Dinuclear Palladacyclic Complexes Derived from C−N Cleavage of an Imidazolium Salt: Synthesis, Structural Characterization, and Their Uses for C−C Coupling

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Cleavage of a C−N bond of 3,6-(*N*-*n*-butylimidazolidenyl)pyridazine salt in its reactions with Ag_2O and $Pd(OAc)_2$ was observed. Subsequent palladation of the resultant *N*-*n*-butylimidazole resulted in the isolation of two novel dinuclear palladacyclic complexes. Both complexes consist of a $Pd_2C_2N_2$ core with two palladium doubly bridged by anionic imidazoles in *N,C*5- or *N,C*2-coordination fashion. Accompanied with the C−N bond cleavage and palladation processes, addition of imidazole C−H to the C≡N bond of acetonitrile occurred in the reaction of $Pd(OAc)_2$ and 3,6-(*N*-*n*-butylimidazolidenyl)pyridazine. All compounds have been fully characterized by the usual spectroscopic techniques, and their X-ray molecular structures are described. The two palladacyclic complexes show good catalytic activities in Heck−Mizoroki and Suzuki coupling reactions of activated aryl bromides.

Introduction

Transition metal complexes of N-heterocyclic carbenes (NHCs) have been the focus of considerable interest because such complexes containing NHC ligands have found wide applications in many organic transformations.[1–4] Because of the strong σ-donating and negligible π-accepting character, NHCs can form stable bonds with various metals from main group to transition metals in different oxidation states and stabilize catalytically active intermediates that are coordinatively unsaturated, and thus NHCs are valuable alternatives to tertiary phosphines.[3] Palladium readily forms thermally stable NHC complexes that are exceptionally efficient catalysts for a variety of C−C[3c,4] and C−N[5] coupling reactions. A number of mono-[6] and bis(NHC)[7] palladium complexes have been prepared and structurally characterized in the recent decade. The most often used procedures for the preparation of Pd-NHC complexes are (1) the reactions of palladium(II) acetate with corresponding imidazolium salts[8] and (2) the carbene transfer reactions of palladium halides with silver-NHC complexes.[9] Such methodologies usually lead to metal bonding at the C2 position of the

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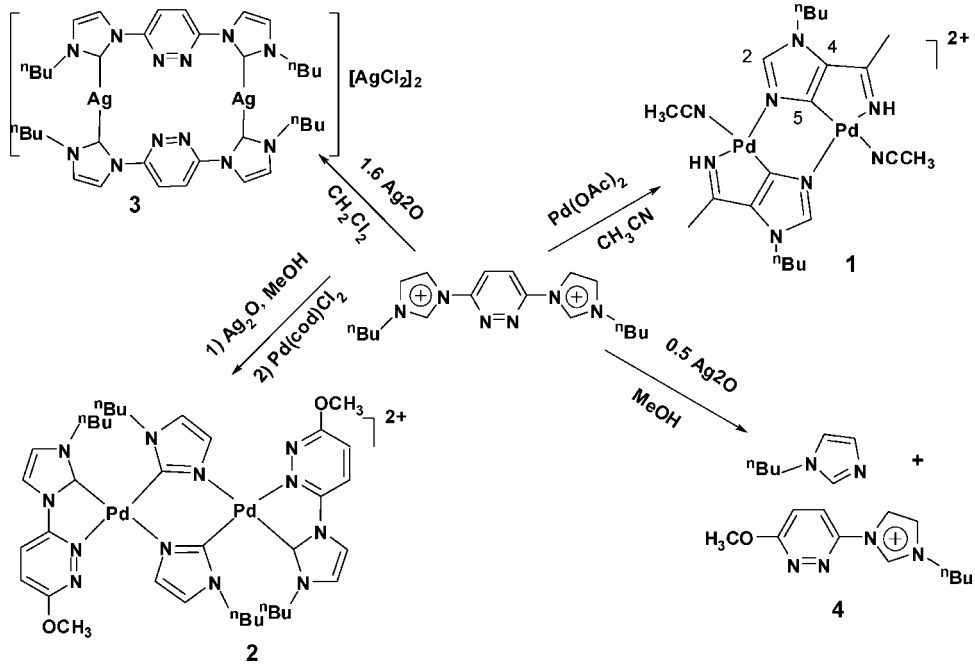
Scheme 1. Synthesis of the Dinuclear Palladium Complexes



imidazolylidene ring. Occasionally, such procedures can yield abnormally bound carbenes, i.e., ligands bound through a backbone C4 carbon, and the C4 -bound carbene palladium complexes are better catalysts for Suzuki coupling reactions.[10] The C−H activation of the backbone C4/5 position of the imidazolium ring forming abnormal NHC complexes has been observed in the case where the C2 position is blocked.[11,12] Many metal-NHC complexes in homogeneous catalysis are made by *in situ* deprontonation of imidazolium salts with the real catalytically active species uninvestigated.[13] In such cases the conclusion based on the expected metal-NHC complexes might not always be reliable.

We have been interested in the synthesis and structures of metal complexes supported by pyridine-, pyrazole-, and naphthyridine-functionalized bis(*N*-heterocyclic carbene) ligands. The resultant multinuclear silver-NHC complexes show Ag−Ag interactions and interesting luminescent properties,[14] and nickel and palladium complexes are good precatalysts for C−C coupling reactions.[15] As a continuation, here we report the unusual reactions based on pyridazine-functionalized bisimidazolium salts leading to two dinuclear palladacyclic complexes. The resultant novel palladium complexes as catalysts for Mizoroki−Heck and Suzuki coupling reactions are also described.

Results and Discussion

Synthesis and Characterization. The deprontonation of 3,6-(*N*-*n*-butylimidazolium)pyridazine was believed to generate a CNNC dinucleating bis(NHC) ligand, forming bimetallic complexes in a bis-chelate fashion. However, attempts to synthesize dinuclear palladium complexes supported by 3,6-(*N*-*n*-butylimydazolylidenyl)pyridazine (L) using the two routes mentioned above are not successful; instead, two unusual palladacylic complexes, **1** and **2**, were obtained (Scheme 1).

We first attempted the reaction of palladium(II) acetate with 3,6-(*N*-*n*-butylimidazoliumyl)pyridazine dihexafluorophosphate ($H_2L(PF_6)_2$) in refluxing acetonitrile. Unexpectedly, complex **1** was afforded as a pale yellow solid in 70% yield, whereas the expected palladium complex containing 3,6-(*N*-*n*-butylimidazolylidenyl)pyridazine or other palladium-containing species were not detected by *in situ* NMR spectroscopy. The ^{1}H NMR spectrum of **1** in DMSO-d_6 shows the resonance signals at 9.95 and 7.81 ppm assignable to the NH proton and C2 proton, respectively. Two methyl groups appear as singlets at 2.51 and 2.07 ppm corresponding to $CH_3C{=}NH$ and CH_3CN, respectively. The metalated carbon (C5) appears at 176.18 ppm as a singlet in the ^{13}C NMR spectrum, whereas $CH_3C{=}NH$, C2, and C4 resonance signals are observed at 159.4, 138.4, and 134.7 ppm, respectively (see Scheme 1). Both ^{1}H and ^{13}C NMR data illustrate the C=N double bond character of the $CH_3C{=}NH$

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group. The anionic bridging imidazolyl moiety obviously results from the deterioration of the imidazolium, evidenced by the reaction of $H_2L(PF_6)_2$ with Ag_2O discussed below. The imino group is formed due to addition of a C−H bond to the triple bond of an acetonitrile molecule.

As expected, the deprontonation of the bis(imidazolium) salt with 1 equiv of Ag_2O in dichloromethane yielded $[Ag_2L_2][AgCl_2]_2$ (**3**), which is light sensitive. The compound has been characterized by elemental analysis, NMR spectroscopy, and X-ray diffraction. The structure of **3** consists of a macrocyclic disilver cation and two $[AgCl_2]^-$ (see Figure S1). The disilver complex is characterized by the appearance of a carbenic carbon resonance at 180.2 ppm in its ^{13}C spectrum, and the chemical shift is consistent with those of silver-NHC complexes having a linear $Ag(NHC)_2$ conformation.[16]

The carbene transfer reaction has proven to be the most convienent route to prepare palladium-NHC complexes, and the reaction is usually facile and clean.[8] However, attempts to prepare the corresponding palladium complex by using **3** were not successful. Treatment of **3** with $Pd(cod)Cl_2$ in acetonitrile did not yield any palladium-NHC complex, but led to the decomposition of the Ag-NHC complex to the starting imidazolium salt, 3,6-(*n*-butylimidazoliumyl)pyridazine, as confirmed by the ^1H NMR spectrum. Simultaneously, silver mirror was found on the wall of the reaction tube.

When the imidazolium salt was treated with 0.5 equiv of Ag_2O in MeOH, facile C−N cleavage was observed due to nucleophilic substitution of one *N*-*n*-butylimidazole by a methoxyl group, affording 6-methoxyl-3-(*N*-*n*-butylimidazoliumyl)pyridazine chloride (**4**) and *N*-*n*-butylimidazole in 82.5% yield. In this case, no silver carbene species was isolated. Compound **4** has also been characterized by NMR spectroscopy and X-ray diffraction analysis (Figure S2). When the reaction of 3,6-(*n*-butylimidazoliumyl)pyridazine dichloride with 1.6 equiv of Ag_2O was conducted in MeOH and the resultant solution was subsequently treated with $Pd(cod)Cl_2$, compound **2** was obtained in 52.4% yield. Again, the cleavage of the C−N bond between *N*-*n*-butylimidazole and pyridazine of the imidazolium salt was observed. One of the imidazolyl groups was substituted by a methoxyl group. The ^1H NMR spectrum of **2** shows a singlet at 4.12 ppm assignable to a methoxyl group. Two sets of resonance signals due to *n*-butyl groups of anionic imidazole and the NHC ring were observed. The two pyridazinyl protons appear as two doublets at 8.43 and 7.81 ppm, respectively. The resonances of two imidazolilydene backbone protons were observed at 8.23 and 7.57 ppm as singlets, whereas the backbone protons of the anionic bridging imidazolyl groups give two singlets at 7.37 and 7.25 ppm, respectively. In the ^{13}C NMR spectrum of **2** the resonance signals at 166.1 and 164.8 ppm can be ascribed to a normal carbenic carbon and the palladated C2 carbon of the bridging imidazolyl ligand, respectively. The chemical shifts of carbenic carbons of **2** appear in the normal range 195−160 ppm for palladium-NHC complexes.[17] Based on the reactions discussed above, one plausible mechanism for the formation of **1** is from the palladation of imidazole of *in situ* generated $[Pd(N\text{-}n\text{-butylimidazole})_2]$ species under basic conditions. However, neither $[Pd(N\text{-}n\text{-butylimidazole})_2Cl_2]$[18] nor $[Pd(N\text{-}n\text{-butylimidazole})_2(OAc)_2]$[19] yielded **1** upon treatment with Ag_2O or other bases in acetonitrile. Another possible route is via **2** by losing its NHC ligands, but so far efforts to convert **2** to **1** have not been successful.

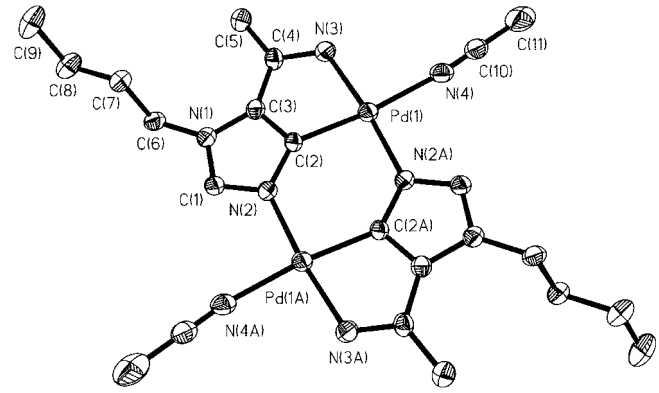

Figure 1. ORTEP drawing of the cationic section of dinuclear palladacyclic complex **1** showing the atomic numbering scheme with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd(1)−C(2) 1.954(4), Pd(1)−N(2)#1 2.025(3), Pd(1)−N(3) 2.038(4), Pd(1)−N(4) 2.091(4), C(2)−Pd(1)−N(2)#1 94.21(15), C(2)−Pd(1)−N(3) 79.74(16), N(2)#1−Pd(1)−N(3) 173.94(14), C(2)−Pd(1)−N(4) 170.76(16), N(2)#1−Pd(1)−N(4) 94.30(14), N(3)−Pd(1)−N(4) 91.73(15). Symmetry code: #1 $-x$, y, $-z+1/2$.

Structural Description of 1 and 2. The structures of **1** and **2** were unambiguously established by X-ray diffraction analysis. An ORTEP diagram of **1** is shown in Figure 1. The structure reveals that **1** is dinuclear, and the two palladium atoms display a square-planar geometry and are bridged by two anionic imino-imidazole ligands in tridentate mode. The coordination sphere of each palladium consists of three different N-bound ligands and a C5-bound imidazole ring. The Pd−C distance is 1.954(4) Å, which is slightly shorter than normal Pd−C(NHC) bonds,[8,9] but consistent with the known values of Pd−C(aryl) bonds.[20] The three different Pd−N bonds in the range 2.025(3)−2.091(4) Å are normal. The C(4)−N(3) bond distance (1.308 Å) and the coplanarity of the C(5)C(4)N(3) moiety with its attached imidazole ring reflect its double-bond character (Figure 1). In addition, another notable structural feature is that the two palladium and the anionic imino-imidazole ligands are essentially coplanar. The distance between the two metals is 4.079 Å, excluding any metal−metal interaction. Obviously, the formation of **1** arises from the C−N bond cleavage, simultaneous double C−H activation of C4 and C5 positions, and subsequent insertion of the C≡N bond of an acetonitrile molecule into the C5−H bond.

The C4/5-H activation of imidazolium salts forming abnormal metal-NHC complexes has been known for a few transition

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(19) $[Pd(N\text{-}n\text{-butylimidazole})_2(OAc)_2]$ was generated *in situ* in acetonitrile by mixing $Pd(OAc)_2$ and 2 equiv of *N*-*n*-butylimidazole.

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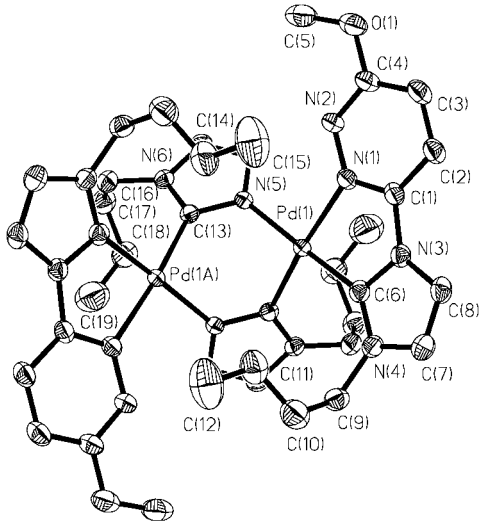

Figure 2. ORTEP diagram of the cationic section of palladacyclic complex **2** showing the atomic numbering scheme with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd(1)−C(6) 1.978(6), Pd(1)−C(13)#1 1.982(6), Pd(1)−N(5) 2.043(4), Pd(1)−N(1) 2.093(5), C(6)−Pd(1)−C(13)#1 98.2(2), C(6)−Pd(1)−N(5) 173.5(2), C(13)#1−Pd(1)−N(5) 86.3(2), C(6)−Pd(1)−N(1) 78.8(2), C(13)#1−Pd(1)−N(1) 174.4(2), N(5)−Pd(1)−N(1) 97.05(18). Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z+1/2$.

metal complexes,[10,21] and this has been summarized by Arnold and Pearson recently.[12] However, the simultaneous double C−H activation of both the C4 and C5 positions of an imidazole ring is quite rare.[21c] The formation of the imine resulting from the addition of a C(sp^2)−H of imidazole to a C≡N triple bond of acetonitrile has not been known so far. That multiple bond cleavage and formation involing C−N cleavage, C−H bond activation, palladation, and addition of a C≡N bond occurred in one flask is remarkable.

The X-ray crystal structure of **2** is shown in Figure 2. Complex **2** is also a dinuclear complex consisting of the palladacyclic $Pd_2C_2N_2$ core. The two palladium ions are doubly bridged by two anionic *N*-*n*-butylimidazolyl ligands forming a six-membered $Pd_2C_2N_2$ ring. However, palladium is bound to the C2 atom of *N*-*n*-butylimidazole rather than the C5 atom as observed in **1**. Each palladium is surrounded by a neutral chelate pyridazinyl-NHC ligand and two anionic *C,N*-bidentate imidazole ligands. Unlike **1**, the two anionic bridging imidazoles are not coplanar with the coordination planes of the two palladium(II) centers because of the steric hindrance of the N-substitutent. As a consequence, the $Pd_2C_2N_2$ ring displays a boat conformation and the distance (3.493 Å) between the two palladiums becomes much shorter than that of complex **1**. The dihedral angles between the coordination planes and the imidazole rings are 50.3°, whereas the dihedral angle between the two coordination planes is 85.90°, indicating the two coordination planes are nearly perpendicular. The Pd−$C_{carbene}$ and Pd−$C_{imidazolyl}$ bond distances (1.978(6) and 1.982(6) Å) are slightly longer than those of **1**, whereas the Pd−N distances are comparable.

Catalytic Activities. The palladium-catalyzed C−C coupling reaction is one of the most powerful methodologies to construct C−C bonds. The Heck−Mizoroki reaction often requires high temperature.[22] Palladium complexes of NHCs are suitable catalyst precursors for this reaction since they have shown good thermostability at the required temperature.[1] So far a few nitrogen-, oxygen-, and sulfur-containing palladacyclic complexes have proven to be excellent catalyst precursors in homogeneous catalysis.[23] Palladacyclic complexes containing NHC ligands have also demonstrated to serve as highly efficient catalysts in C−C coupling reactions.[17a,24]

With palladacyclic complexes **1** and **2** in hand, we tested their catalytic activities for the Heck reaction of different aryl bromides with styrene and acrylic acid esters. All reactions were run in dimethyl acetamide (DMAc) as solvent and NaOAc as the base with a catalyst loading of 0.5 mol % Pd. The results are summarized in Table 1. Under these Heck reaction conditions often used for other palladium catalysts,[22] both **1** and **2** exhibit excellent catalytic activities for aryl bromides bearing electron-withdrawing substituents. The Heck reactions with 4-bromoacetophenone and 4-bromobenzaldehyde using **1** or **2** are facile, giving the desired products in quantitative yields within 30 min (Table 1, entries 1−4). Unfortunately, both complexes show low activity for unactivated aryl bromides such as bromobenzene, 4-bromotoluene, and 4-bromoanisole with yields of 9−39% for **1** and 33−48% for **2**, respectively. Even the reaction time was extended to 18 h. Complex **1** is totally ineffective for the coupling reactions of 2-bromotoulene with styrene and *n*-butyl acrylate, whereas complex **2** is more active, affording the coupling products in ca. 30% yields.

It has been known that the additive *n*-Bu_4NBr can promote palladium-catalyzed Heck couplings of deactivated aryl halides.[7d,17a,25] Actually, when 20 mol % *n*-Bu_4NBr (vs ArX) was added, the coupling yields of electron-rich and deactivated bromides were substantially improved. Representative catalytic results are summarized in Table 1. In the presence of *n*-Bu_4NBr even the inactive 2-bromotoulene can be successfully coupled to the desired product, but the yield is still poor (entries 17 and 18). The yields for deactivated substrates such as 4-bromotoluene and 4-bromoanisole are more than doubled compared to those in the absence of *n*-Bu_4NBr. It was observed that under the same reaction conditions the Pd-NHC complex (**2**) is more active than **1**. With addition of *n*-Bu_4NBr, 4-bromoanisole and 4-bromotoluene can be coupled, affording the corresponding products in moderate to good yields (entries 33−40).

In addition to Heck reactions, the Suzuki cross-coupling reactions of aryl halides and arylboronic acids are of general interest to organic synthesis. The Suzuki reaction has been the most versatile and important method for the synthesis of

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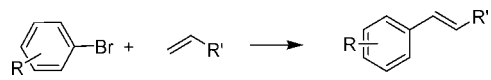
Table 1. Heck−Mizoroki Coupling of Aryl Halides with Olefins[a]



entry	aryl halide	olefin	cat.	additive	time (h)	yield (%)
1	4-bromoacetophenone	*n*-butyl acrylate	**1**		0.5	100
2	4-bromoacetophenone	styrene	**1**		0.5	100
3	4-bromobenzaldehyde	*n*-butyl acrylate	**1**		0.5	100
4	4-bromobenzaldehyde	styrene	**1**		0.5	100
5	bromobenzene	*n*-butyl acrylate	**1**		18	39
6	bromobenzene	styrene	**1**		18	32
7	4-bromotoluene	*n*-butyl acrylate	**1**		18	25
8	4-bromotoluene	styrene	**1**		18	12
9	2-bromotoluene	*n*-butyl acrylate	**1**		18	0
10	2-bromotoluene	styrene	**1**		18	0
11	4-bromoanisole	*n*-butyl acrylate	**1**		18	9
12	4-bromoanisole	styrene	**1**		18	10
13	bromobenzene	*n*-butyl acrylate	**1**	*n*-Bu_4NBr	18	75
14	bromobenzene	styrene	**1**	*n*-Bu_4NBr	18	74
15	4-bromotoluene	*n*-butyl acrylate	**1**	*n*-Bu_4NBr	24	69
16	4-bromotoluene	styrene	**1**	*n*-Bu_4NBr	24	65
17	2-bromotoluene	*n*-butyl acrylate	**1**	*n*-Bu_4NBr	24	35
18	2-bromotoluene	styrene	**1**	*n*-Bu_4NBr	24	30
19	4-bromoanisole	*n*-butyl acrylate	**1**	*n*-Bu_4NBr	24	53
20	4-bromoanisole	styrene	**1**	*n*-Bu_4NBr	24	50
21	4-bromoacetophenone	*n*-butyl acrylate	**2**		0.5	100
22	4-bromoacetophenone	styrene	**2**		0.5	100
23	4-bromobenzaldehyde	*n*-butyl acrylate	**2**		0.5	100
24	4-bromobenzaldehyde	styrene	**2**		0.5	100
25	bromobenzene	*n*-butyl acrylate	**2**		18	37
26	bromobenzene	styrene	**2**		18	43
27	4-bromotoluene	*n*-butyl acrylate	**2**		18	48
28	4-bromotoluene	styrene	**2**		18	42
29	2-bromotoluene	*n*-butyl acrylate	**2**		18	30
30	2-bromotoluene	styrene	**2**		18	33
31	4-bromoanisole	*n*-butyl acrylate	**2**		18	33
32	4-bromoanisole	styrene	**2**		18	38
33	bromobenzene	*n*-butyl acrylate	**2**	*n*-Bu_4NBr	24	85
34	bromobenzene	styrene	**2**	*n*-Bu_4NBr	24	78
35	4-bromotoluene	*n*-butyl acrylate	**2**	*n*-Bu_4NBr	24	75
36	4-bromotoluene	styrene	**2**	*n*-Bu_4NBr	24	72
37	2-bromotoluene	*n*-butyl acrylate	**2**	*n*-Bu_4NBr	24	45
38	2-bromotoluene	styrene	**2**	*n*-Bu_4NBr	24	33
39	4-bromoanisole	*n*-butyl acrylate	**2**	*n*-Bu_4NBr	24	78
40	4-bromoanisole	styrene	**2**	*n*-Bu_4NBr	24	86

[a] Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol), catalyst (0.5 mol%), NaOAc (2.0 mmol), DMAc (3 mL), temperature (130 °C).

unsymmetrically substituted biaryl compounds.[26] The reactions of different aryl bromides with *p*-tolylboronic acid were studied at 90 °C in dioxane using K_3PO_4 as base. It should be noted that K_3PO_4 is a better base than Cs_2CO_3, which is often the best in other Pd-catalyzed Suzuki reactions. At a catalyst loading of 0.5 mol % palladium catalyst, the reactions of 4-bromoacetophenone and 4-bromobenzaldehyde proceeded smoothly, yielding the corresponding biaryls in good to excellent yield (85−96%) in 3 h. The results are summarized in Table 2. The catalytic activity with aryl bromides depends on the substitution of the aryl moiety. Bromobenzenes containing electron-donating groups (Table 2, entries 3−6 and 10−13) required longer reaction time. The coupling of bromobenzene, bromotoluene, and 4-bromoanisole in 6 h afforded the corresponding products in 25−45% yields for **1** and 64−80% yields for **2**, respectively.

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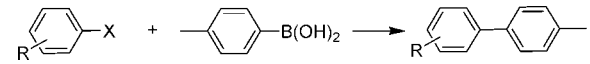
Table 2. Suzuki Coupling of Aryl Halides with *p*-Tolylboronic Acid[a]



entry	aryl halide	cat.	additive[b]	time (h)	yield (%)[c]
1	4-bromoacetophenone	**1**		3	87
2	4-bromobenzaldehyde	**1**		3	85
3	bromobenzene	**1**		6	45
4	4-bromotoluene	**1**		6	39
5	2-bromotoluene	**1**		6	33
6	4-bromoanisole	**1**		6	25
7	4-chloroacetophenone	**1**		6	0
8	4-bromoacetophenone	**1**	PPh_3	0.5	100
9	4-bromobenzaldehyde	**1**	PPh_3	0.5	100
10	bromobenzene	**1**	PPh_3	24	100
11	4-bromotoluene	**1**	PPh_3	24	100
12	2-bromotoluene	**1**	PPh_3	24	100
13	4-bromoanisole	**1**	PPh_3	24	100
14	4-chloroacetophenone	**1**	PPh_3	24	40
15	4-bromoacetophenone	**2**		3	96
16	4-bromobenzaldehyde	**2**		3	96
17	bromobenzene	**2**		6	80
18	4-bromotoluene	**2**		6	68
19	2-bromotoluene	**2**		6	65
20	4-bromoanisole	**2**		6	64
21	4-chloroacetophenone	**2**		6	9
22	4-bromoacetophenone	**2**	PPh_3	0.5	100
23	4-bromobenzaldehyde	**2**	PPh_3	0.5	100
24	bromobenzene	**2**	PPh_3	6	100
25	4-bromotoluene	**2**	PPh_3	24	100
26	2-bromotoluene	**2**	PPh_3	24	100
27	4-bromoanisole	**2**	PPh_3	24	100
28	4-chloroacetophenone	**2**	PPh_3	24	50

[a] Reaction conditions: aryl halide (1.0 mmol), 4-methylphenylboronic acid (1.5 mmol), palladium 0.5 mol %, $K_3PO_4 \cdot 3H_2O$ (2.0 mmol), 1,4-dioxane (3 mL), temperature (90 °C). [b] 2 equiv. [c] Yields were determined by gas chromatography.

Unfortunately, complex **1** did not show any activity for aryl chloride or even activated 4-chloroacetophenone, whereas the catalytic activity of **2** is also poor.

The catalytic efficiency can be significantly improved by adding 2 equiv of PPh_3 (Pd/PPh_3 = 1). Both **1** and **2** can couple 4-bromoacetophenone and 4-bromobenzaldehyde in quantitative yields, giving selectively the corresponding *E*-cinnamate, and the reactions can be completed within 0.5 h (Table 2, entries 8−13 and 22−27). The coupling of electron-rich and deactivated bromides can also proceed cleanly with the addition of PPh_3, affording the coupled products in quantitative yields when the reaction was extended to 24 h. In the case of 4-chloroacetophenone, although the activity has been remarkably improved compared to that in the absence of phosphine, the yield of the coupled product is still low. We have not been able to clarify the role of PPh_3 at present because attempts to identify the possible Pd-NHC-PPh_3 species were not successful.

Both complexes are air and moisture stable. Their pronounced thermal stability was also demonstrated by the absence of Pd-black precipitation and Pd mirror after heating the catalysts in a DMAc solution at 130 °C for 24 h without any additives such as PPh_3 and *n*-Bu_4NBr.

In conclusion, we have reported the structural characterization of two unusual palladacyclic compounds both containing a $Pd_2C_2N_2$ core. The formation of **1** represents an unprecedented set of palladium-promoted reactions for an imidazolium salt. Especially, the C−H bond addition to a C≡N bond leading to an imine is of great interest. The Ag_2O-induced C−N cleavage is also observed for the first time. These results reveal that the discussion on the nature of metal-NHC complexes in homogeneous catalysis in which the carbene is made by an *in situ*

Table 3. Summary of X-ray Crystallographic Data for Complexes 1 and 2

	1	2
formula	$C_{22}H_{32}F_{12}N_8P_2Pd_2$	$C_{38}H_{70}Cl_2N_{12}O_{10}Pd_2$
fw	911.30	1138.76
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a/Å	7.7026(12)	23.109(4)
b/Å	19.112(2)	9.8636(18)
c/Å	11.4095(14)	22.869(4)
β/deg	104.382(2)	91.755(2)
V/Å^3	1627.0(4)	5210.2(17)
Z	2	4
D/g cm^{-3}	1.860	1.452
no. of reflns collected	8224	13 099
no. of ind reflns, R_{int}	2847 (0.0218)	4581 (0.0276)
goodness-of-fit on F^2	1.051	1.102
R1, wR2 [$I > 2\sigma(I)$]	0.0329, 0.0808	0.0474, 0.1186
R1, wR2 (all data)	0.0462, 0.0921	0.0664, 0.1372

deprotonation of an imidazolium salt can be risky. The deterioration of the imidazolium salts should be considered. Furthermore, the palladium complexes are efficient catalysts for Heck and Suzuki coupling of activated aryl bromides.

Experimental Section

All the chemicals were obtained from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta = 0$ ppm, and coupling constants (J) are expressed in Hz. Elemental analyses were performed on a Flash EA1112 instrument.

3,6-Bis(*N*-*n*-butylimidazoliumyl)pyridazine Dichloride. The compound was prepared according to the reported procedure.[27] Yield: 40%. Anal. Calcd for $C_{18}H_{26}Cl_2N_6$: C, 54.41; H, 6.60; N, 21.15. Found: C, 54.15; H, 6.95; N, 20.98. ^{1}H NMR (DMSO-d_6): 10.79 (s, NCHN, 2H), 9.12 (s, $C_4N_2H_2$, 2H), 8.81, 8.24 (s, NCHCHN, each 2H), 4.39 (t, $J = 7.2$ Hz, CH_2CH$_2$CH$_2$CH$_3$, 4H), 1.92 (m, $J = 7.2$ Hz, CH$_2$CH_2CH$_2$CH$_3$, 4H), 1.37 (m, $J = 7.2$ Hz, CH$_2$CH$_2$CH_2CH$_3$, 4H), 0.94 (t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH_3, 6H).

3,6-Bis(*N*-*n*-butylimidazoliumyl)pyridazine Dihexafluorophosphate. To a solution of 3,6-bis(*N*-*n*-butylimidazoliumyl)pyridazine dichloride (3.97 g, 0.01 mol) in water (15 mL) was added NH_4PF_6 (4.0 g, 0.025 mol). The mixture was stirred for 1 h. The resulting precipitate was collected and washed with water and dried *in vacuo*. Yield: 5.8 g (94%). Anal. Calcd for $C_{18}H_{26}F_{12}N_6P_2$: C, 35.08; H, 4.25; N, 13.63. Found: C, 35.03; H, 4.19; N, 13.55. ^{1}H NMR (DMSO-d_6): 10.33 (s, NCHN, 2H), 9.04, 8.38 (both d, $J =$ 8.8 Hz, NCHCHN, 2H), 8.67, 8.14 (s, $C_4N_2H_2$, each 2H), 4.37 (t, $J = 7.2$ Hz, CH_2CH$_2$CH$_2$CH$_3$, 4H), 1.92 (m, $J = 7.2$ Hz, CH$_2$CH_2CH$_2$CH$_3$, 4H), 1.39 (m, $J = 7.2$ Hz, CH$_2$CH$_2$CH_2CH$_3$, 4H), 0.96 (t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH_3, 6H).

Synthesis of 1. A solution of 3,6-bis(*N*-*n*-butylimidazoliumyl)pyridazine hexafluorophosphate (124 mg, 0.2 mmol) in 4 mL of CH_3CN was treated with $Pd(OAc)_2$ (90 mg, 0.4 mmol). The mixture was refluxed for 14 h. The resultant yellow-brown solution was filtered. Addition of 20 mL of diethyl ether to the filtrate afforded a pale yellow solid. Yield: 110 mg (71.5%). Anal. Calcd for $C_{22}H_{34}F_{12}N_8P_2Pd_2$: C, 28.93; H, 3.75; N, 12.27. Found: C, 29.33; H, 3.29; N, 11.67. ^{1}H NMR (DMSO-d_6): 9.95 (s, NH, 2H), 7.81 (s, 2H), 4.21 (t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH$_3$, 4H), 2.51 (s, CH$_3$C=NH, 6H), 2.07 (s, CH$_3$CN, 6H), 1.69 (m, CH$_2$CH$_2$CH$_2$CH$_3$, 4H), 1.29 (m, CH$_2$CH$_2$CH$_2$CH$_3$, 4H), 0.91 (t, $J = 7.6$ Hz, CH$_2$CH$_2$CH$_2$CH$_3$, 6H). ^{1}H NMR (acetone-d_6): 9.47 (s, NH, 2H), 7.68 (s, 2H), 4.26 (t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH$_3$, 4H), 2.60 (s, CH$_3$C=NH, 6H), 2.04 (s, CH$_3$CN, 6H), 1.78 (m, CH$_2$CH$_2$CH$_2$CH$_3$, 4H), 1.35 (m, CH$_2$CH$_2$CH$_2$CH$_3$, 4H), 0.89 (t, $J = 7.6$ Hz, CH$_2$CH$_2$CH$_2$CH$_3$, 6H). ^{13}C NMR (DMSO-d_6): 176.17, 159.44, 138.38, 134.69, 118.35, 46.20, 32.70, 20.88, 19.32, 13.55, 1.36.

Synthesis of 2. A solution of 3,6-bis(*N*-*n*-butylimidazoliumyl)pyridazine dichloride (160 mg, 0.40 mmol) in 5 mL of CH_3OH was treated with Ag_2O (152 mg, 0.66 mmol). After the mixture was stirred at room temperature overnight, $Pd(COD)Cl_2$ (114 mg, 0.40 mmol) was added. The solution was allowed to react for 12 h. The resulting AgCl was filtered off, and the filtrate was reduced to 2 mL. Addition of 10 mL of diethyl ether afforded a white solid. Yield: 108 mg, (52.4%). Anal. Calcd for $C_{38}H_{70}Cl_2N_{12}O_{10}Pd_2$: C, 40.08; H, 6.20; N, 14.76. Found: C, 40.33; H, 5.97; N, 14.55. ^{1}H NMR (DMSO-d_6): 8.43, 7.81 (both d, $J = 9.6$ Hz, pyridazine, each 2H), 8.23, 7.57 (both d, $J = 2.2$, imidazolylidene, each 2H), 7.37, 7.25 (both s, imidazolyl, each 2H), 4.23, 4.00, 3.85 (all m, CH_2CH$_2$CH$_2$CH$_3$, each 2H), 4.12 (s, OCH$_3$, 6H), 3.52, 3.49 (both m, CH$_2$CH_2CH$_2$CH$_3$, each 2H), 1.80, 1.56 (both m, CH$_2$CH$_2$CH_2CH$_3$, each 4H), 1.13−0.97 (m, CH$_2$CH$_2$CH_2CH$_3$, 8H), 0.80, 0.45 (both t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH_3, each 6H). ^{13}C NMR (DMSO-d_6):166.1, 164.8, 155.0 152.1, 130.0, 124.5, 123.7, 122.0, 119.5, 118.1, 55.2, 50.0, 48.5, 33.3, 32.4, 19.3, 19.1, 12.5, 12.2.

Reactions of 3,6-Bis(*N*-*n*-butylimidazoliumyl)pyridazine Dichloride with Ag_2O in MeOH. A solution of 3,6-bis(*n*-butylimidazoliumyl)pyridazine dichloride (234 mg, 0.6 mmol) in 5 mL of methanol was treated with Ag_2O (70 mg, 0.3 mmol). After it was stirred for 30 min, the mixture was filtered. The filtrate was concentrated to ca. 1 mL, and addition of 10 mL of diethyl ether afforded 3-(*N*-*n*-butylimidazoliumyl)-6-methoxylpyridazine chloride as a white solid. Yield: 133 mg, 82.5%. Anal. Calcd for $C_{12}H_{17}ClN_4O$: C, 53.63; H, 6.38; N, 20.85. Found: C, 53.42; H, 6.42; N, 20.52. ^{1}H NMR (DMSO-d_6): 10.27 (s, NCHN, 1H), 8.54, 8.10 (both s, imidazolium, each 1H), 8.34, 7.68 (both d, $J = 9.2$ Hz, pyridazine, each 1H), 4.32 (t, CH_2CH$_2$CH$_2$CH$_3$, 2H), 4.11 (s, OCH$_3$, 3H), 1.88 (m, CH$_2$CH_2CH$_2$CH$_3$, 2H), 1.36 (m, CH$_2$CH$_2$CH_2CH$_3$, 2H), 0.93 (t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH_3, 3H). ^{13}C NMR (DMSO-d_6): 166.0, 148.0, 135.7, 124.1, 124.0, 121.3, 120.0, 55.7, 49.8, 31.5, 19.2, 13.7.

Reactions of 3,6-Bis(*N*-*n*-butylimidazoliumyl)pyridazine Dichloride with Ag_2O in CH_2Cl_2. A suspension of 3,6-bis(*N*-*n*-butylimidazoliumyl)pyridazine dichloride (117 mg, 0.3 mmol) in 5 mL of CH_2Cl_2 was treated with Ag_2O (80 mg, 0.35 mmol), and the mixture was stirred for 30 min. The filtrate was concentrated to ca. 2 mL. Addition of 10 mL of diethyl ether yielded **3** as a white solid. Yield: 128 mg, 81.5%. Anal. Calcd for $C_{36}H_{48}Ag_4Cl_4N_{12}$: C, 35.38; H, 3.96; N, 13.75. Found: C, 35.62; H, 3.72; N, 13.18. ^{1}H NMR (DMSO-d_6): 8.62, 8.15 (both s, imidazolylidene, each 4H), 7.83 (s, pyridazine, 4H), 4.27 (t, $J = 7.2$, CH_2CH$_2$CH$_2$CH$_3$, 8H), 1.85 (m, CH$_2$CH_2CH$_2$CH$_3$, 2H), 1.33 (m, CH$_2$CH$_2$CH_2CH$_3$, 2H), 0.91 (t, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$CH_3, 12H). ^{13}C NMR (DMSO-d_6): 180.2, 150.6, 124.2, 123.9, 120.8, 52.4, 33.1, 19.6, 13.8.

X-ray Structural Determination. Single crystals of the silver complexes were obtained by slow diffusion of diethyl ether into their acetonitrile solutions. Crystals with dimensions 0.29 × 0.25 × 0.21 mm and 0.16 × 0.15 × 0.12 mm for **1** and **2** were mounted onto glass fibers. X-ray diffraction data were collected on a Bruker Smart/CCD area-detector diffractometer with a Mo Kα radiation ($\lambda = 0.71073$ Å) by using an $\omega-2\theta$ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the *SMART* and *SAINT* software.[28] The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F_2 using

(27) Scheele, U. J.; Dechert, S.; Meyer, F. *Inorg. Chim. Acta* **2006**, *359*, 4891.

the SHELXTXL package.[29] Hydrogen atom positions attached to C atoms were calculated and allowed to ride on their respective C atoms with C−H distances of 0.93−0.97 Å and $U_{iso}(H) = -1.2 - 1.5U_{eq}(C)$.

General Procedure for the Heck Reaction. Aryl halide (1.0 mmol), olefin (1.5 mmol), NaOAc (2.0 mmol), catalyst (0.5 mmol %), and DMAc (3 mL) were subsequently added to a Schlenk tube. The solution was heated to 130 °C. The mixture was cooled to room temperature after the desired reaction time. Water was added, and the product was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over $MgSO_4$, and the filtrate was analyzed by GC.

General Procedure for the Suzuki Reaction. Aryl halide (1.0 mmol), additive (1.5 mmol), K_3PO_4 (2.0 mmol), catalyst (0.5 mmol %), and dioxane (3 mL) were subsequently added to a Schlenk tube. The solution was heated to 90 °C. The mixture was cooled to room temperature after the desired reaction time. Water was added, and the product was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over $MgSO_4$, and the filtrate was analyzed by GC.

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Supporting Information Available: Experimental details and crystallographic data for **1**−**4** as cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800272K

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