N-Heterocyclic Carbene Sulfonamide Palladium Complexes and Their Catalytic Activities in Suzuki−Miyaura Coupling Reaction

Tao Zhang,[†] Wenfeng Wang,[†] Xingxing Gu,[†] and Min Shi*[,†,‡]

School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 MeiLong Road, Shanghai 200237, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China

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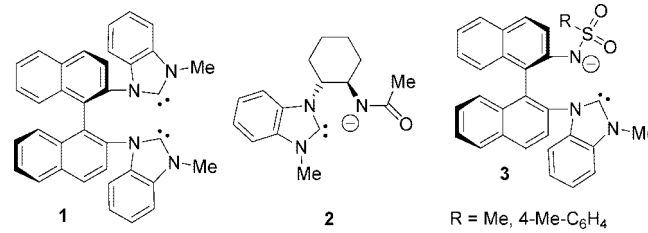
Novel N-heterocyclic carbene sulfonamide ligands derived from binaphthyl-2,2′-diamine (BINAM) and their tridentate NHC−Pd(II) complexes as well as their corresponding NHC−Pd(II) complexes bearing weakly coordinating acetate counterions have been successfully synthesized in good yields. These NHC−palladium(II) complexes have been characterized by X-ray crystal structure diffraction. Moreover, we found that these NHC−Pd(II) complexes bearing weakly coordinating acetate counterions are quite effective in Suzuki−Miyaura coupling reaction to give the corresponding products in good to excellent yields in most cases at room temperature in 2-propanol in the presence of sodium *tert*-butoxide.

Introduction

Since the isolation and characterization of the stable free N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991,[1] much attention has been paid toward their properties and applications. NHCs have been developed rapidly in the latest decade due to their stability to air and moisture and their strong σ-donor but poor π-acceptor abilities.[2] Thus far, they have been reported in numerous transition metal-mediated reactions as excellent supporting ligands because they can be used to replace phosphine ligands in such catalytic reactions.[3] Most significantly, a number of NHC−palladium complexes have emerged as effective catalysts for a variety of coupling reactions.[4] Furthermore, recent studies have revealed that NHC−Pd(II) complexes bearing weakly coordinating counterions, such as acetate, are highly efficient catalysts for C−H activation,[5a] aerobic oxidation of alcohols,[5b,c] hydroarylation of alkynes,[5d] and Suzuki−Miyaura coupling reaction.[5e] Previously, we reported the synthesis of a novel bisNHC ligand **1** based on binaphthyl-2,2′-diamine (BINAM) and its *cis*-chelated bisNHC−palladium complex (Chart 1).[6a] In addition, we also synthesized a NHC acetylamide ligand **2** from *trans*-cyclohexane-1,2-diamine and its NHC−palladium complex (Chart 1).[6b] Interestingly, NHC acetylamide ligand **2** only coordinates the metal center through NHC to form a dimeric monocoordinated NHC−Pd(II) complex rather than a *cis*-chelated NHC−palladium complex. These interesting NHC−Pd(II) complexes have been used as catalysts in the Suzuki−Miyaura coupling reaction. However, it was found that all these coupling reactions were carried out upon heating in tetrahydrofuran (THF), toluene, or *N*,*N*-dimethylacetamide (DMAc) to give the corresponding biaryls in high yields. As a continuing investigation on the preparation of more efficient NHC−Pd(II) complexes in coupling reactions, we turned our

Chart 1.



* Corresponding author. Fax: 86-21-64166128. E-mail: Mshi@mail.sioc.ac.cn.
† East China University of Science and Technology.
‡ Shanghai Institute of Organic Chemistry.

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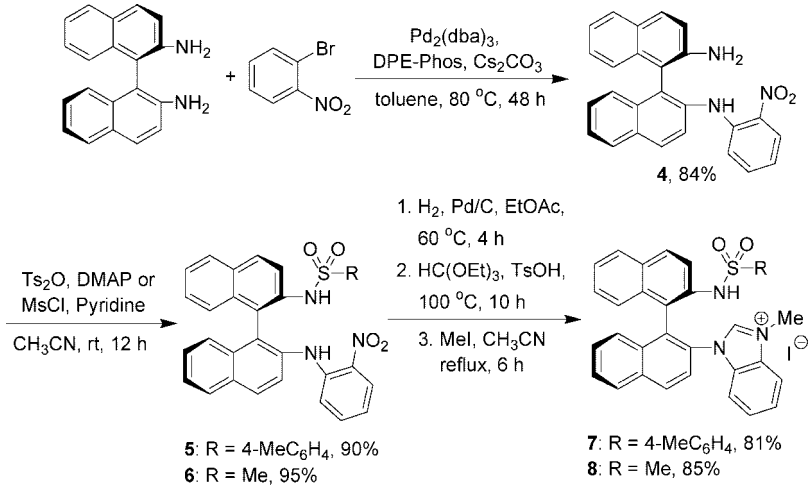
Scheme 1. Synthesis of the Benzimidazolium Salts as Ligand Precursors for the N-Heterocyclic Carbenes



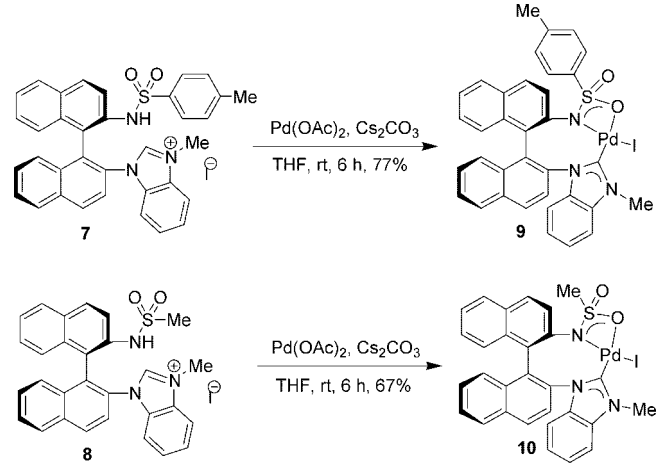
research interest to NHC sulfonamide ligand **3**[7] derived from BINAM (Chart 1). In this paper, we wish to report the synthesis of a variety of NHC sulfonamide palladium(II) complexes and these corresponding NHC−Pd(II) complexes bearing weakly coordinating acetate counterions as well as their catalytic abilities in the Suzuki−Miyaura coupling reactions.

Results and Discussion

Synthesis of the Benzimidazolium Salts as Ligand Precursors for the N-Heterocyclic Carbenes. The synthesis of these benzimidazolium salts **7** and **8** is shown in Scheme 1. Using BINAM as the starting materials for the 2.5 mol % Pd-catalyzed coupling reaction with 2-bromonitrobenzene (1.0 equiv) in toluene in the presence of Cs_2CO_3 (3.2 equiv) and bis(2-diphenylphosphinophenyl)ether (DPE-phos) (7.5 mol %) at 80 °C for 48 h, the desired product **4** was obtained in 84% yield. The reaction of **4** with *p*-toluenesulfonic anhydride in the presence of *p*-*N*,*N*-dimethylaminopyridine (DMAP) or methanesulfonyl chloride in the presence of pyridine produced the corresponding products **5** and **6** in 90 and 95% yield, respectively, at room temperature (20 °C) in acetonitrile. The desired benzimidazolium salts **7** and **8** were obtained in 81 and 85% yield in a similar manner to that described previously (Scheme 1).[6]

Synthesis of NHC−Palladium(II) Complexes. At first, we found that when benzimidazolium salt **7** was treated with $Pd(OAc)_2$ at 90 °C in DMSO for 3 h in the presence of NaI, the corresponding NHC−palladium complex **9** was produced in low yield (30%). After several examinations, it was found that in the presence of Cs_2CO_3 the corresponding NHC−Pd(II) complexes **9** and **10** were produced in 77 and 67% yield, respectively, by treatment of benzimidazolium salts **7** and **8** with $Pd(OAc)_2$ at room temperature (20 °C) in THF for 6 h (Scheme 2). These NHC−Pd(II) complexes are air and moisture stable in the solid state and even in the solution state. Their structures were determined by microanalysis, IR and NMR spectroscopic data, and ESI-MS spectroscopy. The crystal structures of **9** and

Scheme 2. Synthesis of NHC−Palladium Complexes 9 and 10



10 were also unambiguously determined by X-ray diffraction.[8] The single crystals of these complexes suitable for X-ray crystal structure analysis were grown from the mixed solvent petroleum ether/CH_2Cl_2 (2:3). Figure 1 depicts the X-ray crystal structure of NHC−Pd(II) complex **9**. The crystal structure of **9** revealed a distorted-square-planar geometry around the metal center. The NHC ligand and iodide anion ligand coordinate to the palladium center, respectively, and the sulfonamide anion chelates with the metal center through the nitrogen atom and one of two oxygen atoms, stabilizing a 16-electron configuration around the metal center. The bond length of Pd−C(1) (1.927(3) Å) is comparable to those of ligand **1** and **2** analogues.[6] The S(1)−O(1) bond length (1.487(3) Å) is longer than that of S(1)−O(2) (1.428(3) Å, a typical S=O double bond length[7b,9],), suggesting partial π-conjugation between O(1), S(1), and N(3) (N(3)−S(1) bond length: 1.577(3) Å). The most remarkable feature of this structure is a face-to-face interaction ($\pi-\pi$ stacking) between the aryl ring of the Ts group and the naphthyl ring connected with the NHC ligand.

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(8) The crystal data of **9** have been deposited in the CCDC with number 281154. Empirical formula: $C_{35}H_{26}N_3O_2SIPd$; formula weight: 785.95; crystal color, habit: colorless, prismatic; crystal dimensions: 0.307 × 0.236 × 0.170 mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 12.7991(8) Å, b = 12.0372(8) Å, c = 20.4634(13) Å, α = 90°, β = 97.8740(10)°, γ = 90°, V = 3123.0(3) Å^3; space group: $P2(1)/n$; Z = 4; D_{calc} = 1.672 g/cm^3; F_{000} = 1552; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0437, 0.1039.

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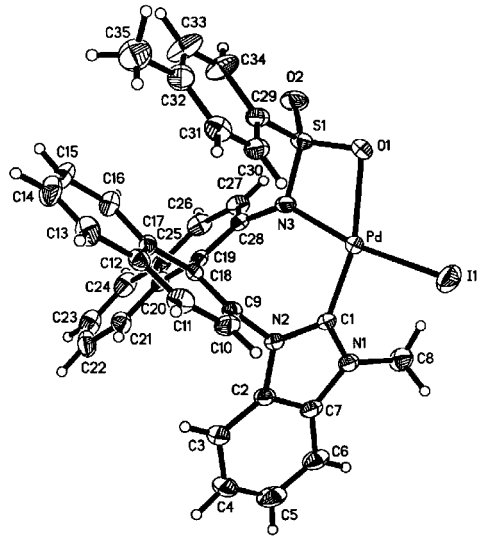


Figure 1. ORTEP drawing of NHC−Pd(II) complex **9** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd−C1 = 1.927(3), Pd−N3 = 2.040(3), Pd−O1 = 2.212(2), Pd−I1 = 2.5600(4), O1−S1 = 1.487(3), N3−S1 = 1.577(3), N3−C28 = 1.402(4); O1−Pd−N3 = 67.15(10), C1−Pd−N3 = 96.54(12), C1−Pd−I1 = 93.78(10), I1−Pd−O1 = 102.44(7), O1−Pd−C1 = 163.66(12), I1−Pd−N3 = 169.03(7).

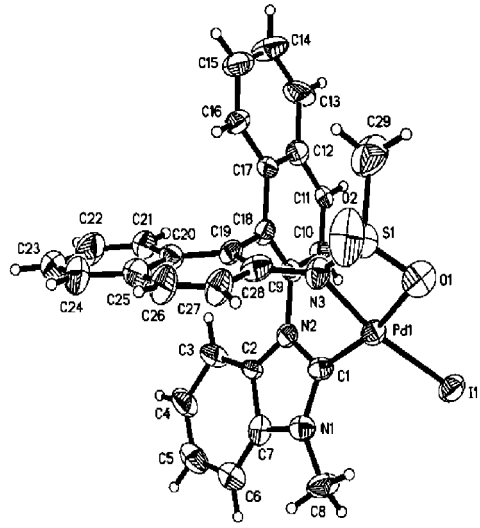
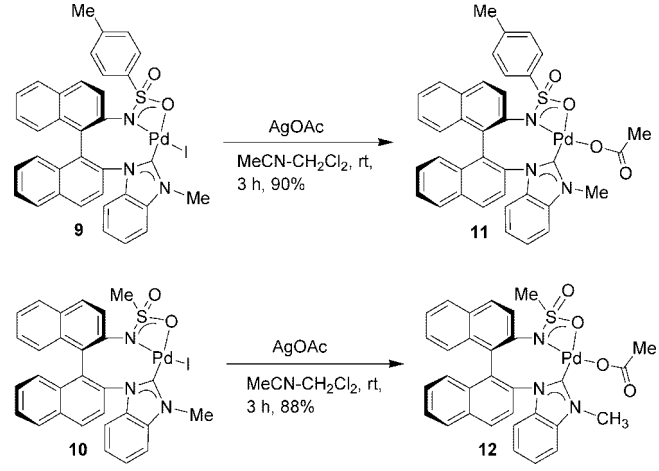


Figure 2. ORTEP drawing of NHC−Pd(II) complex **10** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd1−C1 = 1.888(13), Pd1−N3 = 2.031(11), Pd1−O1 = 2.180(9), Pd1−I1 = 2.5605(13), O1−S1 = 1.510(12), N3−S1 = 1.558(11), N3−C28 = 1.408(19); O1−Pd1−N3 = 68.0(4), C1−Pd1−N3 = 97.2(5), C1−Pd1−I1 = 90.2(4), I1−Pd1−O1 = 104.9(3), O1−Pd1−C1 = 164.8(5), I1−Pd1−N3 = 170.5(3).

The X-ray structure of NHC−Pd (II) complex **10** is shown in Figure 2,[10] which also adopts a distorted-square-planar geometry around the palladium center and is similar to that of complex **9**. The S(1)−O(1) bond length (1.510(12) Å) is longer than that of S(1)−O(2) (1.385(12) Å, typical S=O double bond length), also suggesting partial π-conjugation between O(1), S(1), and N(3) (N(3)−S(1) bond length: 1.558(11) Å). Due to the lack of a face-to-face interaction ($\pi-\pi$ stacking) between the aryl ring of the Ts group and the naphthyl ring connected with the NHC ligand in the structure, the bond length of Pd−C(1) of complex **10** (1.888(13) Å) is shorter than that of complex **9** (1.927(3) Å).

Scheme 3. Synthesis of Palladium Complexes 11 and 12



Upon treatment of NHC−Pd(II) complexes **9** and **10** with silver acetate in the mixed solvent MeCN/CH_2Cl_2 (1:2) at room temperature for 3 h, the corresponding NHC−Pd(II) complexes **11** and **12** bearing weakly coordinating acetate counterions were obtained in 90 and 88% yield, respectively (Scheme 3). The complexes **11** and **12** are also air and moisture stable in the solid state and even in the solution state. Their structures were confirmed by elemental analysis, IR and NMR spectroscopic data, and ESI-MS spectroscopy. The single crystals of NHC−Pd (II) complex **11** suitable for X-ray diffraction study were grown from the mixed solvent petroleum ether/CH_2Cl_2 (1:4). Figure 3 shows the X-ray crystal structure of this complex.[11] The acetate anion acts as monodentate ligand instead of iodide anion in the structure of **9** coordinating to the palladium center. The binding angle of O(1)−Pd−N(3) in complex **11** (65.7(3)°) is smaller than that in complex **9** (67.15(10)°). In addition, the length of Pd−C(1) (1.922(11) Å) in complex **11** is the same as that in complex **9** (1.927(3) Å), indicating that the weakly coordinating counterion does not affect the coordination between NHC and the metal center.[5d]

Suzuki−Miyaura Coupling Reaction. The application of NHC−Pd(II) complexes **9**–**12** (1.0 mol %) as catalysts for the Suzuki−Miyaura coupling reaction was examined where $NaOBu^t$ was used as a base and 2-propanol (IPA) was used as solvent in the reaction of phenylboronic acid with 1-bromo-4-methylbenzene at room temperature (20 °C) under an argon atmosphere.[12] The results are summarized in Table 1, including

(10) The crystal data of **10** have been deposited in the CCDC with number 299485. Empirical formula: $C_{29.5}H_{24}ClIN_3O_{2.5}SPd$; formula weight: 761.33; crystal color, habit: colorless, prismatic; crystal dimensions: 0.485 × 0.102 × 0.063 mm; crystal system: monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 9.0358(7)Å, b = 20.9256(16)Å, c = 18.2528(14)Å, α = 90°, β = 98.456(2)°, γ = 90°, V = 3413.7(5)Å^3; Space group: P2(1)/n; Z = 4; D_{calc} = 1.481 g/cm^3; F_{000} = 1496; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0733, 0.1961.

(11) The crystal data of **11** have been deposited in CCDC with number 623870. Empirical Formula: $C_{37}H_{33}N_3O_6SPd$; Formula Weight: 754.12; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.218 × 0.166 × 0.049 mm; Crystal System: Monoclinic; lattice type: primitive; lattice parameters: a = 15.5903(17) Å, b = 16.9096(19) Å, c = 13.1433(15) Å, α = 90°, β = 103.032(2)°, γ = 90°, V = 3375.7(7) Å^3; space group: $P2(1)/n$; Z = 4; D_{calc} = 1.484 g/cm^3; F_{000} = 1544; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0963, 0.2326.

(12) (a) These reaction conditions were discovered by Nolan's group. See: Hillier, A. C.; Nolan, S. P. *Platinum Met. Rev.* **2002**, *46*, 50. (b) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (c) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181.

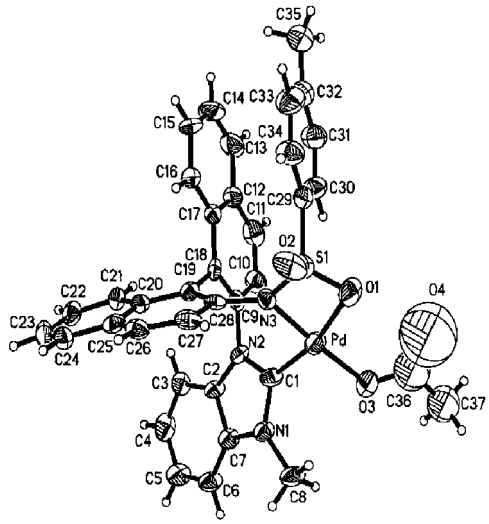
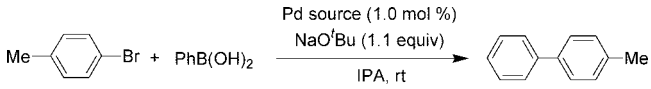


Figure 3. ORTEP drawing of NHC−Pd(II) complex **11** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd−C1 = 1.922(11), Pd−N3 = 2.036(8), Pd−O1 = 2.248(8), Pd−O3 = 2.084(11), O1−S1 = 1.476(8), N3−S1 = 1.568(8), N3−C28 = 1.416(12); O1−Pd−N3 = 65.7(3), C1−Pd−N3 = 98.0(4), C1−Pd−O3 = 86.4(4), O3−Pd−O1 = 110.0(4), O1−Pd−C1 = 163.6(4), O3−Pd−N3 = 175.6(4).

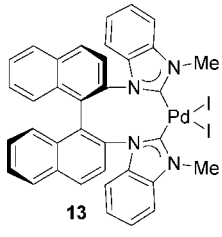
Table 1. NHC−Pd(II) Complex-Catalyzed Suzuki−Miyaura Coupling Reaction of 1-Bromo-4-methylbenzene with Phenylboronic Acid[a]



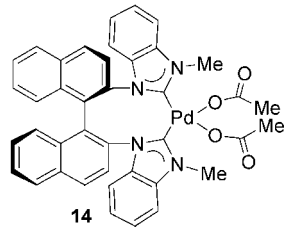
15a

entry	Pd source	time (h)	yield (%)[b] **15a**
1	**9**	6	61
2	**10**	6	85
3	**11**	6	90
4	**12**	6	89
5	**13**	6	17
6	**14**	6	86
7	**9**	72	80
8	**11**	4	88

[a] Reaction conditions: 1.0 mmol of 1-bromo-4-methylbenzene, 1.2 mmol of phenylboronic acid, 1.1 mmol of NaO^{t}Bu, 0.01 mmol of Pd source, and 2.0 mL of IPA. [b] Isolated yields.



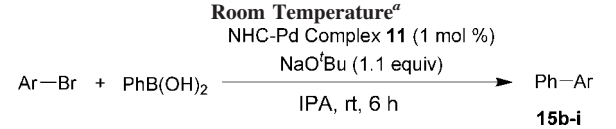
13



14

the results using these previously reported NHC−Pd(II) complexes **13**[4] and **14** bearing two acetate counterions as the catalysts.[7] We found that under these reaction conditions, NHC−Pd(II) complexes **11**, **12**, and **14** bearing weakly coordinating acetate counterions gave the coupled product biaryl **15a** in higher yields than those of NHC−Pd(II) complexes **9**, **10**, and **13** after 6 h, although NHC−Pd(II) complex **10** is fairly effective in the Suzuki coupling reaction (Table 1, entries 1–6). Furthermore, as a clear comparison, using NHC−Pd(II) complex **9** as the catalyst, **15a** was obtained in 80% yield after 72 h under identical conditions (Table 1, entry 7). However, **15a** could be formed in 88% yield after 4 h under identical conditions using NHC−Pd(II) complex **11** as the catalyst (Table 1, entry 8).

Table 2. NHC−Pd(II) Complex 11-Catalyzed Suzuki−Miyaura Coupling Reaction of Aryl Bromides with Phenylboronic Acid at Room Temperature[a]



15b-i

entry	Ar	Ph−Ar	yield (%)[b] **15**
1	C_6H_5	**15b**	91
2	2-ClC_6H_4	**15c**	94
3	3-MeC_6H_4	**15d**	86
4	2-MeC_6H_4	**15e**	83
5	3,5-Me$_2C_6H_3$	**15f**	82
6	4-C(O)MeC_6H_4	**15g**	99
7	3-N$O_2C_6H_4$	**15h**	99
8	4-MeOC_6H_4	**15i**	80

[a] Reaction conditions: 1.0 mmol of aryl bromide, 1.2 mmol of phenylboronic acid, 1.1 mmol of NaO^{t}Bu, 0.01 mmol of NHC−Pd(II) complex **11**, and 2.0 mL of IPA. [b] Isolated yields.

Using these optimized reaction conditions, the Suzuki−Miyaura coupling reaction of a variety of arylbromides with phenylboronic acid was examined using NHC−Pd(II) **11** as a catalyst. The results are summarized in Table 2. As can be seen from Table 2, the corresponding coupling products **15b−i** were obtained in 80–99% yields within 6 h at room temperature (20 °C), indicating that this NHC−Pd(II) complex bearing a weakly coordinating acetate counterion is a quite effective catalyst in the Suzuki−Miyaura coupling reaction (Table 2, entries 1–8).

A plausible explanation of why NHC−Pd(II) complexes **11**, **12**, and **14** are so effective in this reaction is proposed as below: the weakly coordinating counterions such as acetate on the palladium center facilitate the oxidative addition step and transmetalation step and, therefore, increase the catalytic ability of the active Pd species and subsequently accelerate the reaction rate in the Suzuki coupling reation.[13]

Conclusion

In conclusion, we have developed a new class of NHC sulfonamide ligands and their tridentate palladium complexes **9**, **10**, **11**, and **12**. These NHC−Pd(II) complexes have been isolated and characterized by IR, NMR spectroscopic data, and ESI-MS spectroscopy. Moreover, three of them have been characterized by X-ray crystal structure analysis. These interesting NHC sulfonamide complexes have been tested in the Suzuki−Miyaura coupling reaction. NHC−Pd(II) complexes **11** and **12** bearing weakly coordinating acetate counterions are quite effective catalysts in this reaction to give the corresponding coupled products in good to high yields in most cases under very mild conditions. Efforts are underway to elucidate the mechanistic details of this C−C bond forming reaction catalyzed by Pd(II)−NHC complexes and the use of **11** and **12** to catalyze other C−C bond forming transformations as well as asymmetric catalysis.

Experimental Section

Synthesis of NHC−Pd(II) Complex 9. Compound **7** (136 mg, 0.20 mmol), Cs_2CO_3 (62 mg, 0.20 mmol), and $Pd(OAc)_2$ (44 mg,

(13) (a) Solin, N.; Kjellgren, J.; Szabó, K. J. *J. Am. Chem. Soc.* **2004**, *124*, 7026. (b) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752. (c) Huynh, H. V.; Neo, T. C.; Tan, G. K. *Organometallics* **2006**, *25*, 1298.

0.20 mmol) were stirred at room temperature in THF (10 mL) for 20 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate, 4:1) to give Pd(II)−NHC complex **9** (120 mg, 77%) as a yellow solid. The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2/petroleum ether. Mp > 250 °C; $[\alpha]^{20}_D$ 234 (*c* 0.52, $CHCl_3$); IR (KBr) ν 3391, 2923, 1574, 1404, 1384, 1274, 1030, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.13 (s, 3H, CH_3), 4.15 (s, 3H, CH_3), 6.17 (d, J = 8.4 Hz, 2H, ArH), 6.47 (d, J = 8.4 Hz, 2H, ArH), 6.71–6.81 (m, 2H, Ar), 6.93–7.11 (m, 3H, ArH), 7.20–7.26 (m, 5H, ArH), 7.46 (t, J = 7.5 Hz, 1H, ArH), 7.62 (d, J = 8.1 Hz, 1H, Ar), 7.69 (t, J = 7.8 Hz, 2H, ArH), 7.85 (d, J = 9.0 Hz, 1H, ArH), 8.00 (d, J = 8.1 Hz, 1H, ArH), 8.26 (d, J = 8.7 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 21.4, 37.3, 109.9, 110.9, 123.6,123.7, 124.8, 125.2, 125.3, 126.1, 126.2, 126.3, 126.5, 126.8, 126.9, 127.7, 127.8, 128.6, 129.2, 130.4, 130.7, 133.28, 133.33, 133.6, 133.9, 134.2, 135.3, 135.4, 138.2, 138.8, 142.2, 161.5; MS (ESI) *m/e* 808.0 (M^+ + Na);. Anal. Calcd for $C_{36}H_{31}IN_3O_2PdS$: C 53.84, H 3.89, N 5.23. Found: C 54.00, H 3.87, N 5.19.

Synthesis of NHC−Pd(II) Complex 11. Complex **9** (157 mg, 0.20 mmol) was dissolved in CH_3CN/CH_2Cl_2 (3:1) (10 mL). Then AgOAc (24.5 mg, 0.20 mmol) was added, and the mixture was stirred at room temperature for 3 h. The resulting suspension was filtered through Celite to remove AgI, and then the solvent was removed under reduced pressure to give Pd(II)−NHC complex **11** (129 mg, 90%) as a white solid. The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2/petroleum ether. Mp > 250 °C; $[\alpha]^{20}_D$ 195 (*c* 0.86 $CHCl_3$); IR (KBr) ν 3410, 2924, 1585, 1509, 1438, 1382, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.92 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 4.09 (s, 3H, CH_3), 6.56–6.61 (m, 2H, Ar), 6.65–7.17 (m, 9H, ArH), 7.39–7.69 (m, 6H, ArH), 7.92 (d, J = 8.7 Hz, 1H, ArH), 7.90 (d, J = 8.7 Hz, 1H, ArH), 8.27 (d, J = 8.7 Hz, 1H, ArH); MS (ESI) *m/e* 679.1 (M^+ − OAc + Na). Anal. Calcd for $C_{38}H_{33}N_3O_4PdS \cdot 1/2C_6H_{14}$: C 63.36, H 5.19, N 5.41. Found: C 63.70, H 4.84, N 5.69.

Synthesis of NHC−Pd(II) Complex 10. Compound **8** (182 mg, 0.30 mmol), Cs_2CO_3 (93 mg, 0.30 mmol), and $Pd(OAc)_2$ (66 mg, 0.30 mmol) were stirred at room temperature in THF (15 mL) for 20 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate, 3:1) to give Pd(II)−NHC complex **10** (120 mg, 67%) as a red solid. The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2/petroleum ether solutions. Mp > 250 °C; $[\alpha]^{20}_D$ 306 (*c* 0.82, $CHCl_3$); IR (KBr) ν 3538, 1583, 1509, 1382, 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.15 (s, 3H, CH_3), 4.08 (s, 3H, CH_3), 6.99–7.36 (m, 10H, ArH), 7.63–7.76 (m, 4H, ArH), 8.12 (d, J = 8.4 Hz, 1H, ArH), 8.31 (d, J = 8.7 Hz, 1H, ArH); MS (ESI) *m/e* 731.9 (M^++23); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) 37.3, 42.3, 110.0, 110.8, 123.6, 123.8, 125.1, 125.2, 125.8, 126.0, 126.5, 126.6, 126.8, 127.5, 127.7, 127.8, 128.6, 129.5, 130.7, 130.9, 133.3, 133.57, 133.61, 133.9, 134.1, 135.1, 135.4, 138.3, 160.5. Anal. Calcd for $C_{29}H_{22}IN_3O_2PdS \cdot 1/2CH_2Cl_2 \cdot H_2O$: C 45.99, H 3.27, N 5.45. Found: C 46.12, H 3.33, N 5.76.

Synthesis of NHC−Pd(II) Complex 12. Complex **10** (142 mg, 0.20 mmol) was dissolved in CH_3CN/CH_2Cl_2 (3:1) (10 mL). Then AgOAc (24.5 mg, 0.20 mmol) was added, and the mixture was stirred at room temperature for 3 h. The resulting suspension was filtered through Celite to remove AgI, and then the solvent was removed under reduced pressure to give Pd(II)−NHC complex **12** (113 mg, 88%) as a white solid. Mp > 250 °C; $[\alpha]^{20}_D$ 386 (*c* 0.81, $CHCl_3$); IR (KBr) ν 3410, 2924, 1585, 1509, 1438, 1382, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.86 (s, 3H, CH_3), 3.57 (br, 3H, CH_3), 4.06 (s, 3H, CH_3), 6.87–7.13 (m, 7H, ArH), 7.38–7.67 (m, 6H, ArH), 8.02–8.12 (m, 2H, ArH), 8.33 (d, J = 9.0 Hz, 1H, ArH); MS (ESI) *m/e* 664.1 (M^+ + 23), 614.1 (M^+ − OAc + 23). Anal. Calcd for $C_{31}H_{25}N_3O_4PdS$: C 57.99, H 3.92, N 6.54. Found: C 58.22, H 3.84, N 6.69.

Typical Procedure for the Suzuki−Miyaura Cross-Coupling Reaction of Aryl Bromides with Phenylboronic Acids. A typical procedure is given below for the reaction expressed in entry 3 of Table 1. A mixture of NHC−Pd(II) complex **11** (7.2 mg, 0.01 mmol), $NaOBu^t$ (105.6 mg, 1.1 mmol), 1-bromo-4-methylbenzene (171.6 mg, 1.0 mmol), and phenylboronic acid (146 mg, 1.2 mmol) was dissolved in IPA (2.0 mL). The mixture was stirred at room temperature (20 °C) for 6 h. The reaction mixture was filtered and then evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether) to give **15a** (151 mg, 98%) as a white solid.

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