Heck Reaction in Ionic Liquids and the in Situ Identification of *N*-Heterocyclic Carbene Complexes of Palladium

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The Heck reaction was found to proceed markedly more efficiently in the ionic liquid 1-butyl-3-methylimidazolium bromide ([bmim][Br]) than in the analogous tetrafluoroborate salt ([bmim][BF$_4$]). In relation to this observation, 1-butyl-3-methylimidazol-2-ylidene (bmiy) complexes of palladium [PdBr(μ-Br)(bmiy)]$_2$ (**1**) and [PdBr$_2$(bmiy)$_2$] (**2**) have been isolated in [bmim][Br] but not in [bmim][BF$_4$] under conditions similar to those employed for the Heck reaction. In both the ionic liquid [bmim][Br] and molecular solvents, complex **2** was formed via the intermediate **1**. **2** has been shown to be active in the Heck reaction in [bmim]-[Br] but much less so in [bmim][BF$_4$] due to transformation by the latter into less active species.

Introduction

Ionic liquids are attractive alternatives to volatile organic solvents for catalytic reactions and separation processes.[1–4] Among various ionic liquids used as reaction media, those based on dialkylimidazolium salts have attracted particular attention, as they possess wide liquid range and are easy to prepare and handle.[1] A number of transition metal catalyzed reactions have been performed in these and related ionic liquids.[2] Interesting examples include nickel- and palladium-catalyzed olefin dimerization and oligomerization,[2e,h,l,o] rhodium- and ruthenium-catalyzed hydrogenation and hydroformylation,[2d,g,j,k,m,p] and palladium-catalyzed Heck and allylation reactions.[2a–c,f,n] While it is clear from these studies that the ionic liquid anion and cation can exert marked effects on the rate of a reaction, the mechanistic details of the effects are far from clear. In the hydrogenation of 1-alkenes catalyzed by rhodium complexes in dialkylimidazolium ionic liquids, the difference in hydrogenation rates was attributed to the coordinating ability of the ionic liquid anion to cationic rhodium species[2g] and to halide impurities difficult to remove in some of the ionic liquids.[2p] The imidazolium cation is usually presumed to be a simple inert component of a solvent system, and its possible involvement in a catalytic cycle has rarely been an issue. There appears to be only one case where the imidazolium ring was found to undergo dealkylation during a hydrodimerization reaction catalyzed by palladium.[2h]

We have now found that the ionic liquid [bmim][Br], when used as a solvent for the Heck reaction, reacts readily with Pd(OAc)$_2$ to give *N*-heterocyclic carbene complexes of palladium. In contrast, no carbene species were observed with Pd(OAc)$_2$ in [bmim][BF$_4$]. We describe herein our results on the first isolation of the *N*-heterocyclic carbene complexes under conditions similar to those used for the Heck reaction and discuss the implications of the findings to catalysis by metal complexes in imidazolium ionic liquids. The Heck reaction in related ionic liquids has recently been reported by other research groups while this study was in progress, and in particular, Seddon has suggested the possible involvement of *N*-heterocyclic carbenes in the reaction.[2a,f]

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Table 1. Heck Olefination Reactions of Aryl Halides with Acrylates[a]

substrate	ionic liquid[b]	$T/°C$	conversion[c] (%)	selectivity[d] (%)
iodobenzene	[bmim][Br]	90	100	99
	[bmim][Br]	90	71	99[e]
	[bmim][BF$_4$]	90	43	68
4-bromobenzaldehyde	[bmim][Br]	100	88	97
	[bmim][BF$_4$]	100	26	82
4-bromoacetophenone	[bmim][Br]	110	90	98
	[bmim][BF$_4$]	110	36	88
bromobenzene	[bmim][Br]	125	6	90
	[bmim][BF$_4$]	125	<1	

[a] All reactions were carried out with 5.0 mmol of a substrate, 1.4 equiv of *n*-butyl acrylate except with iodobenzene, where ethyl acrylate was used, 1.1 equiv of NaOAc, and 1 mol % Pd(OAc)$_2$ in 5.0 mL of ionic liquid for 24 h. [b] bmim = 1-butyl-3-methylimidazolium. [c] Of the halide. Determined by GC using octadecane as internal standard. [d] To *trans*-cinnamate. [e] 1×10^{-2} mol % Pd(OAc)$_2$, 90 h.

Table 2. Heck Olefination Reactions of Aryl Halides with Styrene[a]

substrate	ionic liquid	$T/°C$	conversion[b] (%)	selectivity[c] (%)
iodobenzene	[bmim][Br]	100	100	99
	[bmim][BF$_4$]	100	21	92
4-bromobenzaldehyde	[bmim][Br]	100	100	90
	[bmim][BF$_4$]	100	45	71
1-bromo-4-fluorobenzene	[bmim][Br]	100	100	90
	[bmim][BF$_4$]	100	<1	
4-bromoacetophenone	[bmim][Br]	110	79	88
	[bmim][BF$_4$]	110	<1	

[a] The reaction conditions were the same as those given in Table 1, except that 1.4 equiv of styrene was used. [b] Of the halide. [c] To *trans*-stilbene.

Results and Discussion

Heck Reaction in Ionic Liquids. The palladium-catalyzed Heck reaction is one of the most powerful tools for the coupling of olefins with aryl and vinyl halides.[5] The reaction is usually carried out in polar solvents such as DMF and MeCN. For the less reactive bromides and chlorides, phosphine ligands are normally required to stabilize catalytically active palladium species. Salt additives such as ammonium and phosphonium chlorides and bromides have been found to stabilize, probably via formation of zerovalent palladium halide species, the palladium catalysts and accelerate the olefination reaction with or without phosphines.[5,6] With a view toward stabilizing and immobilizing palladium compounds for efficient C−C bond forming reactions, we carried out the olefination of aryl halides in [bmim]-[Br] and [bmim][BF$_4$], which themselves are ammonium salts. A typical procedure consisted of heating a mixture of 5.0 mmol of an aryl halide, 1.4 equiv of an acrylate or styrene, 1.1 equiv of NaOAc, and 1 mol % Pd(OAc)$_2$ in 5.0 mL of an ionic liquid for 24 h; the resultant *trans*-cinnamate or *trans*-stilbene was solvent-extracted and characterized by GC and NMR and by comparison with authentic samples. With both ionic liquids, a homogeneous yellow solution was formed during the reaction. But in the case of [bmim][BF$_4$], palladium black slowly precipitated, indicating decomposition of active palladium species. The results are summarized in Tables 1 and 2. Our results corroborate those published recently; that is, the Heck reaction can be performed without additive phosphine ligands in ionic liquids.[2a,f,n] In addition, as is usually observed in molecular solvents, the Heck reaction proceeded more efficiently with aryl

iodides and activated aryl bromides in the ionic liquids. With the less reactive bromobenzene, conversion was low at the chosen conditions. Chlorobenzene was not activated even at 140 °C in either ionic liquid. However, the most interesting conclusion that can be drawn from Tables 1 and 2 is that the coupling reactions are markedly more efficient in [bmim][Br] than in [bmim]-[BF$_4$] under otherwise identical reaction conditions, as can be judged by the higher conversion of halides and better selectivity to the *trans* products with the former. Consider as an example the coupling of iodobenzene with styrene. A 100% conversion of the halide was reached with 99% selectivity to *trans*-stilbene when the reaction was conducted in [bmim][Br]. By way of contrast, a much lower conversion of 21% and lower selectivity of 92% were observed with [bmim][BF$_4$]. While the effects of ionic liquids on the activity of metal catalysts have been noted in several recent studies, no explanations with experimental support have been put forward.[2] We therefore decided to take a closer look at the reaction in an attempt to determine if the catalytically active palladium species in the Heck reaction might be different in the two ionic liquids.

Isolation of Carbene Complexes of Palladium. The C$_2$−H proton of the imidazolium ring is acidic and can be deprotonated to form carbenes by basic ligands of a metal compound.[7] A number of dialkylimidazol-2-ylidene complexes of transition metals have been prepared on the basis of this reaction in solvents such as THF, and of particular relevance, the palladium carbene complexes have been shown to be active catalysts for the Heck and related C−C bond forming reactions in molecular solvents.[7,8a,b] When Pd(OAc)$_2$ (45 mg) was heated in [bmim][Br] (5 mL) in the absence of an olefin

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Scheme 1

cis-anti-**2**   cis-syn-**2**   trans-anti-**2**   trans-syn-**2**
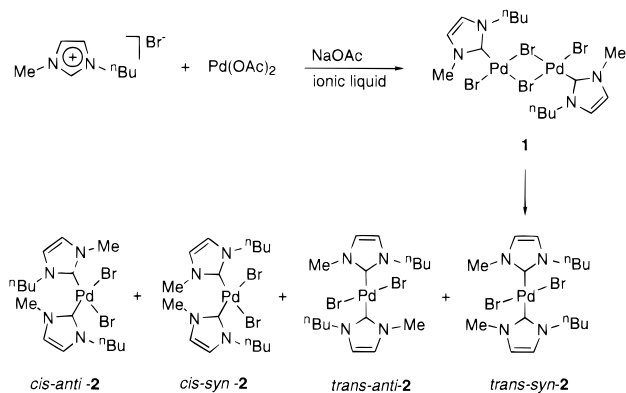
and aryl halide under conditions otherwise similar to those used for the Heck reaction, a color change from dark brown to red and then to yellow was observed in a few minutes. The NMR spectrum of the compounds extracted from the yellow solution suggests the formation of a mixture of palladium bmiy complexes, as indicated by the characteristic chemical shifts of the olefinic protons of the ylidene ligands at ca. δ 7 and those of the carbene carbons at ca. δ 160−170 in the ^{1}H and ^{13}C NMR spectrum, respectively.[7,8] In sharp contrast, heating Pd(OAc)$_2$ in [bmim][BF$_4$] under the same conditions yielded no such carbene species that were detectable in the ^{1}H NMR spectrum. Because *N*-heterocyclic carbene complexes of palladium, including those isolated from [bmim][Br], are catalytically active for C−C bond forming reactions (vide infra), and because the Pd−C bonds of the carbene complexes are known to be strong,[7] the easy formation of the carbene species in [bmim][Br] but not in [bmim][BF$_4$] explains at least partly the different activity and stability of palladium in the Heck reaction in the two ionic liquids.

The mixture formed by heating Pd(OAc)$_2$ in [bmim]-[Br] under conditions close to those used in the Heck reaction contains the dimeric and monomeric carbene complexes [PdBr(μ-Br)(bmiy)]$_2$ (**1**) and [PdBr$_2$(bmiy)$_2$] (**2**) (Scheme 1). Further reaction resulted in rapid transformation of **1** into **2**. Both **1** and **2** were also observed as the major species along with new, unidentified species under the true Heck reaction conditions, that is, in the presence of an acrylate and aryl halide, when the reaction of Pd(OAc)$_2$ with [bmim][Br] was stopped within a short period of reaction time. Longer reaction time led to the disappearance of **1** and only traces of **2** observable in the ^{1}H NMR spectrum, which is consistent with **2** being the immediate catalyst precursor. The unidentified species may result from the reaction of reduced **2** with the substrates. For the Heck reaction in molecular solvents using palladium carbene

complexes as catalysts, the likely active catalytic species is a zerovalent biscarbene complex generated by in situ reduction of divalent palladium biscarbene complexes such as **2**.[8f,9] The same active species may also be involved in the Heck reaction in [bmim][Br].

Complexes **1** and **2** could more easily be isolated in normal solvents such as THF. Thus, treating Pd(OAc)$_2$ with 2 equiv of [bmim][Br] in THF at 45 °C for 1−2 h resulted in a red solution, from which complex **1** was isolated as red crystals in 50% yield. Prolonged heating converted the complex **1** into **2**, accompanied with a color change from red to yellow. The latter could more quickly be obtained at a higher temperature. Evidently, the binuclear complex **1** is an intermediate species in the formation of **2** in both the ionic liquid and THF. Analogous intermediate binuclear species have recently been isolated in the preparation of related carbene complexes of palladium and mercury.[10,11] Binuclear carbene complexes of palladium can also be prepared by reacting Pd(OAc)$_2$ with imidazolium salts in the presence of NaI and KO^{t}Bu.[12]

The characterization of the complexes **1** and **2** has been accomplished by NMR, MS, and microanalysis. For complex **2**, ^{1}H NMR spectrum indicates the existence of four isomers, described as *trans-syn-*, *trans-anti-*, *cis-syn-*, and *cis-anti-***2** on the basis of the relative arrangement of the bmiy ligands and their *N*-substituents. The *trans* and *cis* isomers can easily be separated by chromatography as yellow and white crystalline solids,[13] but attempted separation of their rotation isomers has not been successful. Assignment of the NMR spectrum to an individual rotamer was thus tentative and was only based on its relative stability (vide infra). While the ^{1}H NMR spectra of **1** and *trans-***2** are similar and straightforward to interpret, that of *cis-***2** is more complicated. The geminal N−CH$_2$ protons of *cis-syn-* and *cis-anti-***2** are no longer identical; geminal and vicinal proton−proton couplings are clearly exhibited, indicating that rotation about the N−C bond is restricted. In the ^{13}C NMR spectrum, the two rotamers of *trans-***2** show only one singlet for the carbene carbons (δ 169), and the same is also observed with the two rotamers of its *cis* counterpart (δ 161). The carbene carbon of **1** comes into resonance at a significantly higher field (δ 145).

The interconversion between isomers of **2** was studied by NMR. The ^{1}H NMR spectrum revealed that the *trans* isomer was first formed from the dimeric **1** and subsequently isomerized into the *cis* isomer in the ionic liquid [bmim][Br]. The isomerization occurred in solution at both high and ambient temperatures. The reverse reaction appeared to be much slower, however. Thus, while 50% of *trans-***2** isomerized into *cis-***2** when the former was left in CDCl$_3$ for 2 days at ambient temper-

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Table 3. Heck Reaction Catalyzed by Isolated Carbene Complex 2[a]

substrate	ionic liquid	T/°C	conversion[b] (%)	selectivity[c] (%)
iodobenzene[d]	[bmim][Br]	90	94	99
4-bromobenzaldehyde[e]	[bmim][Br]	100	71	90
iodobenzene[f]	[bmim][Br]	100	93	98
4-bromobenzaldehyde[f]	[bmim][Br]	100	64	93
iodobenzene[d]	[bmim][BF$_4$]	90	35	56
4-bromobenzaldehyde[e]	[bmim][BF$_4$]	100	3	
iodobenzene[f]	[bmim][BF$_4$]	100	11	93
4-bromobenzaldehyde[f]	[bmim][BF$_4$]	100	<1	

[a] The reaction conditions were the same as those given in Tables 1 and 2, except that 1 mol % *trans*-**2** was used. [b] Of the halide. [c] To *trans* cinnamate or stilbene. [d] Reaction with ethyl acrylate. [e] Reaction with *n*-butyl acrylate. [f] Reaction with styrene.

ature, refluxing *cis*-**2** in CDCl$_3$ overnight led to only a trace of *trans*-**2**, with the rest remained unchanged. For *trans*-**2**, the ratio of its rotation isomers varied in solution, becoming in favor of one rotamer with time. For example, a 1:1 solution of *trans-anti-* and *trans-syn*-**2** turned into 5:1 after standing for 24 h in CDCl$_3$ at ambient temperature. On the contrary, a CHCl$_3$ solution of *cis*-**2** with an *anti*/*syn* ratio of 1:1.6 changed only slightly after refluxing for 12 h, reflecting the greater rotation barrier of the carbene ligands in the case of the *cis* isomers. By comparison with previous studies where the *trans-anti* and *cis-syn* rotamers of related carbene complexes were found to be the more stable isomers,[11,12] the thermodynamically favored rotamer of *trans*-**2** may tentatively be assigned to the *anti* isomer, while the dominant rotamer of *cis*-**2** may be assigned to the *syn* one. The existence of the *syn* and *anti* rotation isomers for **2** is due to the sterically demanding *N*-alkyl substituents. With less bulky substituents, rotation about the Pd–C bond is free.[7] Similar rotation and *cis*–*trans* isomerization have been observed with other asymmetrically substituted carbene complexes of palladium.[12,14]

Heck Reaction with Isolated Carbene Complexes. As closely related 1,3-dimethylimidazol-2-ylidene complexes of palladium have been demonstrated to be active catalysts for the Heck reaction,[7,8a] it is not surprising that complex **2** catalyzes the olefination reactions of aryl halides (Table 3). Thus, under conditions similar to those used for Pd(OAc)$_2$, the olefination of iodobenzene and 4-bromobenzaldehyde by acrylates in the presence of *trans*-**2** in [bmim][Br] completed with 94 and 71% conversions, respectively; the selectivity to the expected *trans* product was 99 and 90%. The olefination by styrene with *trans*-**2** proceeded similarly well in the same ionic liquid. Clearly, the carbene complex of palladium formed between Pd(OAc)$_2$ and the solvent [bmim][Br] is catalytically active for the C–C bond formation reaction in the ionic liquid. The lower yields observed with **2** compared with using Pd(OAc)$_2$ in [bmim][Br] is probably due to the presence of other active palladium species in the ionic liquid.

Surprisingly, however, the complex **2** showed very low activity in the Heck reaction in [bmim][BF$_4$], as can be seen in Table 3. As it is known that related dihalobiscarbene complexes of palladium can be converted into tetrakiscarbene species in molecular solvents in the presence of an imidazolium salt and NaOAc, which functions as a base and generates in situ the ylidene ligands from the imidazolium ion,[15] the possible trans-

formation of *trans*-**2** in [bmim][BF$_4$] was investigated. The yellowish **2**, when heated at 100 °C in the ionic liquid in the presence of NaOAc, turned rapidly into a white solid, reminiscent of the formation of tetrakiscarbenes reported before.[15] The ^{1}H NMR spectrum showed the solid to be a mixture containing palladium carbene species, but attempted separation met with failure. As expected, the solid displayed very low catalytic activity in the Heck reaction in [bmim][BF$_4$]. Evidently, the lower activity of **2** in [bmim][BF$_4$] results from its transformation into less active species by the solvent. Similar transformation in [bmim][Br] of the biscarbene **2** into an inactive tetrakiscarbene is less likely; the complex is expected to be stabilized by the bromide ions. One remaining puzzle is the observed activity of Pd-(OAc)$_2$ in [bmim][BF$_4$]. Clearly, it is not due to some carbene species of palladium. One possible explanation may be that the activity stems from the decomposed palladium, which could form colloidal palladium particles active for the Heck reaction.[16]

Summary

Ionic liquids have attracted a great deal of attention as alternative solvents for catalysis in the past few years. A number of reactions catalyzed by transition metal complexes have successfully been demonstrated in the imidazolium ionic liquids.[1,2] While it is true that in most cases the imidazolium cation is inert and not directly involved in a catalytic cycle, our study shows for the first time that the imidazolium ion can react with a catalyst precursor to form *N*-heterocylic carbene complexes via deprotonation in the imidazolium-based ionic liquids under catalytic conditions and the carbene complexes so generated are active for C–C bond coupling reactions. The higher activity and stability of palladium in the Heck reaction in [bmim][Br] than in [bmim][BF$_4$] can be explained at least partly in terms of the easy formation of stable palladium carbene complexes in the former. Perhaps more intriguingly, the activity of the carbene complexes toward Heck coupling varies with the choice of an ionic liquid; they are active in [bmim][Br] but much less so in the analogous [bmim]-[BF$_4$] due to reaction with the latter. The lesson to be learned is that imidazolium ionic liquids not only function as solvating media but can also act as reactive

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reagents, and so a catalyst in an ionic liquid may completely differ from its established form in molecular solvents.

Experimental Section

All reactions were carried out in oven-dried glassware under argon. Solvents were degassed and dried before use. The ionic liquids were prepared according to published procedures and vacuum-dried and stored under argon.[17] Reagents were used as received. NMR spectra were recorded on a Gemini 300 spectrometer at 300.10 (^{1}H) and 75.46 MHz (^{13}C) in ppm with reference to TMS internal standard in CDCl$_3$. Abbreviations for NMR spectral multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Elemental analyses were performed by the Microanalysis Laboratory, Department of Chemistry, the University of Liverpool. Mass spectra were recorded on a VG7070E mass spectrometer.

General Procedures for Heck Reaction in Ionic Liquids. In a 50 mL two-necked flask fitted with a septum and reflux condenser were placed an ionic liquid (5 mL), aryl halide (5.0 mmol), anhydrous sodium acetate (451 mg, 5.5 mmol), and palladium acetate (1 mol % of the aryl halide). After repeated degassing under oil pump vacuum and flushing with argon, an acrylate or styrene (7.0 mmol) was injected through the septum, and the mixture heated to the reaction temperature. After 24 h reaction time, the mixture was cooled to room temperature and diluted with water. The product was then extracted with ethyl acetate. The combined organics were washed with water and brine, dried over MgSO$_4$, and analyzed by NMR and GC (internal standard: octadecane).

[PdBr(μ-Br)(bmiy)]$_2$ (1). Pd(OAc)$_2$ (50 mg, 0.22 mmol) and [bmim][Br] (102 mg, 0.47 mmol) were dissolved in THF (15 mL) in a two-necked flask. After heating at 45 °C for 2 h and cooling to room temperature, the mixture was filtered through a pad of silica gel. Crystallization from hexane/CHCl$_3$ afforded **1** as red crystals (45 mg, 50%). ^{1}H NMR: 6.94 (m, 4H, NCH), 4.53 (br, 4H, NCH_2), 4.15 (s, 6H, CH_3), 2.06 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.06 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR: 144.6 (N$_2$CH), 123.6 (NCH), 122.2 (NCH), 51.1 (NCH_3), 38.6 (NCH_2), 32.3 (CH_2), 19.9 (CH_2), 13.7 (CH_3). MS (FAB): m/z 729 ([M$^+$ − Br], 2.5). Anal. Calcd for C$_{16}$H$_{28}$N$_4$Br$_4$Pd$_2$: C, 23.76; H, 3.49; N, 6.93. Found: C, 23.79; H, 3.49; N, 6.75.

[PdBr$_2$(bmiy)$_2$] (2). Pd(OAc)$_2$ (201 mg, 0.90 mmol) and [bmim][[Br] (413 mg, 1.88 mmol) were dissolved in 30 mL of THF in a two-necked flask. After refluxing for 2 h under argon and cooling to room temperature, the mixture was filtered through a pad of silica gel. The solvent was removed under vacuo to give a yellow solid. The product was separated by column chromatography (silica gel, EtOAc/hexane, 1:1) as white crystals (*cis*-**2**, 90 mg, 19%) and yellow crystalline solids (*trans*-**2**, 265 mg, 55%).

^{1}H NMR (*trans-anti*-**2**): 6.84 (m, 4H, NCH), 4.46 (t, $^3J_{HH}$ = 7.5 Hz, 4H, NCH_2), 4.09 (s, 6H, NCH_3), 2.06 (m, 4H, CH_2), 1.48

(m, 4H, CH_2), 1.02 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3,). ^{13}C{^{1}H} NMR: 169.3 (N$_2$CH), 122.0 (NCH), 120.8 (NCH), 50.7 (NCH_3), 37.9 (NCH_2), 32.8 (CH_2), 20.1 (CH_2), 13.7 (CH_3). The ^{1}H NMR spectrum of the *trans-syn* isomer overlaps that of the *trans-anti* isomer except at 4.44 (t, $^3J_{HH}$ = 7.2 Hz, 4H, NCH_2), 4.06 (s, 6H, NCH_3), and 1.01 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3). No difference was observed in the ^{13}C NMR spectrum for the two rotamers. The *trans-anti*/*trans-syn* ratio was 1:1, but it varied with time in solution with the *trans-anti* rotamer gaining intensity as shown by the ^{1}H NMR spectrum. The *anti* and *syn* assignment was only tentative for both *trans*- and *cis*-**2**. Attempted separation of the rotamers was not successful. MS (FAB) (trans-**2**): m/z 463 ([M$^+$ − Br], 2.5). Anal. Calcd for C$_{16}$H$_{28}$N$_4$Br$_2$Pd: C, 35.41; H, 5.20; N, 10.32. Found: C, 35.28; H, 5.19; N, 10.28.

^{1}H NMR (*cis-syn*-**2**): 7.00, 6.90 (AB q, $^3J_{HH}$ = 1.8 Hz, 4H, NCH), 4.16 (s, 6H, NCH_3), 4.01 (m, 2H, NCHH), 3.96 (m, 2H, NCHH), 1.76 (m, 2H, CHH), 1.42 (m, 2H, CHH), 1.33 (m, 4H, CH_2), 0.94 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR: 161.4 (N$_2$CH), 123.2 (NCH), 50.7 (NCH_3), 39.5 (NCH_2), 32.5 (CH_2), 20.0 (CH_2), 13.7 (CH_3). ^{1}H NMR (*cis-anti*-**2**): 6.96, 6.94 (AB q, $^3J_{HH}$ = 1.8 Hz, 4H, NCH), 4.60 (ddd, $^2J_{HH}$ = −13.2 Hz, $^3J_{HH}$ = 10.2, 5.4 Hz, 2H, NCHH), 4.15 (m, 2H, NCHH), 1.96 (m, 2H, CHH), 1.55 (m, 2H, CHH), 1.42 (m, 4H, CH_2), 0.98 (t, $^3J_{HH}$ = 7.3 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR: 161.4 (N$_2$CH), 121.1 (NCH), 120.8 (NCH), 51.1 (NCH_3), 38.8 (NCH_2), 32.3 (CH_2), 19.9 (CH_2), 13.7 (CH_3). The *cis-anti*/*cis-syn* ratio was 1:1.2 in solution. Anal. Calcd for C$_{16}$H$_{28}$N$_4$Br$_2$Pd: C, 35.41; H, 5.20; N, 10.32. Found: C, 35.83; H, 5.23; N, 10.22.

Isolation of 2 in Ionic Liquid. A mixture of Pd(OAc)$_2$ (45 mg, 0.20 mmol), NaOAc (1.641 g, 20.0 mmol), and [bmim][Br] (5 mL) was stirred at 100 °C for 4 h. After cooling to ambient temperature, water (60 mL) and CH$_2$Cl$_2$ (30 mL) were added. The organic layer was separated, washed with water (3 × 50 mL) and brine (30 mL), dried with MgSO$_4$, and evaporated under reduced pressure to give **2** as a mixture of *cis* and *trans* isomers (68 mg, 63%, *cis*/*trans* = 6:1, *cis-anti*/*cis-syn* = 1:1.7, *trans-anti*/*trans-syn* = 1.5:1). When the above reaction was stopped in 3 min reaction time and quenched immediately with water, the only carbene complexes observed in the ^{1}H NMR spectrum were **1**, *trans-anti*-**2**, and *trans-syn*-**2** and in a 50:1: 50 ratio. The same complexes were also observed, when the reaction was stopped in a few minutes, in the presence of iodobenzene and ethyl acrylate under the Heck reaction conditions, along with new, unidentified species.

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