Benzenimidazole-Functionalized Imidazolium-Based N-Heterocyclic Carbene Complexes of Silver(I) and Palladium(II): Isolation of a Ag_3 Intermediate toward a Facile Transmetalation and Suzuki Coupling

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A new benzenimidazole-functionalized imidazolium-based N-heterocyclic carbene complex of Pd(II) has been prepared from facile transmetalation via a Ag(I) precursor. The latter was obtained from a condensation reaction between Ag_2O and benzenimidazolium salt. Single-crystal X-ray crystallography revealed an unusual trinuclear $Ag_3Cl_2(\mu\text{-Cl})(\mu\text{-N-C})_2$ (N-C = 3-methyl-1-(1-ethyl-2-methylbenzoyl)imidazolin-2-ylidene) intermediate in which the central carbene-supported Ag(I) is flanked by two imidazole-coordinated Ag(I). The hybrid ligand (N-C), carrying two heterodonors of benzenimidazole and carbene, is bridging in Ag(I) but chelating in Pd(II). The latter mononuclear $PdCl_2(\eta\text{-N-C})$ is active toward Suzuki−Miyaura coupling of aryl bromides and boronic acids, giving a TON up to 11 750 within 4 h at rt.

Introduction

Research on N-heterocyclic carbenes (NHCs) continues to advance at a blistering pace.[1] We have recently reported a system in which the NHC is functionalized by an allyl pendant.[2] This reflects our current interest in the design and isolation of catalytically active complexes that are supported by hemilabile ligands.[3] A major incentive of such work is to promote a reversible coordination-and-dissociation mechanism whereby the metal–ligand bond can respond actively to the different needs of the metal at different stages of the catalytic cycle.[4] Although most of such designs are still confined to phosphine-based system, there are emerging examples of NHCs that carry pendants ranging from spectating to hemilabile and coordinative, such as pyridyl, thioether, picolyl, amine, and alcohol.[5] In this report, we use a simple and known method to create a new imidazole-rich heterofunctional ligand. This is achieved by attaching an active (coordinative) benzenimidazole function to the imidazolium-based NHC. The coordinative ability of the resulting hybrid ligand (N-C) is demonstrated by the isolation and characterization of the transmetalation intermediate $Ag_3Cl_2(\mu\text{-Cl})(\mu\text{-N-C})_2$ (N-C = 3-methyl-1-(1-ethyl-2-methylbenzoyl)imidazolin-2-ylidene). Several structural motifs of the intermediate Ag(I) carbenes have been highlighted in the literature,[6] notably AgX(NHC), $[Ag(NHC)_2][AgX_2]$, and their dinuclear forms.[7] It is nevertheless unexpected to witness a trinuclear Ag(I) framework stabilized by the C- and N-donors of the benzenimidazole-based functions. Using this hybrid ligand, we achieved a facile transmetalation, isolated both Ag(I) and Pd(II) NHC complexes, and observed a high-yielding catalysis of $PdCl_2(\eta\text{-N-C})$ toward C−C coupling of aryl halides and boronic acids at rt.

Results and Discussion

Synthesis of a New Benzenimidazole-Functionalized Imidazolium Salt (2). The synthesis of the imidazolium ligand precursor of the new C/N-bidentate ligand was carried out by direct N-alkylation of *N*-methylimidazole with 2-chloromethyl-

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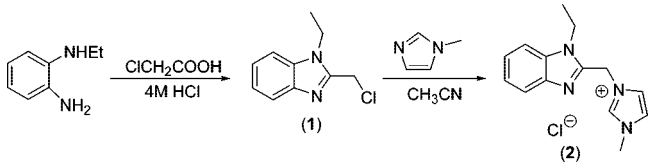
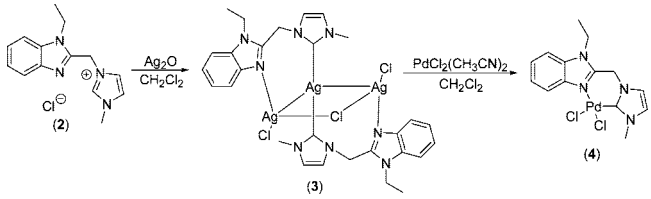
Scheme 1. Synthesis of New N-Functionalized Benzenimidazolium Salt 2



Scheme 2. Synthesis of the Pd(II) Complex 4 from the Hybrid Ligand Precursor 2 from a Transmetalation Method via a Ag_3 Intermediate (3)



1-ethyl-benzenimidazole (**1**), which in turn was obtained as a pink solid in a one-step procedure from commercially available *N*-ethylbenzene-1,2-diamine with 80% yield (Scheme 1).[8] Adding 1-methylimidazole to a solution of **1** in CH_3CN at 90 °C for 48 h led to the formation of the 1-ethyl-2-methylbenzenimidazole-imidazolium salt H[C-N]Cl (**2**), which was precipitated and isolated as a white solid in 87% yield. The formation of H[C-N]Cl was confirmed by a characteristic downfield signal in the ^{1}H NMR spectrum at 9.45 ppm for the NCHN proton and a base peak in the ESI mass spectrum at $m/z = 241$ for the $H[C\text{-}N]^+$ fragment.

Synthesis of Ag(I) and Pd(II) Complexes. Compound **2** essentially serves as a carbene precursor that delivers the NHC carbene to palladium via silver in a transmetalation method developed by Lin et al.[9] Mixing the imidazolium salt **2** with Ag_2O in CH_2Cl_2 at rt for 12 h afforded the silver N-heterocyclic complex $[Ag_3(N\text{-}C)_2Cl_3]$, **3** (Scheme 2). The ESI mass spectrum of **3** in CH_2Cl_2 shows a molecular ion peak at $m/z = 587$, which corresponds to the silver bis(carbene) monocation, $[Ag(N\text{-}C)_2]^+$. The Ag-NHC coordination was established by the ^{13}C NMR shift at δ 180.16 ppm, assignable to the 2C-imidazol-2-ylidene carbon, and absence of the ^{1}H resonance for the 2H-imidazolium proton.

Single crystals suitable for X-ray crystallography of **3** were obtained by slow diffusion of Et_2O into its CH_2Cl_2 solution. X-ray diffraction analysis revealed an unusual trinuclear imidazole-carbene-bridged Ag_3 with approximately perpendicular alignment of the metals ($\angle$Ag1−Ag2−Ag3 84.54(1)°) (Figure 1 and Table 1). The central Ag(I) carries the carbene moiety (Ag1−C1 2.094(3) and Ag1−C15 2.099(3) Å), whereas the external Ag(I) centers are supported by the N-bonded imidazole. As a result, the hybrid ligand links the internal to the external silver atoms, whereas the latter is bridged by chloride and also carries a terminal chloride each. The bridging imidazole-carbene brings the metals to close proximity and results in an overall rhombic $\{Ag_3Cl\}$ core, with Cl being 0.494 Å out of the Ag_3 plane.

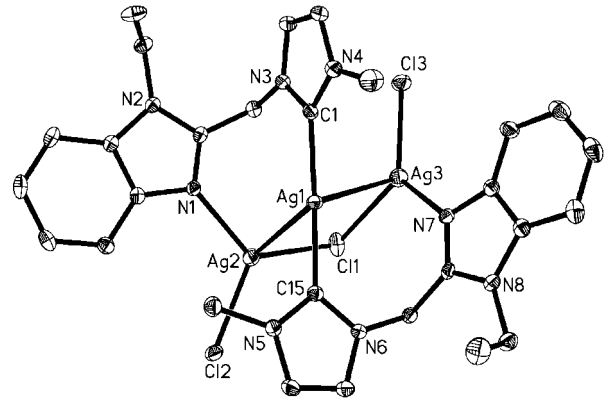


Figure 1. ORTEP view of the molecule $[Ag_3(N\text{-}C)_2Cl_3]$ (**3**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity.

The Ag···Ag contacts of 3.0074(4) and 3.1056(4) Å are within those recorded in many Ag−Ag bonded systems (2.8–3.3 Å) but slightly longer than that of the unsupported Ag−Ag bond (2.954(4) Å) in Lin's original carbene $(NHC)_2Ag\text{-}AgBr_2$ and the orthogonal d^{10}−d^{10} argentophilic interaction (2.815(4) Å) in the aggregate $\{Pt_4Ag_2S_4\}$ system.[9, 10] The Ag−Ag interactions contribute to the stability of this 50-e cluster with near-tetrahedral Ag(I).

Complex **3** undergoes transmetalation with $PdCl_2(CH_3CN)_2$ by giving the corresponding chelating benzenimidazole-carbene-palladium(II) complex **4** in ca. 67% yield (Scheme 2). The use of other palladium precursors (such as $[PdCl_2(COD)]$) is possible but would not improve the yields significantly. ESI mass spectral analysis in CH_3CN gives a $m/z = 424$ peak that could be assigned to $\{[PdCl(CH_3CN)(N\text{-}C)]^+\}$. In MeOH solution, there are peaks at $m/z = 415$ corresponding to $\{[PdCl(MeOH)(C\text{-}N)]^+\}$. NMR analysis is consistent with a mononuclear $PdCl_2(N\text{-}C)$ complex with NHC carbene and imidazole coordination at nitrogen. Chelation of the hybrid ligand imposes a hindered ligand rotation, thereby differentiating the two hydrogen atoms on the unique carbon that links the NHC to benzenimidazole (C5 in the crystal structure depicted in Figure 2). One of the protons on C5 is intermolecularly H-bonded to both chlorides of the neighboring molecule. These analogous protons are equivalent in **3**, giving a single ^{1}H proton resonance even down to −80 °C in CD_3OD. This possibly suggests a fast dynamic bond cleavage at Ag−N and that the solid-state structure is not retained in solution.

The molecular structure of **4** was determined by X-ray single-crystal diffraction (Figure 2 and Table 2). It shows the expected chelating benzenimidazole-derivatized NHC at an essentially square-planar Pd(II) (C1−Pd1−N1, 85.58(19)°; C1−Pd1−Cl2, 92.04(15)°; N1−Pd1−Cl1, 91.46(13)°; Cl2−Pd1−Cl1, 90.76(6)°). The Pd1−Cl1 bond [2.376(17) Å] *trans* to the carbene is significantly longer than that *trans* to the benzoimdazole-N donor atom [2.300(15) Å], which indicates the strong *trans* influence of the N-heterocyclic carbene ligand. This is consistent with previous structural studies on related complexes.[11]

Examination of the crystal packing revealed that each mononuclear Pd-NHC complex of **4** is associated with its neighbors through H-bonding between the chlorides and two

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

		Bond Lengths			
Ag1−C1	2.094(3)	Ag1−C15	2.099(3)	Ag1−Ag2	3.0074(4)
Ag1−Ag3	3.1056(4)	Ag2−N1	2.242(2)	Ag2−Cl2	2.5019(9)
Ag2−Cl1	2.5227(9)	Ag3−N7	2.242(3)	Ag3−Cl3	2.4734(9)
Ag3−Cl1	2.5874(9)	Ag2···Ag3	4.112(5)		
		Bond Angles			
C1−Ag1−C15	173.19(11)	C1−Ag1−Ag2	112.44(8)	C15−Ag1−Ag2	71.57(8
C1−Ag1−Ag3	78.30(8)	C15−Ag1−Ag3	107.90(8)	Ag1−Ag2−Ag3	84.535(12)
N1−Ag2−Cl2	117.31(6)	N1−Ag2−Cl1	124.76(7)	Cl2−Ag2−Cl1	116.22(3)
N1−Ag2−Ag	77.84(6)	Cl2−Ag2−Ag1	123.31(2)	Cl1−Ag2−Ag1	84.28(2)
N7−Ag3−Cl3	125.92(7)	N7−Ag3−Cl1	112.69(7)	Cl3−Ag3−Cl1	121.28(3)
N7−Ag3−Ag1	69.43(6)	Cl3−Ag3−Ag1	114.14(2)	Cl1−Ag3−Ag1	81.26(2)
Ag2−Cl1−Ag3	107.16(3)				

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

		Bond Distances			
Pd(1)−C(1)	1.976(6)	Pd(1)−N(1)	2.022(4)	Pd(1)−Cl(2)	2.300(15)
Pd(1)−Cl(1)	2.376(17)				
		Bond Angles			
C(1)−Pd(1)−N(1)	85.58(19)	C(1)−Pd(1)−Cl(2)	92.04(15)	N(1)−Pd(1)−Cl(2)	176.24(11)
C(1)−Pd(1)−Cl(1)	175.85(17)	N(1)−Pd(1)−Cl(1)	91.46(13)	Cl(2)−Pd(1)−Cl(1)	90.76(6)
		Hydrogen Bonds			
C−HCl[a]	C−H	CCl	HCl	∠C−HCl	
C5−H5···Cl1A	0.97	3.5462	2.74	141	
C5−H5···Cl2A	0.97	3.5468	2.75	140	
C13−H13···Cl1B	0.97	3.7109	2.79	160	

[a] Symmetry codes: A, $1-x$, $2-y$, $1-z$; B, $x-1$, y, z.

kinds of methylene protons. Through the H-bonds between the bridgehead methylene (C5) proton and the chlorides, two mononuclear units come together to form a dinuclear framework, in which the two coordinative planes of [$PdCl_2(\eta$-N-C)] are coplanar to each other with a Pd···Pd separation of 4.497 Å (Figure 3). These dimers are further aligned side-by-side in the *a* direction by H-bonding between the ethyl methylene (C13) proton and one of the chlorides, giving a one-dimensional coordination chain of dimers. Between the chains is $\pi-\pi$ stacking between benzenimidazole groups from neighbor chains in the *b* direction with an interplanar distance of 3.383 Å. The entire assembly therefore comprises a two-dimensional supermolecular network of interconnecting dimers through two levels of H-bonding and $\pi-\pi$ stacking (Figure 3). Although such a solid-state network usually disintegrates in solution, it is notable that there is ESI-MS evidence of dimer formation with a peak around $m/z = 801$ for the $[Pd_2Cl_3(\eta$-C-N)$_2]^+$ fragment in CH_3CN solution.

Jin recently reported a similar method to prepare pyridine-functionalized NHC complexes.[5h] Similar to our outcomes is the formation of a Ag_3 intermediate and the mononuclear Pd(II)

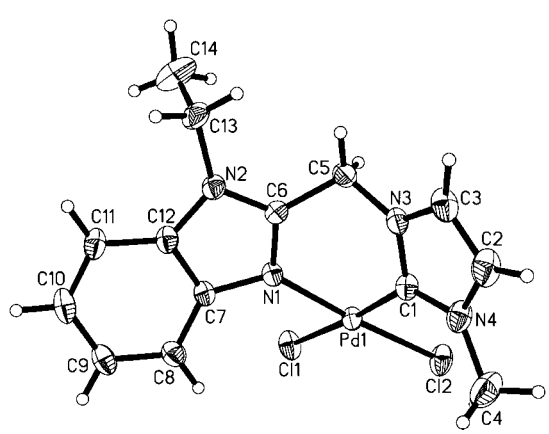

Figure 2. ORTEP view of the molecular structure of [$PdCl_2(\eta$-C-N)] (**4**) with 30% thermal ellipsoids and labeling scheme.

with a six-membered N-C chelate. However, there are notable and intriguing differences. Jin's intermediate is an "all-carbene" dicationic complex with dangling pyridyl functions and no Ag−Ag bonds. Our trinuclear Ag(I) is a mixed ligand and electronically neutral system with a central carbene-ligated Ag(I) flanked by two imidazole-ligated Ag(I) and supported by Ag···Ag interactions. Both systems are also different from Cavell's[5a] $Ag(NHC)_2 \cdot AgI_2$ intermediate, which yields a Pd(II) dicarbene.

It is interesting to note that the hybrid ligand chooses to be chelating toward Pd(II) but opts to be bridging in the Ag_3 structure, even though in the latter case it results in a seemingly less stable seven-membered ring framework. This could be attributed to the strength of the $d^{10}-d^{10}$ metal interactions that augments the bridging ligand well. The stoichiometric product Ag_2Cl_2(N-C)$_2$, or Lin's form of $Ag(NC)_2AgCl_2$, was not observed. Such bicyclic dinuclear species would probably inherit unnecessary strain, which could be relieved by capturing adventitious AgCl (from its precursor AgCl(N-C)) to yield the observed **3**.

Suzuki−Miyaura Coupling Reaction. The Suzuki cross-coupling of aryl bromides with arylboronic acids catalyzed by Pd-NHC complexes is well-documented.[11] However, most of the reported cases were carried out under higher reaction temperature, air-free conditions, or extended reaction time. We found that **4** is a highly active precatalyst toward the Suzuki−Miyaura cross-coupling reaction of aryl bromides with arylboronic acid.

A model coupling reaction of 4-bromoacetophenone with phenylboronic acid was used to test the solvent and base effects (Table 4). Use of absolute MeOH gives 60% coupling yield at rt in 1 h and 72% in 2 h (entries 1 and 2). Addition of 20% water pushes the isolated yield to near-quantitative within 1 h (entry 3). The higher activity is attributed to the better solubility of K_2CO_3 in the aqueous MeOH mixture and rapid reduction of Pd(II) to Pd(0).[12] Use of pure water as solvent is however less desirable, giving ~70% yield in 2 h (entry 11). Other polar solvents such as DMF and DMA give similar yields compared

Table 3. Summary of Crystallographic Data for 3 and 4

	3·3H$_2$O	**4**
formula	$C_{28}H_{38}Cl_3N_8O_3Ag_3$	$C_{14}H_{17}Cl_2N_4Pd$
fw	964.62	418.64
temp (K)	223(2)	295(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$
unit cell dimens		
a (Å)	12.8342 (13)	8.665(4)
b (Å)	15.2235 (16)	12.094(5)
c (Å)	17.2827 (17)	12.339(5)
α (deg)	90	72.050(9)
β (deg)	94.801 (2)	73.639(9)
γ (deg)	90	71.962(9)
V (Å^3)	3364.9 (6)	1144.5(8)
Z	4	2
D_{calcd} (Mg/m^3)	1.904	1.705
abs coeff (mm^{-1})	2.011	1.521
F(000)	1912	584
cryst size (mm)	0.54 × 0.34 × 0.08	0.40 × 0.28 × 0.06
θ range for data collecn (deg)	1.79–27.50	1.77 to 27.50
No. of rflns collected	23475	11047
No. of indep rflns	7707 [R(int) = 0.0339]	5208 [R(int) = 0.0591]
completeness to θ = 27.50° (%)	99.7	99.2
max., min. transmn	0.8557, 0.4098	0.9143, 0.5814
refinement method	full-matrix least-squares on F^2	
no. of data/restraints/params	7707/6/434	5208/0/250
goodness of fit on F^2	1.023	1.070
final R indices [$I > 2\sigma(I)$]		
R1	0.0335	0.0617
wR2	0.0727	0.1722
largest diff peak, hole (e/Å^3)	0.625, −0.486	1.978, −1.160

to MeOH; addition of water also raises the yields (entry 6). Less polar solvents such as THF and CH_2Cl_2 generally give poorer yields. Solvents with higher polarity and donicity are expected to provide a better solubility and homogeneity to the catalyst. Unsaturated species formed in the catalytic cycle can also be stabilized better in the presence of solvents with good donor characters. The common and less expensive inorganic bases, such as K_2CO_3, Na_2CO_3, and NaOH are the reagents of choice (Table 4). $Ba(OH)_2$ gives poor yield due to its poor solubility in the aqueous media. Although the use of NaOAc and NEt_3 is common in typical Heck coupling reactions, they are less effective in this Suzuki system, perhaps because they are less effective in promoting the transmetalation step.

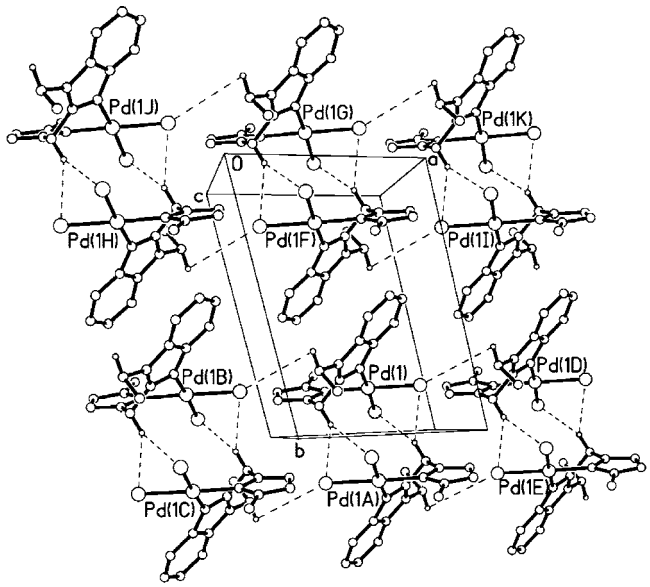

Figure 3. Intermolecular hydrogen bonding of **4**. Noncontributing hydrogen atoms are omitted for clarity.

The above optimized conditions were used to examine a representative range of aryl halides for the reaction. The results are summarized in Table 5. In general, complex **4** effectively catalyzes the cross-coupling of various aryl bromides with arylboronic acids in MeOH/H_2O at rt, giving high to near-quantitative yields. The coupling reaction of activated or deactivated aryl bromide with phenylboronic acid or naphthalyboronic acid could be preformed smoothly, even down to a catalyst load as low as 0.008 mol %. All the substrates with an electronic withdrawing substituent could be transformed to the biaryl products with >95% yields within a short time (Table 5, entries 1–7). The deactivated aryl bromides with an electronic donating moiety also could be coupled with phenylboronic acid easily with high yield at rt (Table 5, entries 8–11). This catalytic system shows good tolerance toward a wide range of sensitive functional groups, and the high efficiency of **4** at rt also makes it a valuable precatalyst for thermally sensitive substrates.

The catalyst is also effective toward the coupling of activated aryl chloride with phenylboronic acid. In the presence of 1.0 mol % of **4**, 43% yield was obtained from the reaction of

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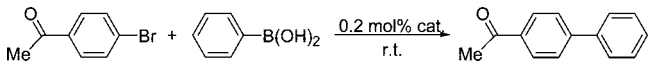
(13) (a) Li, F. W.; Xia, C. G.; Xu, L. W.; Sun, W.; Chen, G. X. *Chem. Commun.* **2003**, 2042. (b) Li, F. W.; Xiao, L. F.; Xia, C. G.; Hu, B. *Tetrahedron Lett.* **2004**, *45*, 8307. (c) Migowski, P.; Dupont, J. *Chem. Eur. J.* **2007**, *13*, 32. (d) Li, F. W.; Xia, C. G. *Tetrahedron Lett.* **2007**, *48*, 4845.

(14) (a) For the representative papers on TBAB-promoted cross coupling reactions, see: Selvakumar, K.; Zapf, A.; Beller, M. *Org. Lett.* **2002**, *4*, 3031. (b) Bedford, R. B.; Blake, M. E.; Butts, C. P.; Holder, D. *Chem. Commun.* **2003**, 466. (c) Yang, D.; Chen, Y. C.; Zhu, N. Y. *Org. Lett.* **2004**, *6*, 1557. (d) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267. (e) Li, S. H.; Lin, Y. J.; Cao, J. G.; Zhang, S. B. *J. Org. Chem.* **2007**, *72*, 4067.

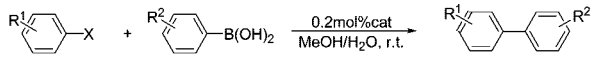
Table 4. Solvent and Base Effects on the Coupling Reaction[a]

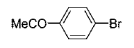
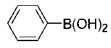
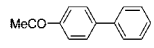
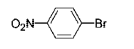
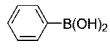
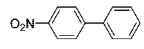
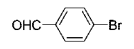
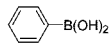
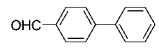
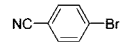
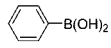
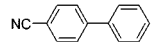
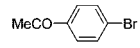
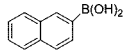
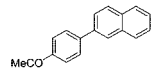
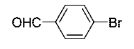
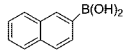
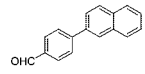
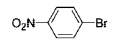
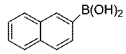
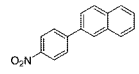
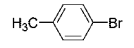
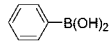
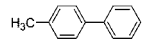
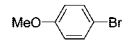
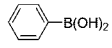
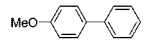
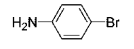
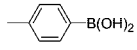
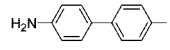
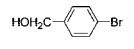
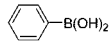
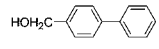
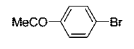
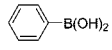
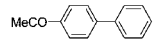
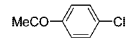
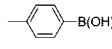


entry	solvent	base	time (h)	yield (%)[b]
1	MeOH	K_2CO_3	1	60
2	MeOH	K_2CO_3	2	72
3[c]	MeOH/H_2O	K_2CO_3	1	97
4	DMF	K_2CO_3	1	50
5	DMF	K_2CO_3	2	73
6[c]	DMF/H_2O	K_2CO_3	2	96
7	THF	K_2CO_3	2	48
8	CH_2Cl_2	K_2CO_3	2	25
9	CH_3CN	K_2CO_3	2	69
10	DMA	K_2CO_3	2	80
11	H_2O	K_2CO_3	2	71
12[c]	MeOH/H_2O	Na_2CO_3	1	95
13[c]	MeOH/H_2O	NaOH	1	98
14	MeOH/H_2O	$Ba(OH)_2$	2	57
15	MeOH/H_2O	NaOAc	2	65
16	MeOH/H_2O	NEt_3	2	70

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.6 mmol of phenylboronic acid, 1.2 mmol of base, 0.2 mol % of complex **4**, 2.0 mL of organic solvent, 0.5 mL of water (if needed), rt. [b] Analyzed by GC-MS. [c] Isolated yield.

Table 5. Pd-NHC Complex Catalyzed Suzuki−Miyaura Coupling of Aryl Halides with Arylboronic Acids in Aqueous Methanol Solution[a]



entry	ArX	$ArB(OH)_2$	Product	Conversion[b]
1				100%
2				100%
3				98%
4				95%
5				100%
6				97%
7				98%
8				94%
9				83%
10				96%
11				94%
12[c]				94%
13[d]				43%
14[e]				61%

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.6 mmolf of phenylboronic acid, 1.2 mmol of base, 0.2 mol % of complex 4, 2.0 mL of organic solvent, 0.5 mL of water (if needed), room temperature. [b] GC-MS yield. [c] Catalyst loading is 0.008 mol %, reaction time is 4 h and isolated yield. [d] Catalyst loading is 1 mol % and reaction time is 8 h. [e] 1.0 mmol TBAB was added.

4-methylphenylboronic acid with 4-chloroacetophenone (Table 5, entry 13). Addition of $[N(n\text{-}C_4H_9)_4]Br$ (TBAB) improves the cross-coupling yield to 61% (Table 5, entry 14), possibly due to complex stabilization by quaternary ammonium salt formation.[13,14]

The coupling between 4-bromoacetophenone and phenylboronic acid gives a good isolated yield of 94% even at catalyst loadings as low as 0.008 mol % with a TON of 11 750 (mol of product/mol of Pd) (Table 5, entry 12). This thus provides an effective phosphine-free catalyst system for facile coupling of aryl bromides or activated aryl chlorides in good to excellent yields under mild and aerobic conditions.

Conclusions

Although Lin's transmetalation method could experience problems in some other systems when the NHC transfer is incomplete or derouted,[15] we did not experience such difficulty using this method with our "nitrogen-rich" ligand. Herein the metalation at both Ag(I) and Pd(II) occurs at rt with high yields. Although the hybrid imidazole-NHC ligand is bridging in the intermediate Ag(I) complex, it reverts to the expected chelating form in Pd(II). Even though the ligand stabilizes a trinuclear Ag(I), there is no evidence of dinuclear or polynuclear Pd(II) formation. The augmentation of agentophilic interaction in the Ag_3 core offers a possible explanation. The resultant mononuclear Pd(II) has the desirable heterobidentate C/N chelate, is chemically stable, and is catalytically active. The high turnover (TON up to 11 750 at rt within a short duration) has encouraged us to use similar ligand designs to create other active catalysts.

Experimental Section

General Information. All the chemicals and solvents were used as received without purification or drying. *N*-Ethylbenzene-1,2-diamine and $PdCl_2(CH_3CN)_2$ were prepared according to literature procedures. NMR spectra were measured on Bruker ACF300 300 MHz and AMX500 500 MHz FT NMR spectrometers. Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in house.

2-Chloromethyl-1-ethylbenzoimdazole (1). Monochloroacetic acid (8.0 g, 0.085 mol) and N-ethylphenyl-1,2-diamine (6.8 g, 0.05 mol) were refluxed in 50 mL of 4 N HC1 for 7.5 h with stirring. The reaction mixture was left overnight and was then neutralized with aqueous K_2CO_3. The precipitated product was collected by vacuum filtration, and 7.8 g (80% yield) of pink solid **1** was obtained after drying. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (m, 1H, phenyl H), 7.77–7.29 (m, 3H, phenyl H), 4.85 (s, 2H, CH_2), 4.33 (dd, $^3J_{(H,\ H)} = 7.2$, 2H, CH_2CH_3), 1.53 (t, $^3J_{(H,\ H)} = 7.2$, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 149.2, 143.0, 135.7, 124.2, 123.3, 121.1, 110.5(s, Ar-C), 39.8 (s, CH_2), 37.4 (s, CH_2), 15.7 (s, CH_3).

3-Methyl-1-(1-ethyl-2-methylbenzoyl)imidazolium Chloride (2). To a solution of 2-chloromethyl-1-ethyl benzenimdazole (1.94 g, 10 mmol) in CH_3CN (100 mL) was added 1-methylimidzole (1.64 g, 20 mmol). After reflux for 48 h, the solution was reduced to 10 mL by vacuum pump and 20 mL of Et_2O was added to precipitate the product. Then the resultant white powder was collected and washed with 10 mL of ether three times. Yield: 2.4g (87%).

^1H NMR (300 MHz, d_6-DMSO): δ 9.45 (s, 1H, NC(H)N), 7.93 (d, $^3J_{(H,\ H)} = 1.7$, 1H, HCCH), 7.81 (d, $^3J_{(H,\ H)} = 1.5$, 1H, HCCH), 7.65–7.58 (m, 2H, phenyl H), 7.31–7.18 (m, 2H, phenyl H), 6.00 (s, 2H, CH_2), 4.39 (dd, $^3J_{(H,\ H)} = 7.2$, 2H, CH_2CH_3), 3.9 (s, 3H,

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NCH_3), 1.33 (t, $J_{(H, H)} = 7.2$, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, d_6-DMSO): δ 147.82 (s, NCN), 141.85, 137.60, 134.95, 123.57, 123.52, 122.73, 121.94, 119.08, 110.44 (s, Ar-C), 44.98 (s, CH_2), 38.19 (s, CH_2), 35.97 (s, CH_3), 15.02 (s, CH_3). MS (ESI): $m/z = 241.09$ H[C-N]$^+$.

[Ag{3-methyl-1-(1-ethyl-2-methylbenzoyl)imidazolin-2-ylidene}$_2$][Ag_2Cl_3] (3). A solution of **2** (276 mg, 1 mmol) and Ag_2O (116 mg, 0.5 mmol) in $CH_2Cl_2$was stirred at rt for 12 h. Filtration of the reaction mixture through Celite gave a colorless solution, which was then concentrated to about 5 mL. Upon the addition of Et_2O to the crude reaction mixture, complex **3** was precipitated and isolated as a white solid (274 mg, 60%). ^1H NMR (300 MHz, d_6-DMSO): δ 7.60–7.48 (m, 4H, HCCH and phenyl H), 7.29–7.16 (m, 2H, phenyl H), 5.77 (s, 2H, CH_2), 4.37 (dd, $^3J_{(H, H)} = 7.2$, 2H, CH_2CH_3), 3.80 (s, 3H, CH_3), 1.21 (t, $J_{(H, H)} = 7.2$, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, d_6-DMSO): δ 180.16 (s, NCN), 149.41, 141.76, 134.67, 123.00, 122.79, 122.71, 121.94, 119.10, 110.44 (s, Ar-C), 46.92 (s, CH_2), 38.33 (s, CH_2), 29.34 (s, CH_3), 14.94 (s, CH_3). Anal. Calc for $C_{28}H_{40}Cl_3N_8O_3Ag_3$: C, 34.79; H, 4.17; N, 11.59. Found: C, 34.73; H, 3.76; N, 11.60. MS (ESI): $m/z = 587$ [Ag(C-N)$_2$]$^+$.

[Pd{3-methyl-1-(1-ethyl-2-methylbenzoyl)imidazolin-2-ylidene}Cl_2] (4). To a solution of **3** (242 mg, 0.25 mmol) in 20 mL of CH_2Cl_2 was added a CH_3CN suspension of $Pd(CH_3CN)Cl_2$ (130 mg, 0.5 mmol). After it was stirred at rt overnight, the solution was filtered through Celite to remove precipitated AgCl. The solvent was removed *in vacuo* to ca. 5 mL, followed by addition of Et_2O (10 mL), causing a yellow precipitate to form. The product was recrystallized from CH_3CN/Et_2O to give yellow crystals. Yield: 140 mg (67%). ^1H NMR (300 MHz, d_3-MeCN): δ 8.37–8.34 (d, 1H, Ar-H), 7.62–7.59 (m, 1H, Ar-H), 7.45–7.34 (m, 3H, Ar-H), 7.06 (d, 1H, Ar-H), 5.87 (d, $^2J_{(H, H)} = 1.64$, 1H, CH_2), 5.57 (d, $^2J_{(H, H)} = 1.60$, 1H, CH_2), 4.43 (dd, $^3J_{(H, H)} = 7.2$, 2H, CH_2CH_3), 4.05 (s, 3H, CH_3), 1.44 (t, $^3J_{(H, H)} = 7.2$, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (125.77 MHz, d_6-DMSO): δ 158.04, 150.23, 138.84, 133.30, 132.71, 129.98, 124.84, 124.16, 112.49 (s, Ar-C), 45.80 (s, CH_2), 37.60 (s, CH_2), 35.12 (s, CH_3), 16.07 (s, CH_3). MS (ESI): $m/z = 424$ {[Pd(C-N)Cl]$^+$ + CH_3CN}; $m/z = 415$ {[Pd(C-N)Cl]$^+$ + CH_3OH}; $m/z = 801$. [Pd_2Cl_3(C-N)$_2$]$^+$.

General Procedure for the Suzuki−Miyaura Cross-Coupling Reaction. In a typical run, aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (1.1 mmol), and Pd-NHC complex **4** (0.001 mmol) were charged in a reaction tube equipped with a stirring bar. The organic solvent (2 mL) and water (0.5 mL) were then added to the mixture using a syringe. The reaction mixture was vigorously stirred at rt in air. After the desired reaction time, the reaction was stopped. CH_2Cl_2 (10 mL) was added to the reaction mixture, and the organic phase extracted from water and dried over $MgSO_4$. The solution was analyzed by a HP 6890/5973 GC-MS or separated by a column to get the purified products.

X-ray Crystallography. Crystals suitable for X-ray analysis of **3** and **4** were obtained by slow diffusion of Et_2O into CH_2Cl_2 and CH_3CN solutions of the corresponding compounds, respectively. The crystals were mounted on quartz fibers and X-ray data were collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at −50 °C, using Mo Kα radiation ($\gamma = 0.71073$ Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs.[16] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The data collection and processing parameters are given in Tables 3 and 4.

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Supporting Information Available: Crystallographic data for **3** and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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