 Hz), which was similarly detected in the palladium analogues (J_{PC} = 80−190 Hz).[7d−f] However, in the case of the bromide complex **3b**, the corresponding carbene signal was invisible in the room-temperature ^{13}C NMR spectrum. The ^{31}P resonances due to the triphenylphosphine of **3a** and **3b** appeared at δ 13.74 and 22.15, respectively, as broadening signals ($W_{1/2}$ = 110 and 435 Hz, respectively) at room temperature. Herrmann et al. reported that the palladium analogue $[PdI_2(NHC)(PR_3)]$ rapidly isomerized between *cis* and *trans* isomers at room temperature.[7a] Similarly, in the nickel complexes **3**, such fast isomerization may occur. The isomerization rate of **3a** was faster than that of **3b**. As shown in the Supporting Information, the broadening signal of the ^{31}P resonances in **3b** at room temperature was clearly divided into two peaks at −50 °C (δ 17.74 and 15.02) with an integrated ratio of 100:5, respectively; these peaks may be assigned as the *trans* and *cis* isomers, respectively.

The compounds **2a**, **2b**, and **3a** were structurally determined by X-ray crystallography. The crystallographic and measurement data are shown in Table 1, and representative bond lengths and angles are listed in Tables 2 and 3. Figure 1 presents the ORTEP drawings of the structures. In the crystals of **2a** or **2b**, two halogen atoms and one nickel atom were placed on the symmetrical plane, and half of the structure was drawn with symmetrical operations in Figure 1a,b. Because one molecule of hexane, which is highly disordered, was contained in the lattice of **2a** or **2b**, X-ray reflections gradually decayed when each crystal was coated with epoxy resin. In the case of **3a**, two independent molecules of it were included in the crystal and both were refined.

Although compound **3** may have two (*trans* and *cis*) structures in solution, the crystal structure of **3b** revealed that phosphine was located at the *trans* position of the carbene in the solid state. The bond lengths between Ni and $C_{carbene}$ in **2a**, **2b**, and **3a** were 1.933(6), 1.943(9), and 1.912(4) Å, respectively, which were in good agreement with other Ni(II) and Ni(0) NHC complexes.[6,7,9,10] Interestingly, the $C_{carbene}$−Ni−P angles (165.9(1)° and 173.8(1)°) in the independent molecules of **3a** were bent a little compared to those found in typical square planar structures. A similar bent angle was observed in the analogous palladium(II) complexes.[7] In the nickel(II) bisphosphine complex, $[NiCl_2(PPh_3)_2]$, the four ligands reportedly formed a tetrahedral structure (P−Ni−P angle = 111.42(1)°).[11] Two carbene ligands in the Ni(II) complexes **2a** and **2b** changed their coordination structure in the Ni(II) atom to that of a square plane. In the case of **3a**, somewhat bent C−Ni−P angles were induced by

Table 2. Representative Bond Distances (Å) and Angles (deg) for 2a and 2b

2a		**2b**	
Ni(1)−C(1)	1.933(6)	Ni(1)−C(1)	1.943(9)
Ni(1)−Cl(1)	2.167(3)	Ni(1)−Br(1)	2.308(3)
Ni(1)−Cl(2)	2.172(3)	Ni(1)−Br(2)	2.295(3)
N(1)−C(1)	1.338(8)	N(1)−C(1)	1.47(1)
N(1)−C(2)	1.395(9)	N(1)−C(2)	1.49(1)
N(2)−C(1)	1.382(8)	N(2)−C(1)	1.45(1)
N(2)−C(3)	1.390(9)	N(2)−C(3)	1.41(1)
C(2)−C(3)	1.315(11)	C(2)−C(3)	1.32(2)
C(1)$^{\#1}$−Ni(1)−C(1)	179.5(5)	C(1)$^{\#1}$−Ni(1)−C(1)	178.9(7)
C(1)−Ni(1)−Cl(1)	89.7(2)	C(1)−Ni(1)−Br(2)	89.5(4)
C(1)−Ni(1)−Cl(2)	90.3(2)	C(1)−Ni(1)−Br(1)	90.5(4)
Cl(1)−Ni(1)−Cl(2)	180	Br(2)−Ni(1)−Br(1)	180

Table 3. Representative Bond Distances (Å) and Angles (deg) for 3a

Ni(1)−C(1)	1.912(4)	Ni(2)−C(1)
Ni(1)−Cl(1)	2.146(1)	Ni(2)−Cl(1)
Ni(1)−Cl(2)	2.277(1)	Ni(2)−Cl(2)
Ni(1)−P(1)	2.254(1)	Ni(2)−P(1)
N(1)−C(1)	1.370(5)	N(3)−C(1)
N(1)−C(2)	1.391(5)	N(3)−C(2)
N(2)−C(1)	1.342(5)	N(4)−C(1)
N(2)−C(3)	1.385(5)	N(4)−C(3)
C(2)−C(3)	1.332(6)	
C(1)−Ni(1)−P(1)	165.9(1)	
C(1)−Ni(1)−Cl(1)	93.0(1)	
C(1)−Ni(1)−Cl(2)	88.7(1)	
Cl(1)−Ni(1)−Cl(2)	165.78(6)	

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(9) Monocarbene nickel complexes: (a) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490−10491. (b) Dible, B. R.; Sigman, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 872−873.

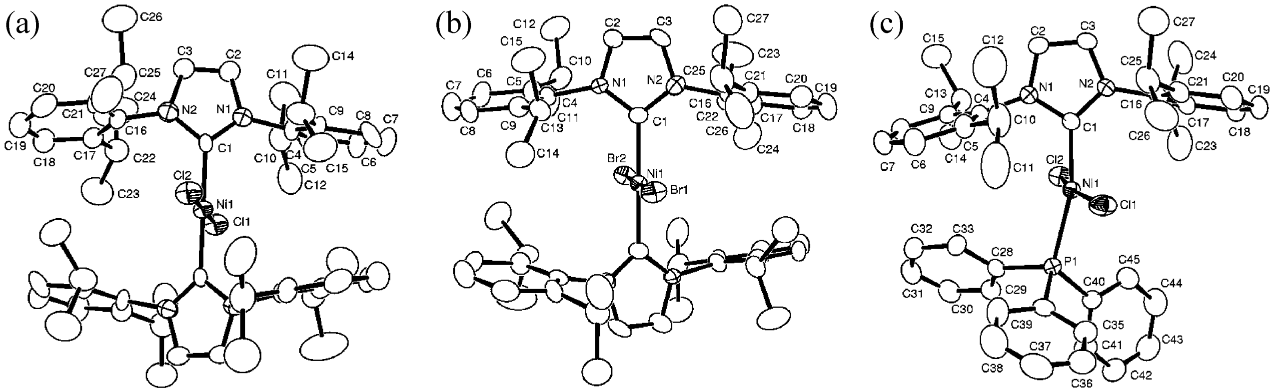
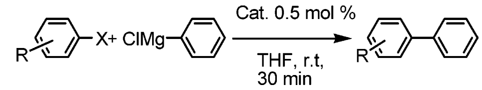


Figure 1. ORTEP drawings of (a) **2a**, (b) **2b**, and (c) **3a** (30% probability thermal ellipsoids; for clarity, one of the two independent molecules (**3a**) is presented, and hexane (**1b** and **2b**) and all hydrogen atoms are omitted).

Scheme 2



the electric and/or steric influences of the triphenylphosphine ligand on the nickel center. In addition, the nickel−phosphorus bond lengths in **3a** were 2.254(1) and 2.263(1) Å and were 0.07 Å shorter than that of [$NiCl_2(PPh_3)_2$], 2.3180(2) Å,[11] indicating the stronger σ-donor ability of the NHC ligand compared to that of triphenylphosphine.

Grignard Coupling with Ni(II) NHC Complexes. Development of the procedure for new, stable nickel(II) NHC complexes **3** made possible a comparison among the bisphosphine complex, the biscarbene complex, and the mixed phosphine/NHC complex in the catalytic activity of Grignard coupling reactions (Scheme 2).[4b,12] The catalyst activity of **3a** was high enough in comparison with the other nickel catalysts. In Table 4 we show the results of the Grignard cross-coupling reactions of several aryl halides catalyzed by **3a** and **2a** at room temperature (about 18 °C). By using only 0.5 mol % of the catalysts, the reactions of phenylmagnesium bromide with several aryl halides gave cross-coupling products, especially in generating a fever in the case of using **3a**. Of interest is that complex **2a**, which has two NHC ligands, showed moderate activity, whereas, in contrast, complex **3a** exhibited high activity. The turnover number in the cross-coupling of aryl bromide by **3a** was over 400 (Table 4, entries 2, 6, 7), whereas that by **2a** was around 200−300 (entries 8, 12, 13). Herrmann et al. demonstrated the catalyst performances in Suzuki−Miyaura cross-coupling among three complexes: an analogous mixed phosphine/NHC complex, a bis(NHC) complex, and a bisphosphine complex of palladium. The bis(NHC) palladium complex had the lowest activity, whereas the bisphosphine complex had the highest activity but was less stable than the mixed PR_3/NHC complex in the reaction medium.[7a] However, in the Grignard coupling reactions with the nickel complexes, [$NiCl_2(PPh_3)_2$], **3a**, and **2a**, the highest activity was observed for the mixed complex **3a** (Table 4, entries 1, 5, 11, respectively). It is important that the simple, easily accessible, stable nickel(II) complexes **3** can exhibit high activity in catalytic cross-coupling reactions, possibly due to the stability provided from the bulky N-heterocyclic ligand and hemilability of the triphenylphosphine ligand on the nickel.

Table 4. Grignard Cross-Coupling in the Presence of 3a and 2a[a]

entry	catalyst	R	X	yield (%)	TON
1	$NiCl_2(PPh_3)_2$	OMe	Cl	11[b]	40
2	**3a**	H	Br	100	>400
3		H	I	100	>400
4		OMe	F	15[b]	60
5		OMe	Cl	39[b]	160
6		OMe	Br	100	>400
7		Ph	Br	100	>400
8	**2a**	H	Br	60	240
9		H	I	86	340
10		OMe	F	0	0
11		OMe	Cl	13[b]	50
12		OMe	Br	34[b]	140
13		Ph	Br	75[b]	300

[a] R and X mean substituents in aryl halides. The reactions were carried out using 0.5 mol % of the catalysts for 30 min at 18 °C in THF. [b] Isolated with silica column chromatography.

Conclusion

We investigated the reactions of NHC ligands with the versatile nickel(II) compound [$NiX_2(PPh_3)_2$] (X = Cl and Br). When only the bulky NHC ligand 2,6-bis(1,3-diisopropylphenyl)imidazol-2-ylidene was employed, we successfully prepared nickel(II) halides **3a** and **3b**, having a triphenylphosphine and an NHC ligand in one molecule. In the formation of **3**, using 1 equiv of the bulky NHC ligand is required at room temperature, and adding 2 equiv led to formation of Ni(II) biscarbene complexes in all cases. Furthermore, these monocarbene complexes were isolated, structurally determined, and revealed to be thermally and air stable in the solid state. One or two carbene ligands in the complexes **1**−**3** changed the coordination structures around the Ni(II) atom to that of a square plane and also made the electric structures diamagnetic from paramagnetic

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(11) Crystal structure of $NiCl_2(PPh_3)_2$: (a) Corain, B.; Longato, B.; Angeletti, R.; Valle, G. *Inorg. Chim. Acta* **1985**, *104*, 15−18. (b) Brammer, L.; Stevens, E. D. *Acta Crystallogr., Sect. C* **1989**, *45*, 400−403.

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bisphosphine complexes.[13] It is of interest that the monocarbene complex showed higher catalytic activity in the Grignard coupling than the biscarbene complex and bisphosphine complex at room temperature. The new, active, stable nickel(II) complexes are easily prepared and have a simple structure, so they should demonstrate valuable applications as various organic catalysts. We are now studying other catalytic organic reactions using these NHC complexes as catalysts.

Experimental Section

General Procedures. All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and a glovebox (MBraun UniLab) unless otherwise noted. THF, ether, hexane, benzene-d_6, and chloroform-*d* were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. KO^tBu was sublimed just before use. Organic reagents used for coupling reactions were distilled just before use. Other reagents were used as received. Column chromatography of organic products was carried out using silica gel (Kanto Kagaku, silica gel 60N (spherical, neutral)). The ^1H, ^{13}C, and ^{31}P NMR spectra were taken with a Varian Mercury Y plus 400 MHz spectrometer at room temperature. Chemical shifts (δ) were recorded in ppm from the internal standard (^1H and ^{13}C: solvent) and the external standard (^{31}P: H_3PO_4). IR spectra were recorded in cm^{-1} on a Perkin Elmer Spectrum One spectrometer equipped with a universal diamond ATR. Elemental analysis was carried out with a Yanaco CHN Corder MT-5 autosampler. The nickel complexes $[NiX_2(PPh_3)_2]$ (X = Cl and Br)[14] and N-heterocyclic carbenes (IMes and I^iPr)[15] were prepared according to the published methods.

Preparation of 1a, 1b, 2a, and 2b. The general procedure for preparation of **1a**, **1b**, **2a**, and **2b** is as follows. In a typical example, bis(2,6-diisopropylphenyl)imidazolium chloride (117.0 mg, 0.270 mmol) and THF (1.5 mL) were added to a 20 mL Schlenk tube and stirred for 15 min, followed by addition of KO^tBu (36.7 mg, 0.327 mmol) and stirring for 20 min. The resulting pale yellow suspension was filtered through a small amount of Celite and added to a THF solution of $[NiCl_2(PPh_3)_2]$ (73.5 mg, 0.112 mmol) with vigorous stirring. The solution was then stirred for 10 min, and the volatile reagents were removed under reduced pressure. After extracting with hexane, sublimation of the evaporated residue at 80−110 °C for 1 h removed the triphenylphosphine, giving **2a** (81.4 mg, 0.089 mmol, 80% yield). No contaminating phosphine was confirmed on the basis of ^1H and ^{31}P NMR spectroscopy.

1a: mp 183 °C (dec). ^1H NMR ($CDCl_3$): δ 7.01 (s, 8H, *meta*-CH), 6.62 (s, 4H, CH═CH), 2.54 (s, 12H, *para*-CH_3), 1.95 (s, 24H, *ortho*-CH_3). ^{13}C NMR: δ 167.48 (NCN), 137.40 (*ipso*-C), 136.45 (*para*-C), 136.24 (*ortho*-C), 128.97 (*meta*-C), 122.43 (CH═CH), 21.29 (CH_3), 19.05 (CH_3). IR (ν, cm^{-1}): 3141 (m), 3008 (m), 2959 (m), 2918 (s), 1609 (m), 1486 (vs), 1404 (s), 1271 (s), 1226 (m), 1165 (m), 1089 (m), 1017 (mbr), 929 (m), 850 (m), 743 (m), 731 (m), 704 (vs). Anal. Calcd for $C_{42}H_{48}N_4Cl_2Ni$: C, 68.31; H, 6.55; N, 7.59. Found: C, 68.15; H, 6.61; N, 7.59.

1b: mp 280−288 °C (dec). ^1H NMR ($CDCl_3$): δ 7.01 (s, 8H, *meta*), 6.63 (s, 4H, CH═CH), 2.52 (s, 12H, *para*-CH_3), 2.00 (24 H, s, *ortho*-CH_3). ^{13}C NMR ($CDCl_3$): δ 168.92 (NCN), 137.64 (*ipso*-C), 136.44 (*para*-C), 136.38 (*ortho*-C), 129.08 (*meta*-C), 123.18 (CH═CH), 21.27 (CH_3), 20.06 (CH_3). IR (ν, cm^{-1}): 3141 (m), 3008 (m), 2959 (m), 2918 (s), 1609 (m), 1486 (vs), 1402 (s), 1267 (s), 1221 (m), 1166 (m), 1089 (m), 1017 (mbr), 927 (m), 850 (m), 730 (m), 704 (vs). Anal. Calcd for $C_{42}H_{48}N_4Br_2Ni$: C, 60.97; H, 5.85; N, 6.77. Found: C, 60.09; H, 5.89; N, 5.57.

2a: mp 253−259 °C (dec). ^1H NMR ($CDCl_3$): δ 7.42 (t, 4H, *para*-CH), 7.14 (d, 8H, *meta*-CH), 6.54 (4H, CH═CH), 2.78 (sept, J = 6.8 Hz, 8H, C*H*(CH_3)$_2$), 0.95 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 0.83 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 168.43 (NCN), 146.71 (*ipso*-C), 136.81 (*ortho*-C), 129.14 (*para*-C), 124.72 (*meta*-C), 123.83 (CH═CH), 28.12 (*C*(CH_3)), 25.95 (CH_3), 22.72 (CH_3). IR (ν, cm^{-1}): 3142 (w), 3068 (m), 2964 (vs), 2928 (sh), 2867 (s), 1464 (vs), 1402 (s), 1382 (s), 1361 (m), 1271 (s), 1201 (m), 1116 (m), 1060 (m), 941 (m), 802 (s), 757 (s), 710 (s). Anal. Calcd for $C_{54}H_{72}N_4Cl_2Ni$: C, 71.53; H, 8.00; N, 6.18. Found: C, 69.46; H, 7.68; N, 6.14. The elemental analysis of **2a** was carried out several times; however, all observed values were not in agreement with the calculated ones possibly due to small amounts of contaminated products that were difficult to separate by recrystallization.

2b: mp 250−260 °C (dec). ^1H NMR ($CDCl_3$): δ 7.41 (t, 4H, *para*-CH), 7.13 (d, 8H, *meta*-CH), 6.58 (s, 4H, CH═CH), 2.91 (sept, J = 6.8 Hz, 8H, C*H*(CH_3)$_2$), 0.98 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 0.82 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 170.40 (NCN), 146.72 (*ipso*-C), 136.75 (*ortho*-C), 129.29 (*para*-C), 124.47 (*meta*-C), 123.92 (CH═CH), 28.34 (*C*(CH_3)), 26.09 (CH_3), 22.92 (CH_3). IR (ν, cm^{-1}): 3143 (w), 3069 (m), 2965 (vs), 2930 (sh), 2868 (s), 1465 (vs), 1399 (s), 1331 (s), 1263 (s), 1201 (m), 1119 (m), 1060 (m), 940 (m), 801 (s), 756 (s), 710 (s). Anal. Calcd for $C_{54}H_{72}N_4Br_2Ni$: C, 60.97; H, 5.85; N, 6.77. Found: C, 60.87; H, 5.90; N, 6.48.

Preparation of 3a and 3b. In a typical example, bis(2,6-diisopropylphenyl)imidazolium chloride (102.7 mg, 0.241 mmol) and THF (2.5 mL) were added to a 20 mL Schlenk tube and stirred for 15 min, followed by addition of KO^tBu (30.2 mg, 0.269 mmol) and stirring for 20 min. The resulting pale yellow suspension was filtered through small amount of Celite and added to a THF solution of $[NiCl_2(PPh_3)_2]$ (158.4 mg, 0.242 mmol) with vigorous stirring. The solution was then stirred for 5 min, and the volatile reagents were removed under reduced pressure. After extracting with hexane, sublimation of the evaporated residue at 80−110 °C for 1 h removed the triphenylphosphine, giving deep purple crystals of **3a** (95.4 mg, 0.124 mmol, 51% yield). No contaminating phosphine was confirmed on the basis of ^1H NMR spectroscopy.

3a: mp 187 °C (dec). ^1H NMR ($CDCl_3$): δ 7.64 (t, 4H, *para*-CH), 7.47 (d, 8H, *meta*-CH), 6.88−7.12 (m, 15H, C_6H_5), 7.02 (s, 2H, CH═CH), 3.09 (sept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.29 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.07 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 165.3 (d, J_{PC} = 137 Hz, NCN), 147.3 (*ipso*-Ph: NHC), 135.9 (*ortho*-Ph: NHC), 134.7 (*ortho*-Ph: PPh_3), 133.7 (*ipso*-Ph: PPh_3), 129.8 (*para*-Ph: PPh_3), 129.2 (*meta*-Ph: NHC), 127.4 (*meta*-Ph: PPh_3), 124.3 (*para*-Ph: NHC), 123.9 (CH═CH), 28.58 (*C*(CH_3)), 26.25 (CH_3), 22.77 (CH_3). ^{31}P NMR ($CDCl_3$): δ 13.74 (br, $W_{1/2}$ = 110 Hz). IR (ν, cm^{-1}): 3074 (s), 3056 (s), 2965 (vs), 2930 (sh), 2868 (s), 1590 (m), 1539 (m), 1439 (vs), 1402 (s), 1333 (s), 1263 (m), 1183 (s), 1120 (vs), 1099 (sh), 1062 (m), 941 (m), 804 (s), 751 (s), 721 (s), 695 (vs). Anal. Calcd for $C_{45}H_{51}N_2PCl_2Ni$: C, 69.25; H, 6.59; N, 3.59. Found: C, 68.96; H, 6.68; N, 3.79.

3b: mp 175 °C (dec). ^1H NMR ($CDCl_3$): δ 7.63 (t, 4H, *para*-CH), 7.45 (d, 8H, *meta*-CH), 6.88−7.12 (m, 15H, C_6H_5), 7.06 (s, 2H, CH═CH), 3.20 (sept, J = 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.31 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.05 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 163.6 (d, J_{PC} = 112.1 Hz, NCN), 147.2 (*ipso*-Ph: NHC), 136.1 (*ortho*-Ph: NHC), 134.9 (*ortho*-Ph: PPh_3), 133.7 (*ipso*-Ph: PPh_3), 129.9 (*para*-Ph: PPh_3), 129.2 (*meta*-Ph: NHC), 127.3 (*meta*-Ph: PPh_3), 125.1 (*para*-Ph: NHC), 124.0 (CH═CH), 28.87 (*C*(CH_3)), 26.38 (CH_3), 22.91 (CH_3). ^{31}P NMR ($CDCl_3$): 22.15 (br, $W_{1/2}$ = 435 Hz). IR (ν, cm^{-1}): 3074 (s), 3056 (s), 2963 (vs), 2929 (sh), 2867 (s), 1589 (m), 1464 (vs), 1434 (vs), 1399 (s), 1330 (s), 1272 (m), 1183 (m), 1119 (s), 1098 (s), 941 (m), 802 (s),

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750 (s), 704 (s), 692 (vs). Anal. Calcd for $C_{45}H_{51}N_2PBr_2Ni$: C, 62.17; H, 5.91; N, 3.22. Found: C, 62.40; H, 6.09; N, 3.20.

Catalytic C−C Bond Coupling Using 3a. In a typical example, complex **3a** (3.0 mg, 0.0038 mmol), *p*-chloroanisol (95 μL, 0.76 mmol), and THF (0.5 mL) were added to a 20 mL Schlenk tube, and the mixture was stirred at room temperature for several minutes. Phenylmagnesium chloride (1.14 mmol, 2.0 M solution in THF) was added to the solution, which was stirred for 30 min. Then, after the reaction was quenched by adding methanol (0.5 mL), water was added. The organic layer was extracted with dichloromethane and dried with magnesium sulfoxide. Removal of the solvents under reduced pressure gave 4-methoxybiphenyl (140 mg, 0.759 mmol, 100% yield).

Catalytic C−C Bond Coupling Using 2a. In a typical example, complex **2a** (3.0 mg, 0.0033 mmol), *p*-bromoanisol (82 μL, 0.66 mmol), and THF (0.5 mL) were added to a 20 mL Schlenk tube, and the mixture was stirred at room temperature for several minutes. Phenylmagnesium chloride (0.99 mmol, 2.0 M solution in THF) was added to the solution, which was stirred for 30 min. Then, after the reaction was quenched by adding methanol (0.5 mL), the mixture was extracted with dichloromethane and dried with magnesium sulfoxide. The solvents were removed under reduced pressure, and the residual mixture was separated by column chromatography by eluting with 20% dichloromethane in hexane to give 4-methoxybiphenyl (41.6 mg, 0.226 mmol, 39% yield).

X-ray Crystallography. Single crystals of **2a**, **2b**, and **3a** for X-ray diffraction studies were grown at −35 °C from a hexane solution. The data were collected on a Rigaku AFC-5R four-cycle axis diffractometer at 293 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares fitting based on F^2 using the program SHELXL 97-2 PC version.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located at ideal positions and were included in the refinement, but were restricted to ride on the atom to which they were bonded.

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Supporting Information Available: Detailed procedures for all nickel compounds **1**−**3**, ^{13}C and ^{31}P NMR spectra for **3a** and **3b**, variable-temperature ^{31}P NMR spectra for **3b**, and cif data for **2a**, **2b**, and **3a**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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