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Facile and Efficient Olefination of Aryl Halides Catalyzed by a Palladium Complex Containing a Heteroarene-Functionalized N-Heterocyclic Carbene

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$[Ag_4(L)_4](PF_6)_4$ and $[Pd(L)_2](PF_6)_2$ (L = 3-(2,4-dimethyl-1,8-naphthyrid-7-yl)-1-picolylimidazolylidene) have been prepared and fully characterized. The silver compound consists of a Ag_4 ring with short Ag−Ag contacts displaying a butterfly conformation. The palladium complex exhibits a helical structure with palladium located in a square-planar environment with two carbene ligands and two pyridines in a cis arrangement. The palladium complex has proven to be a highly efficient catalyst for Heck coupling reactions of aryl bromides with *n*-butyl acrylate. TON values up to 10^6 and TOF values up to 5×10^5 h^{-1} can be achieved.

Introduction

The palladium-catalyzed Heck reaction, i.e. the coupling reaction of aryl halides and olefins, is one of the most important protocols for the preparation of aryl-substituted olefins.[1] Although reactions catalyzed by the combination of palladium and bulky monophosphines and diphosphines have achieved great success in the last decade,[2] the phosphines are normally not easily available, are air-sensitive, and are quite expensive.[3] Therefore, the development of efficient catalyst systems with non-phosphine ligands is of practical interest. So far, a few successful examples, including the use of hydrazone,[4] bis(imidazole) ligands,[5] thioureas,[6] quinoline-8-carboxylate,[7] alanine,[8] and N-heterocyclic carbenes (NHCs),[9] have been reported.

N-heterocyclic carbenes as a class of non-phosphine ligands and alternative to tertiary phosphines are attracting more and more attention, since N-heterocyclic carbene ligands exhibit unique advantages: i.e., their stronger σ-donating characters facilitate oxidative addition of substrates to metals; the strong metal−carbenic bond disfavors ligand dissociation; the presence of sterically encumbering groups bound to the N atoms favors reductive elimination of the product from metals. Hence, the transition-metal complexes of N-heterocyclic carbenes have been widely employed in a number of industrially important organic processes.[10] Especially, metal−NHC complexes exhibit excellent catalytic activity for many C−C bond formation reactions.[9g,11]

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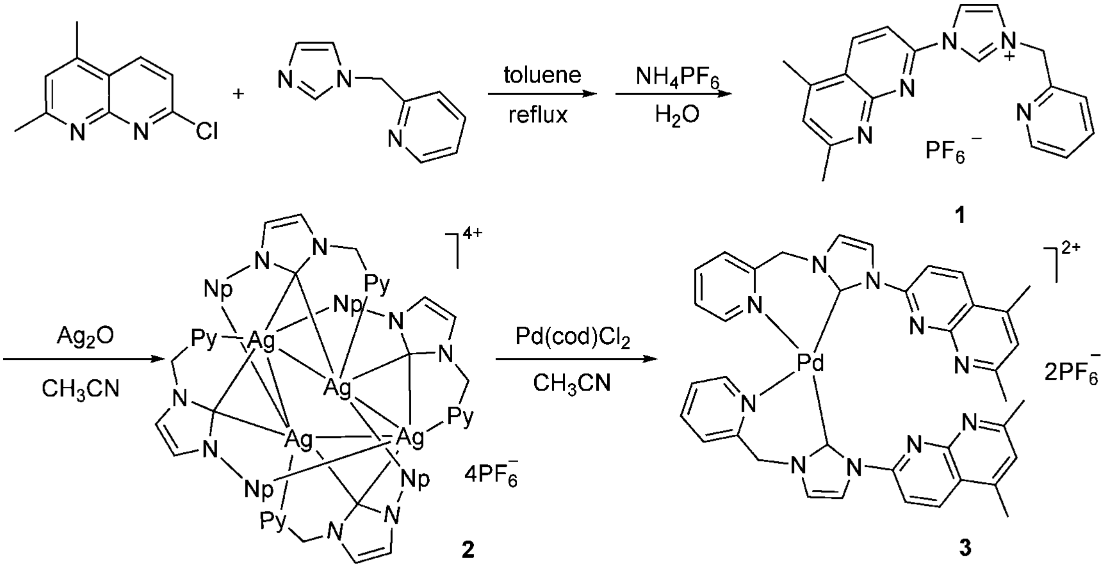
Scheme 1



Np = 2,4-dimethyl-1,8-naphthyridinyl, Py = pyridyl

There are many examples of monodentate NHCs,[10e,12] but only a few examples of chelating NHC ligands have been studied,[13] which are believed to be more useful for the stabilization of the catalysts and enhancement of the catalytic activity.

We have recently reported the preparation and structural characterization of multinuclear metal complexes of pyridine- and pyrazole-functionalized bis(NHC) ligands.[14] It is believed that suitably chosen N substituents of NHCs are crucial to acquire high catalytic efficiency. 3-(2,4-Dimethyl-1,8-naphthyrid-7-yl)-1-picolylimidazolylidene (L), bearing sterically bulky and hemilabile N-substituents, would be a good candidate. In this paper we describe the synthesis and structural characterization of $[Ag_4(L)_4](PF_6)_4$ (**2**) and $[Pd(L)_2](PF_6)_2$ (**3**). The palladium complex is an efficient catalyst for the Heck coupling reactions of aryl bromides with *n*-butyl acrylate.

Results and Discussion

Synthesis and Structural Characterization. The naphthyridyl-functionalized imidazolium salt **1** was prepared by refluxing 7-chloro-2,4-dimethyl-1,8-naphthyridine and *N*-picolylimidazole in toluene and carrying out a subsequent anion exchange reaction in water (Scheme 1). Facile deprotonation of **1** with Ag_2O in acetonitrile led to the isolation of the tetrasilver complex $[Ag_4(L)_4](PF_6)_4$ (**2**). The palladium complex $[Pd(L)_2](PF_6)_2$ (**3**) was obtained from the carbene transfer reaction of the in situ generated silver–NHC complex with $Pd(cod)Cl_2$. The formation of the Ag– and Pd–NHC complexes was confirmed by the absence of the ^1H NMR resonance signal of the acidic imidazolium C2–H at 9.81 ppm, where the resonance signal of **1** is found. The ^1H NMR spectrum of **2** exhibits four singlets of equal intensities for the eight methyl groups and two doublets and one broad singlet with an intensity ratio of 1:1:2 for the four methylene groups. In the range of 7.0–8.6 ppm, eight resonance signals assignable to four pyridyl groups were observed. However, only two broad singlets due to the imidazolylidene backbone protons appear for the four imidazolylidene ligands, illustrating dynamic behavior in solution. Complex **2** in solution is not very stable, and no satisfactory ^{13}C spectrum could be obtained. The ^{13}C NMR spectrum of **3** exhibits a resonance signal at 164.4 ppm ascribed to the carbenic carbon atom, which is consistent with the reported values for Pd–NHC complexes. The ^{13}C chemical shifts of known Pd–NHC complexes appear in the range of 182.4–149.5 ppm, depending upon the ancillary ligands.[15] Compound **3** is stable toward air and moisture in its solid state and in solution. The ESI-MS spectrum of **3** shows peaks at 1056.7, 882.7, and 422.2 assignable to $[PdL_2(CH_3CN)(PF_6)_2]^+$, $[PdL_2(PF_6)]^+$, and $[Pd(L)]^+$, respectively.

Complex **2** and the carbene precursor **1** in acetonitrile are emissive. The emission spectrum of **2** shows a broad band centered at 430 nm that tails out to 520 nm when excited at 355 nm. The imidazolium salt emits at 399 nm upon excitation at 350 nm. The emission spectrum of **2** is similar to those of the previously reported silver clusters also supported by NHC ligands.[14a,b,16a,c]

X-ray diffraction analysis showed that complex **2** is a tetranuclear silver complex which consists of a Ag_4 ring displaying a butterfly conformation. The molecular structure of **2** is depicted in Figure 1. The four silver ions are linked together by four 3-(2,4-dimethyl-1,8-naphthyrid-7-yl)-1-picolylimidazolylidene ligands, and each ligand interacts with three silver ions, with the internal naphthyridyl nitrogen being uncoordinated. Each of the four silver ions are tetracoordinated by two NHCs, one pyridine, and one naphthyridine group. The Ag_4 ring is formed because of argentophilic attraction and the ligand functionality. The four Ag–Ag bonds are buttressed by four NHC ligands forming Ag_2C rings, and thus the Ag–Ag distances ranging from 2.8365(7) to 2.8661(8) Å are relatively shorter than for our previously reported silver complexes.[14] This coordination mode of NHC ligands has recently been observed

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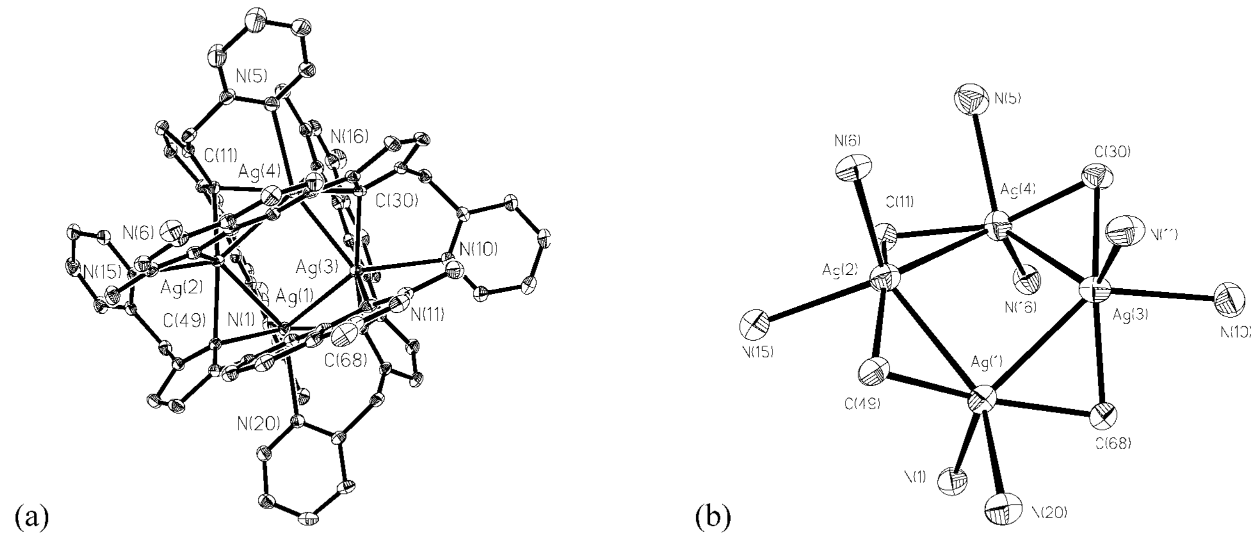

Figure 1. (a) ORTEP drawing of the cationic section of **2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ag(1)−Ag(2) = 2.8405(7), Ag(1)−Ag(3) = 2.8365(7), Ag(2)−Ag(4) = 2.8652(7), Ag(3)−Ag(4) = 2.8661(8), Ag(1)−C(68) = 2.244(6), Ag(1)−C(49) = 2.252(6), Ag(1)−N(20) = 2.597(6), Ag(1)−N(1) = 2.616(5), Ag(2)−C(11) = 2.270(6), Ag(2)−C(49) = 2.279(6), Ag(2)−N(6) = 2.545(5), Ag(2)−N(15) = 2.615(6), Ag(3)−C(30) = 2.280(5), Ag(3)−C(68) = 2.294(6), Ag(3)−N(11) = 2.571(5), Ag(3)−N(10) = 2.618(6), Ag(4)−C(30) = 2.283(6), Ag(4)−C(11) = 2.289(6), Ag(4)−N(16) = 2.531(5), Ag(4)−N(5) = 2.656(6); C(68)−Ag(1)−C(49) = 156.8(2), C(68)−Ag(1)−N(20) = 83.5(2), C(49)−Ag(1)−N(20) = 83.7(2), C(68)−Ag(1)−N(1) = 90.6(2), C(49)−Ag(1)−N(1) = 110.5(2), N(20)−Ag(1)−N(1) = 99.2(2), C(49)−Ag(2)−N(15) = 80.9(2), N(6)−Ag(2)−N(15) = 100.9(2), C(30)−Ag(3)−C(68) = 153.8(2), C(30)−Ag(3)−N(11) = 90.5(2), C(68)−Ag(3)−N(11) = 113.7(2), C(30)−Ag(3)−N(10) = 85.7(2), C(68)−Ag(3)−N(10) = 81.5(2), N(11)−Ag(3)−N(10) = 97.4(2), C(30)−Ag(4)−C(11) = 155.2(2), C(30)−Ag(4)−N(16) = 110.7(2), C(11)−Ag(4)−N(16) = 92.4(2), C(30)−Ag(4)−N(5) = 85.0(2), C(11)−Ag(4)−N(5) = 81.3(2), Ag(3)−Ag(1)−Ag(2) = 84.56(2), Ag(1)−Ag(2)−Ag(4) = 85.36(2), Ag(1)−Ag(3)−Ag(4) = 85.42(2), Ag(2)−Ag(4)−Ag(3) = 83.57(2). (b) Simplified illustration of the coordination environment of the Ag_4 complex.

for a few silver clusters.[14b,16] The Ag−C bond distances fall in the narrow range of 2.244(6)−2.294(6) Å, which are significantly longer than the normal Ag−C bonds of mononuclear silver−NHC complexes,[17] but are consistent with a few trinuclear and tetranuclear silver complexes.[16] The Ag−N (pyridine and naphthyridine) distances in the range of 2.531(5)−2.656(6) Å are relatively long, illustrating that both pyridine and naphthyridine are weakly coordinated. Due to the geometric requirements of the ligands, the C−Ag−C angles are ca. 155°. Although a large number of transition-metal complexes of Ag−NHC have been structurally characterized in the last decade,[17] multinuclear silver clusters supported by NHC ligands have still been scarcely reported.[14,16] The Ag−Ag distances for **2** are also comparable to those of the known silver clusters.

Slow diffusion of diethyl ether into the acetonitrile solution of **3** yielded colorless, nice-looking crystals with the formulation of $[Pd(L)_2](PF_6)_2 \cdot 2CH_3CN$. Although the diffraction data were repeatedly collected in different laboratories at different temperatures, the structure was resolved with quite large *R* factors (R1 = 0.1471 and wR2 = 0.3800). Recrystallization of the crystal sample in DMF afforded single crystals of the composition $[Pd(L)_2](PF_6)_2 \cdot DMF \cdot CH_3CN$, which was quite suitable for an X-ray diffraction study. This study revealed that the complex exhibits a helical structure and crystallizes in the chiral space group $P2_12_12_1$. The Flack factor is 0.02(4), illustrating that the absolute configuration is correct. The molecular structure of **3** determined by X-ray diffraction analysis is shown in Figure 2. Palladium is located in a square-planar geometry surrounded by two imidazolilydenes and two pyridyl groups with the same donating atoms arranged cis to each other. Two naphthyridine groups are not coordinated and are directed up and down the coordination plane of palladium. The Pd−C (1.974(7) and 1.961(6) Å) and Pd−N bond distances (2.073(5) and 2.087(5) Å) are quite normal as compared to those of many known palladium−NHC complexes.[15,18]

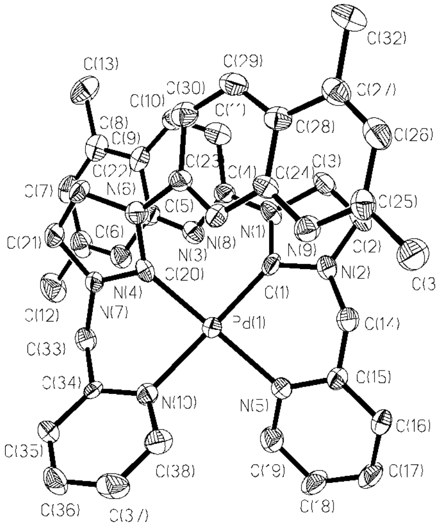

Figure 2. ORTEP drawing of the cation of $[PdL_2](PF_6)_2] \cdot DMF \cdot CH_3CN$. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) = 1.974(7), Pd(1)−C(20) = 1.961(6), Pd(1)−N(5) = 2.073(5), Pd(1)−N(10) = 2.087(5); C(20)−Pd(1)−C(1) = 93.8(2), C(20)−Pd(1)−N(5) = 179.3(2), C(1)−Pd(1)−N(5) = 86.8(2), C(20)−Pd(1)−N(10) = 85.1(2), C(1)−Pd(1)−N(10) = 177.9(3), N(5)−Pd(1)−N(10) = 94.2(2).

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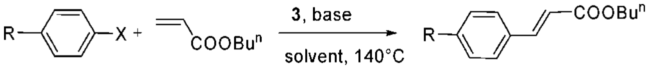
Table 1. Olefination of Aryl Halides with n-Butyl Acrylate[a]



entry	R	X	solvent	base	cat. load (mol %)	time (h)	GC/isolated yield (%)
1	H	Br	DMF	Na_2CO_3	5×10^{-1}	6	37
2	H	Br	DMF	Cs_2CO_3	5×10^{-1}	6	27
3	H	Br	DMF	NaOAc	5×10^{-1}	6	33
4[b]	H	Br	DMF	Na_2CO_3	5×10^{-1}	6	61/57
5[b]	H	Br	DMF	NaOAc	5×10^{-1}	6	72/70
6[b]	H	Br	DMAc	NaOAc	5×10^{-1}	6	85/81
7	H	I	DMAc	NaOAc	5×10^{-1}	0.5	100/98
8	H	I	DMAc	NaOAc	5×10^{-2}	0.5	100/98
9	Cl	I	DMAc	NaOAc	5×10^{-1}	0.5	100/93
10	C(O)CH_3	Br	DMAc	NaOAc	5×10^{-1}	0.5	100/94
11	C(O)CH_3	Br	DMAc	NaOAc	5×10^{-2}	0.5	100/95
12	C(O)CH_3	Br	DMAc	NaOAc	5×10^{-3}	0.5	100/92
13	C(O)CH_3	Br	DMAc	NaOAc	5×10^{-4}	0.5	66/57
14	CHO	Br	DMAc	NaOAc	5×10^{-1}	0.5	100/92
15	CHO	Br	DMAc	NaOAc	5×10^{-2}	0.5	100/96
16	C(O)CH_3	Br	DMF	Na_2CO_3	5×10^{-1}	0.5	100/94
17	CHO	Br	DMF	Na_2CO_3	5×10^{-1}	0.5	100/96
18[b]	CH_3	Br	DMAc	NaOAc	5×10^{-1}	6	91/89
19[b]	CH_3	Br	DMAc	NaOAc	5×10^{-2}	6	61/58
20	CH_3	Br	DMAc	NaOAc	5×10^{-1}	6	38
21[b,c]	CH_3	Br	DMAc	NaOAc	5×10^{-1}	6	83/82
22[b]	OCH_3	Br	DMAc	NaOAc	5×10^{-1}	6	88/85
23[b]	OCH_3	Br	DMAc	NaOAc	5×10^{-2}	6	60/49
24[b,d]	C(O)CH_3	Br	DMAc	NaOAc	5×10^{-1}	14	13
25[b]	2-CH_3	Br	DMAc	NaOAc	5×10^{-1}	6	13
26[b]	C(O)CH_3	Cl	DMAc	NaOAc	5×10^{-1}	6	11

[a] Reaction conditions: aryl halide, 1.0 mmol; *n*-butyl acrylate, 1.5 mmol; base, 2.0 mmol; solvent, 5 mL; 140 °C. [b] With 20 mol % *n*-Bu_4NBr added vs ArX. [c] In air atmosphere. [d] At 80 °C.

Catalytic Heck Coupling Reactions. The coupling reactions of bromobenzene and *n*-butyl acrylate were tested in DMF at 140 °C using 0.5 mol % of **3** (Table 1, entries 1−3). *n*-Butyl (*E*)-cinnamate is the sole product, and no (*Z*)-olefin and other side products were observed by gas chromatography. The target product was obtained in not more than 37% yield when Na_2CO_3, Cs_2CO_3, and NaOAc were used as bases. However, the reactions could be dramatically improved in the presence of tetrabutylammonium bromide (TBAB) under the same conditions. It was observed that when 20 mol % of *n*-Bu_4NBr (vs ArX) was added, the yields were markedly increased to 61% and 70% in the cases of Na_2CO_3 and NaOAc, respectively (Table 1, entries 4 and 5). It has been known that addition of TBAB as a cocatalyst enhances the activity of many catalytic systems, and TBAB is able to activate and stabilize the in situ generated palladium(0) species, which is believed to be the real catalytically active species.[9a,15b,19] In addition, when DMAc was used as solvent instead of DMF, a better yield of 85% could be obtained (Table 1, entry 6).

With these optimized conditions in hand, we continued our investigation of Heck reactions of other substrates. The results show that the catalysis is more efficient for the olefination of aryl iodides and activated bromides (Table 1, entries 7−17). The olefination reactions of aryl iodides and activated bromides with *n*-butyl acrylate could be completed within 30 min with 100% conversion, even in the absence of *n*-Bu_4NBr. Reduction of the catalyst loading to 5×10^{-3} mol % still gave a quantitative yield for 4-acetylphenyl bromide (Table 1, entry 12). Further decrease of the catalyst loading to 5×10^{-4} mol % afforded the coupled product in 66% yield (Table 1, entry 13). When the reaction temperature was lowered to 80 °C for the same substrate, the yield was sharply decreased to 13%, even when the reaction time was extended to 14 h (Table 1, entry 13). The deactivated aryl bromides such as 4-bromotoluene and 4-bromoanisole also gave excellent yields (91% and 88%, Table 1, entries 18 and 22) under the conditions used for unactivated substrates, although these reactions required a longer reaction time. The catalysts showed poor activity even for electron-deficient aryl chloride; the yield in the case of 4-acetylphenyl chloride is only 11% after 11 h. Actually, few catalyst systems show good catalyst activity for the olefination of aryl chlorides.[19a,20]

Table 2. Determination of TON and TOF in the Heck Olefination of Different Aryl Halides with *n*-Butyl Acrylate[a]

entry	R	X	amt of **3** (mol %)	time	yield (%)[b]	TON	TOF (h^{-1})
1	C(O)CH_3	Br	1	5 min	100	10^2	1 200
2	C(O)CH_3	Br	1×10^{-1}	25 min	100	10^3	2 400
3	C(O)CH_3	Br	1×10^{-2}	30 min	100	10^4	20 000
4	C(O)CH_3	Br	1×10^{-3}	10 h	100	10^5	10 000
5	C(O)CH_3	Br	1×10^{-4}	20 h	100	10^6	50 000
6	CHO	Br	1×10^{-3}	6 h	100	10^5	16 666
7	CHO	Br	1×10^{-4}	20 h	100	10^6	50 000
8	H	I	1×10^{-3}	10 h	100	10^5	10 000
9	H	I	1×10^{-4}	20 h	100	10^6	50 000

[a] Reaction conditions: aryl halide, 1.0 mmol; *n*-butyl acrylate, 1.5 mmol; NaOAc, 2.0 mmol; DMAc, 5 mL; 140 °C. [b] GC yield (average of two runs).

As described above, the palladium−bis(NHC) complex shows high catalytic activity for the Heck reactions of various aryl bromides and iodides. To further examine its catalytic efficiency, coupling reactions with different catalyst loadings ranging from 1 to 10^{-4} mol % were performed. The reaction of 4-acetylphenyl bromide and *n*-butyl acrylate in DMAc at 140 °C was chosen to assess the effect of catalyst loading. As shown in Table 2, the catalyst exhibits a very high catalytic activity, and 4-acetylphenyl bromide could be completely converted to the desired product within 5 min at a catalyst loading of 1 mol % (Table 2, entry 1). Surprisingly, reduction of the catalyst loading to 10^{-4} mol % still afforded the coupling product in 100% yield upon extending the reaction time to 20 h. The turnover numbers (TONs) of 10^4−10^6 at catalyst loadings of 10^{-2}−10^{-4} mol % Pd can be achieved (Table 2 entries 3−5), which are among the highest for Heck coupling reactions of aryl bromides. A turnover frequency (TOF) of up to 5×10^4 h^{-1} was observed in the case of a catalyst loading of 10^{-4} mol %, which is also the highest. Similarly, the catalyst also shows high activity for 4-bromobenzaldehyde and iodobenzene. It should be noted that no additives such as TBAB are required for the catalyst to gain extremely high activity. For aryl iodide and activated bromide substrates, the palladium−NHC catalyst is even more effective than most known palladium catalysts such as phosphapalladacycles[15b,21] and Pd−phosphine−imidazolium salt systems.[9b,d,22] The reaction rate (TOF up to 5×10^4 h^{-1}) is also remarkable.

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Table 3. Influence of Air and H_2O on Heck Olefination

entry	R	X	cat. load (mol %)	special conditions	time (min)	yield (%)[a]
1	$C(O)CH_3$	Br	1	air	10	100
2	$C(O)CH_3$	Br	1	N_2	5	100
3	$C(O)CH_3$	Br	1×10^{-1}	air	30/360	70/100
4	$C(O)CH_3$	Br	1×10^{-1}	N_2	30	100
5	$C(O)CH_3$	Br	1×10^{-2}	air	30/1200	23/85
6	$C(O)CH_3$	Br	1×10^{-2}	N_2	30	100
7	H	I	1×10^{-2}	air	30/1200	21/83
8[c]	$C(O)CH_3$	Br	1×10^{-1}	H_2O	30	100
9[c]	$C(O)CH_3$	Br	1×10^{-2}	H_2O	30	100
10[c]	CHO	Br	1×10^{-1}	H_2O	30	100
11[c]	H	I	1×10^{-1}	H_2O	30	100

[a] Reaction conditions: aryl halide, 1.0 mmol; *n*-butyl acrylate, 1.5 mmol; NaOAc, 2.0 mmol; DMAc, 5 mL; 140 °C. [b] GC yield (average of two runs). [c] 100 μL of water was added.

Obviously, the excellent catalytic activity and stability can be ascribed to the strong donating ability of NHC and the weak coordination of heteroaryl groups. The weak coordination abilities of pyridyl groups make them easy to dissociate from the metal center to create catalytically active species with vacant coordination sites. The strong Pd−C bonds can facilitate the oxidative addition of aryl halides to the metal. The dynamic dissociation and association of the heteroaryl groups allow the approach of substrate to the metal center, and the bulky naphthyridyl groups favor the stabilization of the active metal species after reductive elimination of the product.

It is commonly believed that metal−NHC complexes as catalysts are superior to metal−phosphine complexes, because they are stable to air and more tolerant to moisture. It was indeed found that Pd−NHC-catalyzed Heck reactions with the careful exclusion of air and water did not show any significant differences from those carried out in air in commercial solvents.[15b,23] However, our results obviously show that oxygen can remarkably inhibit Heck coupling reactions of bromides and iodides (Table 3). The effect of air is more distinct at lower catalyst loading. For instance, the reaction of 4-acetylphenyl bromide can reach completion within 30 min at catalyst loadings of 0.1 and 0.01 mol % under an N_2 atmosphere. However, the reaction required 6 h to reach 100% conversion using 0.1 mol % catalyst **3** in air. When the catalyst loading is lowered to 0.01 mol %, the yield of the coupling product is only 23% within 30 min and 85% after 20 h (Table 3, entry 5). The same effect of air to decrease the reaction rate is also observed for the coupling reaction of iodobenzene. Further experiments were conducted to examine the influence of water on the reaction rate. Under an N_2 atmosphere, adding 100 μL of water to the reaction mixtures of bromides and iodides did not change the reaction rates, and no other byproducts were detected by gas chromatography. Obviously, the palladium catalyst has good tolerance toward moisture.

The effect of air can be more clearly illustrated by monitoring the reaction course by gas chromatography. Figures 3 and 4 show the time-dependent reaction profiles for the Heck arylation of *n*-butyl acrylate carried out under dried N_2 and air at different catalyst loadings. Under an N_2 atmosphere, the reactions can reach 100% conversion within 25 and 30 min when 0.1 and 0.01 mol % catalyst were employed, respectively. In contrast, when the same reactions were exposed to air, the reactions had to be extended to 400 min to reach completion in the case of 0.1 mol % catalyst loading. When the catalyst loading was decreased to 0.01 mol %, only a ca. 80% yield of *n*-butyl (*E*)-cinnamate can be obtained, even after 20 h. Although it is not clear at present that how oxygen influences the reaction, the results demonstrate that even for the robust catalyst the influence of air cannot be neglected.

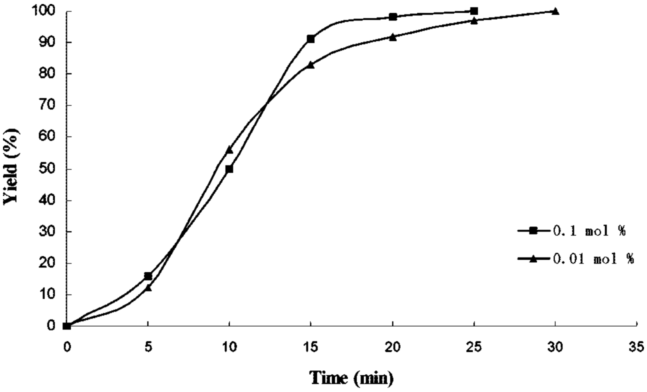

Figure 3. Plot of yields vs time with different catalyst loadings under an N_2 atmosphere. The reaction conditions are the same as in Table 2.

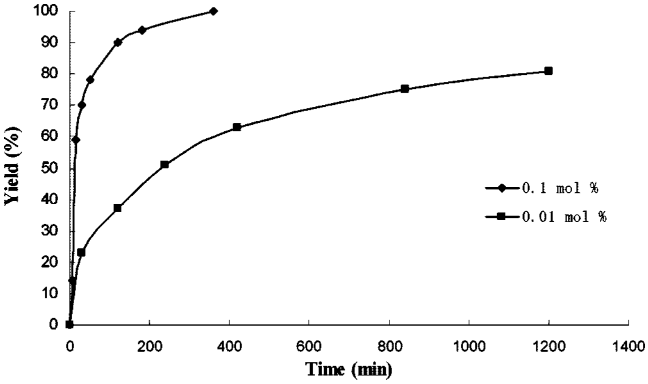

Figure 4. Plot of yields vs time with different catalyst loadings in air. The reaction conditions are the same as in Table 2.

In summary, we have described the synthesis and structural characterization of a new and potentially useful bis(NHC) complex of palladium(II) which shows extremely high catalytic activity for Heck olefination of aryl bromides and iodides without the need for additional ligands. The catalytic efficiency (TON) and reaction rate (TOF) at low catalyst loading are among the highest yet reported for aryl bromides. The work demonstrates that rationally designed NHC ligands with suitable donating ability and steric hindrance may markedly enhance the activity of their corresponding metal complexes.

Experimental Section

General Procedures. All the chemicals were obtained from commercial suppliers and used without further purification. N-Picolylimidazole[24] and 7-chloro-2,4-dimethyl-1,8-naphthyridine[25] were prepared according to the known procedures. The C, H, and N elemental analyses were carried out with a Vario EL III elemental analyzer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from TMS at δ 0 ppm, and coupling constants (*J*) are expressed in Hz.

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Synthesis of 3-(2,4-Dimethyl-1,8-naphthyrid-7-yl)-1-picolylimidazolium Hexafluorophosphate (1). 7-Chloro-2,4-dimethyl-1,8-naphthyridine (1.92 g, 10 mmol) was added to a solution of 1-picolylimidazole (4.2 g, 20 mmol) in 100 mL of toluene. The mixture was refluxed overnight. The resulting precipitate was isolated and washed with toluene (2 × 5 mL) and Et_2O (2 × 5 mL), which was then dissolved in water (20 mL). To the aqueous solution was added an excess of NH_4PF_6 (3.3 g, 20 mmol), resulting immediately in a white precipitate. The white solid was collected, washed with water and Et_2O, and dried under vacuum. Yield: 2.97 g (63%). ^{1}H NMR (400 MHz, $CDCl_3$): 9.81 (s, NCHN, 1H), 8.69, 8.07 (both d, $J = 8.8$, naphthyridine, each 1H), 8.56 (d, $J = 4.8$, pyridyl, 1H), 8.53 (s, naphthyridine, 1H), 7.78, 7.33 (both s, imidazolium, each 1H), 7.75, 7.63, 7.27 (m, pyridyl, each 1H), 5.64 (s, CH_2, 2H), 2.72 (s, CH_3, 3H), 2.78 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.4, 153.9, 151.1, 150.0, 146.4, 146.3, 139.2, 137.8, 134.4, 124.9, 124.2, 124.1, 123.7, 121.7, 119.3, 111.3, 54.8, 25.6, 18.1. Anal. Calcd for $C_{19}H_{18}N_5F_6P$: C, 49.46; H, 3.93; N, 15.18. Found: C, 49.32; H, 4.06; N, 14.90.

[Ag_4(3-(2,4-dimethyl-1,8-naphthyrid-7-yl)-1-picolylimidazolylidene)$_4$](PF_6)$_4$·$2H_2O$ (2). A slurry of Ag_2O (38 mg, 0.17 mmol) in 20 mL of CH_3CN was treated with **1** (138 mg, 0.30 mmol). The mixture was stirred for 5 h with exclution of light at room temperature until nearly all of the Ag_2O was dissolved. The filtrate was concentrated to ca. 2 mL. Addition of Et_2O (20 mL) to the filtrate yielded a white solid. Yield: 159 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.56, 8.21, 7.99, 7.10 (all d, $J = 8.6$, naphthyridine, each 2H), 8.33, 8.10 (both s, naphthyridine, each 2H), 7.85, 7.40 (both s, imidazolium, each 4H), 8.49, 8.42, 7.49, 7.30 (all br, pyridyl, each 2H), 7.68 (t, $J = 7.0$, pyridyl, 2H), 7.61 (d, $J = 4.4$, pyridyl, 2H), 7.24 (t, $J = 6.4$, pyridyl, 2H), 7.13 (d, $J = 7.6$, pyridyl, 2H), 5.82, 5.44 (both d, $J = 14.8$, CH_2, each 2H), 5.50 (s, CH_2, 4H), 2.62, 2.60, 2.44, 1.75 (all s, CH_3, each 6H), 2.78 (s, CH_3, 3H). Anal. Calcd for $C_{76}H_{72}Ag_4F_{24}N_{20}O_2P_4$: C, 39.54; H, 3.14; N, 12.13. Found: C, 39.71; H, 3.40; N, 12.17.

[Pd(3-(2,4-dimethyl-1,8-naphthyrid-7-yl)-1-picolylimidazolylidene)$_2$](PF_6)$_2$ (3). To a solution of **1** (138 mg, 0.3 mmol) in CH_3CN (20 mL) was added Ag_2O (38 mg, 0.165 mmol), and the mixture was stirred at room temperature for 5 h. To the filtrate was added Pd(COD)Cl_2 (43 mg, 0.15 mmol). After it was stirred overnight, the mixture was filtered through Celite, and the filtrate was then concentrated to ca. 2 mL. Addition of Et_2O (20 mL) to the filtrate afforded a white precipitate. Yield: 152 mg (96%). ^{1}H NMR (400 MHz, DMSO-d_6): 8.71, 8.06 (both d, $J = 8.8$, naphthyridine, each 2H), 8.64 (d, $J = 4.2$, pyridine, 2H), 8.31 (t, $J = 8.0$, pyridine, 2H), 7.72 (t, $J = 6.4$, pyridine, 2H), 7.67 (d, $J = 8.0$, pyridine, 2H), 7.57 (s, naphthyridine, 2H), 7.46, 7.27 (d, $J = 2.0$, imidazolilydene, each 2H), 6.73 (d, $J = 15.2$, CH_2, 2H), 5.83 (d, $J = 15.2$, CH_2, 2H), 2.86 (s, CH_3, 6H), 2.78 (s, CH_3, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 164.4, 158.5, 153.8, 153.4, 153.2, 149.4, 146.8, 142.0, 137.5, 126.4, 126.1, 124.6, 123.7, 120.9, 120.5, 115.1, 55.9, 25.5, 18.8. Anal. Calcd for $C_{38}H_{34}N_{10}F_{12}P_2Pd \cdot 2H_2O$: C, 42.93; H, 3.60; N, 13.17. Found: C, 42.99; H, 3.62; N, 13.20. Crystallization of $[Pd(L)_2](PF_6)_2 \cdot 2H_2O$ in acetonitrile yielded nearly colorless crystals of $[Pd(L)_2](PF_6)_2 \cdot 2CH_3CN$. X-ray-quality crystals were obtained by slow diffusion of Et_2O into the DMF solution of $[Pd(L)_2](PF_6)_2 \cdot 2CH_3CN$.

X-ray Structural Determination. Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart-CCD area-detector diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ 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.[26] 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 the SHELXTXL package.[27] Hydrogen atom positions for all of the structures 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) = 1.2−1.5 times U_{eq}(C). Further details of the structural analyses are summarized in Table 4.

Table 4. Summary of X-ray Crystallographic Data for complexes 2 and 3

	$[Ag_4(L)_4](PF_6)_4 \cdot 2H_2O$ (**2**)	$[Pd(L)_2](PF_6)_2 \cdot DMF \cdot CH_3CN$ (**3**)
formula	$C_{76}H_{72}Ag_4F_{24}N_{20}O_2P_4$	$C_{43}H_{44}F_{12}N_{12}OP_2Pd$
fw	2308.91	1141.24
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	15.536(2)	8.4236(9)
b, Å	17.959(2)	12.5375(13)
c, Å	18.176(2)	46.354(4)
α, deg	88.668(2)	
β, deg	86.415(2)	
γ, deg	68.656(1)	
V, Å^3	4714.2(10)	4895.5(8)
Z	2	4
D_{calcd}, Mg/m^3	1.627	1.548
no. of rflns collected	24 101	20 395
no. of unique rflns, R_{int}	16 519, 0.0185	8561, 0.0624
goodness of fit on F^2	1.046	1.019
R1, wR2 ($I > 2\sigma(I)$)	0.0510, 0.1513	0.0613, 0.1240
R1, wR2 (all data)	0.0753, 0.1723	0.0880, 0.1338
largest diff peak, hole, e Å^{-3}	0.865, −0.642	0.490, −0.839

General Procedure for Heck Reactions with 3. 4-Bromoacetophenone (199 mg, 1.0 mmol), *n*-butyl acrylate (192 mg, 1.5 mmol), NaOAc (164 mg, 2.0 mmol), **3** (5 mg, 0.5 mmol %), and 5 mL of DMAc were subsequently added to a Schlenk tube. The solution was heated to 140 °C under an atmosphere of N_2 for 30 min. The mixture was then cooled to room temperature and added to 20 mL of water. The product was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the desired product.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **2** and **3** and figures and text giving spectroscopic data for the coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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