Bis-chelate tetracarbene palladium(II) complex as an efficient and recyclable catalyst precursor for Heck reaction

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Abstract

A homoleptic Pd(II) complex with two chelating di-*N*-heterocyclic carbene (NHC) ligands has been synthesized and its square planar molecular geometry has been determined by X-ray diffraction analysis. The complex proved to be an efficient catalyst having exceedingly high turnover number and good reusability in Heck reaction.
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Keywords: Chelate; *N*-Heterocyclic carbene; Palladium; Heck reaction

1. Introduction

N-Heterocyclic carbenes (NHCs) have proven to be a versatile class of ligands in the present organometallic chemistry to prepare novel metal complexes for a variety of organic transformations [1,2]. Although the metal–NHCs have emerged as a new class of compounds from the pioneering work of Öfele and Wanzlick [3,4], they have gained enormous reputation only after the successful use of metal–NHCs in C–C [5–8], C–N [9,10] bond formations and other catalytic reactions [11–13]. This is driven by the strong σ-donating power of NHCs to the metal centers, which can prevent the catalyst degradation, orthometallation and allow us to carryout the reactions at higher temperature unlike most phosphines. Although palladium–phosphine complexes displayed extreme catalytic performance, the practical difficulties connected with this system such as air and moisture sensitivity, and the possible catalytic degradation have focused attention towards the use of stable metal–NHC catalysts to avoid such difficulties. Moreover NHC ligand precursors are easy to access, and their chemical and topological versatility allows the preparation of a wide variety of complexes whose chemical properties can be easily modulated [14–23]. Although a wide range of monodentate Pd(NHC) catalysts were explored in the literature, a possible reductive elimination with alkyl groups was also

noticed in some cases [24]. In this regard, using chelating NHC as ligand to improve the thermal stability of Pd–NHC complexes has been designed. Heteroleptic and homoleptic Pd(II)–NHC complexes consisting of only one chelating NHC unit has been explored [14,25–28], but the efficiency of those catalysts in Heck reaction is still not satisfactory. Recently, a simple chelating dicarbene metal complex developed by Herrmann et al. [5] was carefully investigated by the Biffis's group [29]. They suggested that the catalytic activity of the dicarbene system might be probably inhibited by the formation of a bis-chelate tetracarbene Pd derivative during the course of reaction, giving a poor yield even after 24 h for activated aryl bromide.

On the contrary to the hypothetical assumption, we herein present the first catalytic examination of a homoleptic bis-chelate tetracarbene complex, bis-(1,1′-di-*n*-butyl-3,3′-methylenediimidazolin-2,2′-diylidene) palladium(II) tetrafluoroborate ([($^{Bu}CC^{meth}$)$_2$Pd][BF$_4$]$_2$), which proves to be an excellent precatalyst for Heck reaction with potential recyclability.

2. Results and discussion

2.1. Preparation and structure of [($^{Bu}CC^{meth}$)$_2$Pd][BF$_4$]$_2$ complex

Similar homoleptic Pd(II)–NHCs with X anions (X = I$^-$, BF$_4$$^-$) were prepared previously by the direct reaction of an

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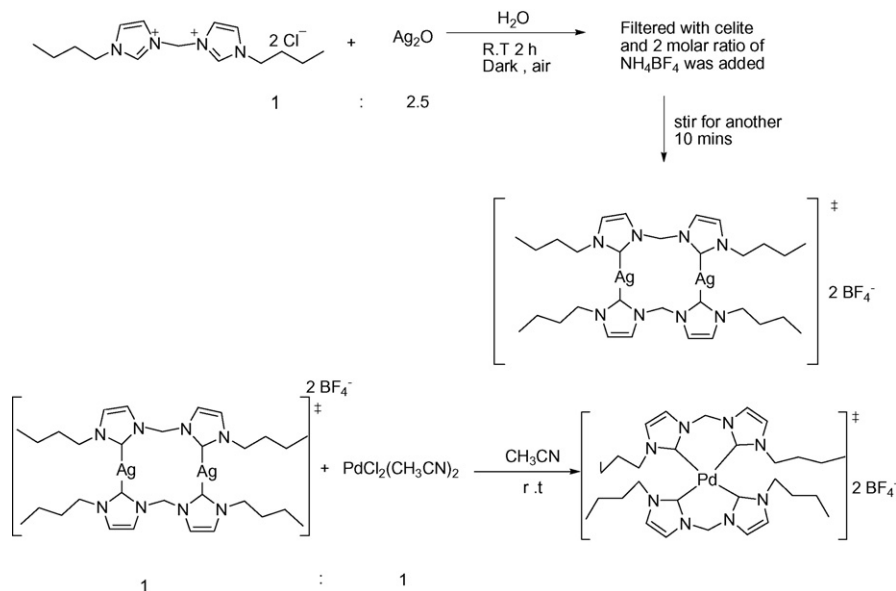
Scheme 1.

alkylene linked di-imidazolium salt with palladium salts [30,31] in the presence of an external base. In those cases relatively low product yields were noted and no attempt on the catalytic reaction was reported. Ag(I)–NHC [32,33] route was employed to synthesize the homoleptic bis-chelate tetracarbene Pd(II) complex to obtain a better yield (Scheme 1).

The bidentate NHC precursor 1,1′-di-*n*-butyl-3,3′-methylenediimidazolium dichloride ([(^{Bu}CC^{meth}-H)_2]Cl_2) reacted readily with Ag_2O in water to give a Ag(I)–NHC complex, which was isolated as the BF_4^- salt ([Ag_2(^{Bu}CC^{meth})_2][BF_4]_2), to avoid the interference of AgX_2^-/X^- ions. The formation of [Ag_2(^{Bu}CC^{meth})_2][BF_4]_2 complex was identified by the disappearance of the imidazolium C_2–H proton in the ^{1}H NMR spectrum. Further reaction of the g(I)–NHC complex with PdCl_2(CH_3CN)_2 in CH_3CN progressed smoothly to produce the [(^{Bu}CC^{meth})_2Pd] [BF_4]_2 in high yield. This Pd(II) complex is air and moisture stable for months in the solid state or in the polar solvent like CH_3CN or DMSO. The cyclic voltammogram of the Pd(II) complex in CH_3CN gave an irreversible peak at +1.20 V and a quasireversible couple with $E_{1/2} = -0.83$ V versus Ag/AgCl (scan rate 50 mV/sec). The latter corresponds to Pd(II)/Pd(0) redox couple indicating the high stability of the Pd(II) and its corresponding Pd(0) complexes.

Single crystals of (^{Bu}CC^{meth})_2Pd(II)(BF_4)_2 suitable for X-ray diffraction study was obtained from diffusion of (CH_3CH_2)_2O into CH_3CN solution of the complex. The molecular structure is depicted in Fig. 1. The complex crystallized in the triclinic crystal system with the $P\bar{1}$ space group. The structural analysis showed that it was a mononuclear Pd(II) complex, chelated by two ^{Bu}CC^{meth} ligands. Each chelated unit constructed a six membered ring upon coordination and the Pd(II) center adopted a square planar coordination geometry with C–Pd–C bite angle 83.16°. The twist angle (41.04(1)° to 45.88(2)°) of the heterocyclic rings relative to the coordination plane defined by

four coordinated carbene carbons indicate that the conformation adopted primarily resulted from minimization of Bu–Bu nonbonding interactions, thereby leading to the chemically nonequivalent methylene protons as observed in the NMR spectrum. The average Pd–C_{carbene} bond distance of 2.024 Å was slightly shorter than that of reported homoleptic Pd(II)–NHC [31]. The short C_{carbene}–N bonds imply a clear consequence of the contributions from σ-donation of the NHC to the metal centre and π-stabilization of the carbene onto the adjacent nitrogen atoms.

2.2. Heck reaction

The Pd(II) complex [(^{Bu}CC^{meth})_2Pd][BF_4]_2 has been tested for its catalytic activity in the Heck reaction with various types of bases. The standard coupling reaction of aryl bromide and styrene was carried out in 2.5 mL *N,N*-dimethylformamide

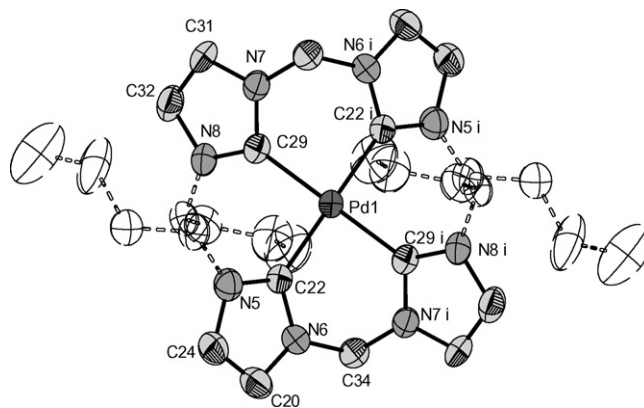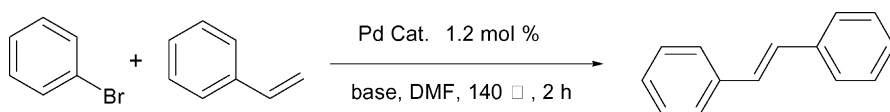
Fig. 1. Cationic part of palladium complex with ellipsoids drawn at 30% probability. Selected bond lengths (Å) and angles (°): Pd1-C22, 2.024(6); Pd1-C29, 2.036(5); Pd1-C22i, 2.024(6); Pd1-C29i, 2.036(5); C22i-Pd1-C22, 180.0; C29i-Pd1-C29, 180.0.

Table 1
Effect of the base on the product yield in a definitive time in Heck coupling reactions of aryl bromide with styrene[a]

Entry	Base	Yield[a,b] (%)	Entry	Base	Yield[a,b] (%)
1	K_3PO_4	80	7	KOH	50
2	Cs_2CO_3	Trace	8	NaOAc	100
3	$Ba(OH)_2$	Trace	9[c]	NaOAc	Trace
4	Na_2CO_3	10	10[d]	NaOAc	Trace
5	NEt_3	10	11[e]	NaOAc	Trace
6	K_2CO_3	Trace	12[f]	NaOAc	84

[a] Reaction condition: 1 mmol aryl bromide, 1.5 mmol styrene, 2 mmol base, 1.2 mol% Pd cat., 2.5 mL DMF, 140 °C and 2 h.
[b] Isolated yield including trace amount of gem-isomer, which was detected by ^{1}H NMR.
[c] Reaction temperature, 90 °C.
[d] Reaction temperature, 90 °C; reaction time, 24 h.
[e] Reaction solvent, 1 mL H_2O; reaction time, 24 h.
[f] Reaction solvent, DMF/H_2O (1.5 mL/1 mL); reaction time, 24 h; temperature, 90 °C.

(DMF) with a 1.2 mol% catalyst loading for 2 h at 140 °C. The results are summarized in Table 1.

Investigation of the effect of various bases on the catalytic reaction reveals that sodium acetate (NaOAc) is the best of choice (Table 1, entry 8). Mechanistically carboxylated anions were thought to function as an optimal base and also as a reducing agent [34,35] in Heck reaction. It was found that the Pd(II) catalyst was activated in situ by NaOAc in DMF at high temperature (140 °C) to achieve a good yield, whereas a moderate yield of coupling product was obtained at low temperature (90 °C) at longer time (Table 1, entries 9 and10). Weak inorganic bases with carbonate anion (Table 1, entries 2, 4 and 6) or organic base (Table 1, entry 5) showed low activity while K_3PO_4 and strong base KOH (Table 1, entries 1 and 7) worked smoothly in the reaction, giving a Pd black precipitation. It has also been reported that H_2O molecule sometimes is required to activate the Pd(II) catalyst or to improve the solubility of inorganic bases [7]. In our case, carrying out the reaction in DMF/H_2O (1.5 mL/1 mL) mixed solvent at low temperature (90 °C) gave a positive effect on the product yield (Table 1, entry 12) in comparison with that in pure DMF (Table 1, entry 10), while in pure aqueous solvent the activity of the catalyst was low even at high temperature (Table 1, entry 11).

As reported earlier, the activity of most Pd–NHC catalytic system can be enhanced by the addition of tetrabutylammonium bromide (TBAB) as a cocatalyst [36]. The effect of TBAB toward our catalytic system is evaluated under the same standard reaction conditions using NaOAc as the base. The kinetic results (Fig. 2) show that the system with or without addition of TBAB quantitatively couples aryl bromide and styrene at 140 °C in 2 h. Although the role of TBAB in the C–C coupling reaction is not completely understood, upon the addition of TBAB a shorter induction period for activation of Pd(II) complex is observed for our system, suggesting more efficient reduction of Pd(II) complex to a catalytically active Pd(0) under Jeffery conditions [37]. Similar phenomenon was also observed in other mono-chelate dicarbene Pd(II) complex system [38].

It has been reported that low concentrations of Pd catalyst are required in some cases because the Pd cluster formation at high concentrations inhibits the catalytic reaction [35,36,39,40]. In our catalytic system, reducing the volume of solvent, DMF, from 2.5 mL to 0.5 mL did not affect the product yield significantly in 2 h. The reaction profiles in these two different volumes of solvent conditions show that the induction period in 0.5 mL of DMF was shorter than that in 2.5 mL of DMF (Fig. 3). Moreover, no Pd black precipitation was observed during the reaction in 0.5 mL DMF. If the solvent volume was less than 0.5 mL, we found that the product yield became gradually lower. Carrying out the reaction with 0.1 mL DMF or without DMF under the same condition gave only 42.6% or trace of the product, respectively.

The recyclability of the Pd(II) catalyst for Heck reaction was examined following a strategy of a repetitive process described in the literature [41]. Originally, the reaction was carried out with 1 mmol aryl bromide, 1.5 mmol styrene, 2 mmol NaOAc, 1 mmol TBAB and 1.2 mol% Pd catalyst in 0.5 mL DMF at 140 °C for 2 h. On completion of the reaction, the reaction mixture was cooled, the same amount of aryl bromide, styrene, and
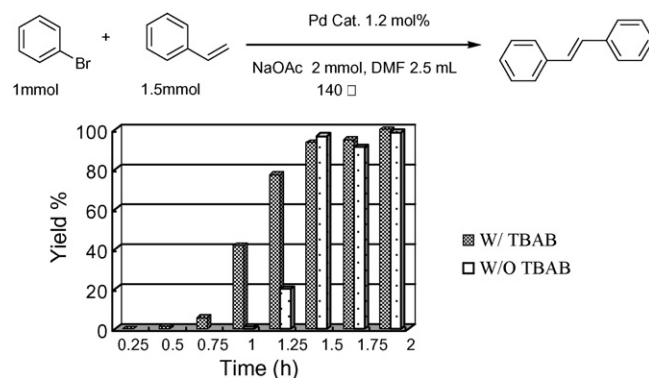

Fig. 2. Time–yield comparison of system with addition of 1 eq. TBAB and system without TBAB in Heck reaction of aryl bormide and styrene.
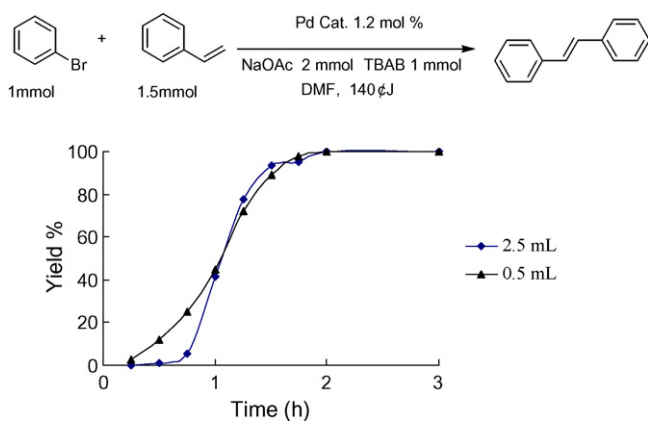
Fig. 3. Reaction profiles for high (▲) and low (♦) [Pd] concentration in Heck reaction.
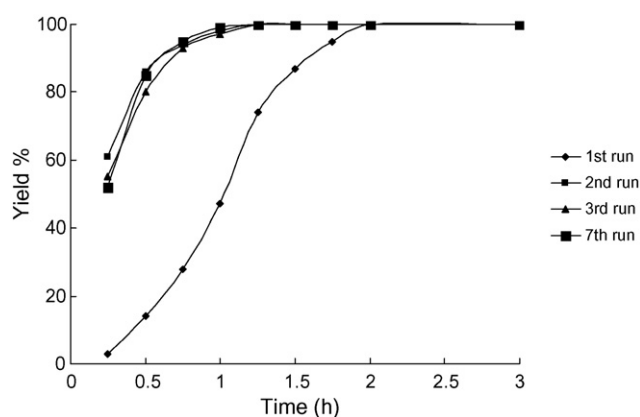

Fig. 4. Reaction profiles of repetitive runs in Heck reaction. First run: 1 mmol aryl bromide, 1.5 mmol styrene, 2 mmol NaOAc, 1.2 mol% Pd cat. and 1 mmol TBAB in 0.5 mL DMF at 140 °C for 2 h. For each of the repetitive runs the same amount of aryl bromide, styrene and NaOAc were added as in original reaction. Isolated yields including trace amount of gem olefin were detected by ^{1}H NMR.

NaOAc were added as in the original reaction, and the reaction was continued for the next run. In this way, six repetitive runs were carried out, each time without addition of more catalyst, solvent and TBAB and the product yield in this gradual diluted system remained constant (~100%) in 2 h of reaction. Furthermore, reaction profiles for recycle process show (Fig. 4) that the induction period of recycling runs was dramatically shorter than that of first run. We also found that the completion time for the repetitive runs was reduced (Fig. 4). These promising results provide evidence for the high catalytic activity and thermal stability of this bis-chelate tetracarbene Pd(II) complex and shows its potential use for recycling Heck reaction. Here, we propose that the extreme basic property on the Pd center, due to the formation of active palladium metal(0) species could be stabilized by chelating effect.

To determine the turnover number (TON) and to investigate the tolerance of the substituted functionality on aryl halide, sim-

ilar optimal reaction conditions were employed (Table 2). Both activated and deactivated aryl bromides underwent the C–C coupling reaction with good yields (Table 2, entries 1–5). In order to realize the differences of the reactions for activated, deactivated and unactivated aryl bromides, we have compared the reaction profiles for 4′-bromoacetophenone, 4-bromoanisole and bromobenzene under the same reaction conditions (Fig. 5). The profiles show that the induction period and completion time were shorter for activated aryl bromide than the other two. Furthermore, this catalyst gave a moderate yield in longer time (24 h) with activated aryl chloride (Table 2, entry 7), while with non-activated aryl chloride only a lower yield was achieved (Table 2, entry 6) in the same time. Extending the reaction time up to 36 h did not give better results for aryl chlorides. The low yields obtained with aryl chloride or substituted aryl chlorides are due

Table 2
Product yield of activated and deactivated aryl halides, Hg(0) poisoning, and low catalyst loading in a definitive time in Heck coupling reactions
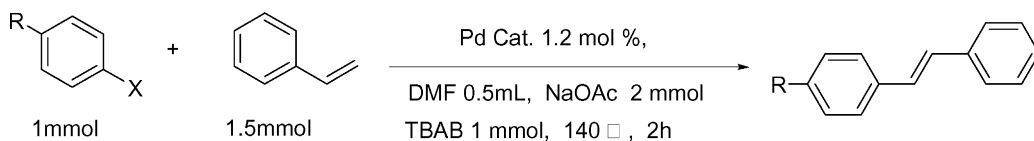
Entry	R	X	Yield[a] (%)	TON
1	4-CH$_3$(O)C	Br	95	79
2	4-CN	Br	97	81
3	4-NO$_2$	Br	94	78
4	4-CH$_3$O	Br	98	82
5	4-CH$_3$	Br	95	79
6	H	Cl	45[b]	38
7	4-CH$_3$(O)C	Cl	85[b]	71
8	4-CH$_3$	Cl	<5[b]	–
9[c]	H	Br	<3	
10[d]	H	Br	81	6.75×10^6
11[e]	H	I	97	8.08×10^8

[a] Isolated yield.
[b] Reaction time, 24 h.
[c] 360 mg Hg(0) was added.
[d] Pd catalyst loading, 1.2×10^{-7} mmol; reaction time, 52 h.
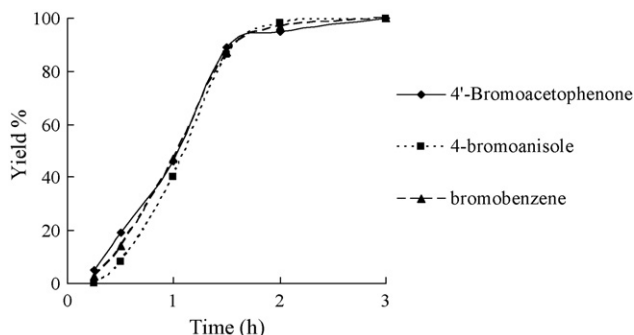[e] Pd catalyst loading, 1.2×10^{-9} mmol; reaction time, 36 h.

Fig. 5. Reaction profiles for Heck reaction of substituted aryl bromides with styrene.

to the stronger C_{sp2}–Cl bonds of aryl chlorides than those of the heavier congeners. Noticeably high activity of our catalyst for non-activated aryl bromide is demonstrated by the extremely high TON of 6.75×10^6 obtained with 1.2×10^{-5} mol% Pd catalyst (Table 2, entry 10), and the result is even better for aryl iodide (Table 2, entry 11) [5–9,27,37,42–47]. In this connection, several review articles [40,48,49] reported the good activity and high TON for the Heck coupling of aryl halides with styrene in ligand free Pd salts like Pd(OAc)$_2$, PdCl$_2$ and Pd(OH)$_2$ under different reaction conditions. Köhler et al. [49], have mentioned that the activity of catalyst depends on several conditions like substrate, nature of the catalyst and reaction conditions (temperature, solvent, base, additives, atmosphere, etc.). Using ligand free Pd salts the authors have also achieved almost similar results like our NHC-catalyst system. The main advantages of our NHC-catalyst under these conditions are its high recyclability and constant reproductivity compared to ligand free catalyst systems [40,48–50].

It has been known that Hg(0) can poison the catalytic property of a metal(0) species by amalgamating the metal or absorbing on the metal surface in a heterogeneous catalysis [51,52]. In our study we also found that the addition of excess Hg(0) (Hg:Pd = 150:1) indeed totally deactivated the coupling reaction (Table 2, entry 9). This result might suggest that the actual catalytic species is Pd(0) species as reported [53]. Furthermore, the cyclic voltammogram of the Pd(II) complex in acetonitrile (CH$_3$CN) gave a quasireversible Pd(II)/Pd(0) redox couple, indicating the high stability of the Pd(0) and also supports the formation of Pd(0) as a possible intermediate in catalytic cycle. We assume that the bis-chelate tetracarbene Pd(II) complex might be reduced to a stable Pd(0)–NHC complex which in a dangling mode generate an active species for the catalytic cycle. Further investigation of the true activation mechanism for this bis-chelate tetracarbene Pd(II) complex and its practical applications are undergoing.

3. Conclusion

A homoleptic Pd(II) complex with two chelating tetracarbene ligands has been synthesized in high yield. The complex shows excellent air and thermal stability at elevated temperature and is an excellent catalyst for Heck reaction. The complex also exibits full recyclability and constant reproductivity with markedly high TONs in the Heck coupling of aryl bromide and aryl iodide with styrene.

4. Experimental

4.1. General

All the reactions were carried out in air. The solvents and reagents were purchased from general sources and were used without further purification. NMR spectra were recorded on a Bruker DX-300 NMR spectrometer (^{1}H, 299.96 MHz; ^{13}C, 75.43 MHz). Mass Spectra were measured on a Micromass Platform II spectrometer. Elemental analyses were carried out using a PerkinElmer 2400, 2400II elemental analyzer. Cyclic voltammetry was carried out using a BAS 100B Electrochemical Analyzer. The measurements were performed at room temperature in deoxygenated acetonitrile (CH$_3$CN) solution containing 0.1 M TBAB and 10^{-3}–10^{-4} M Pd(II) complex. The working, counter and reference electrodes used were a glassy carbon, a platinum coil and a Ag/AgCl electrode, respectively.

4.2. Syntheses of 1,1′-di-n-butyl-3,3′-methylene-diimidazolium dichloride [($^{Bu}CC^{meth}$-H)$_2$Cl$_2$]

n-Butylimidazole (5.00 g, 40.25 mmol) was added to excess of CH$_2$Cl$_2$ and the mixture was stirred at reflux temperature for 1 week. The solution was cooled and added into ether (20 mL), followed by filtration, to give a white powder. Yield: 74% (7.80 g, 29.78 mmol). ^{1}H NMR (D$_2$O): δ 7.62 (d, 2H, J_{H-H} = 2.1 Hz, imidazole H), 7.51 (d, 2H, J_{H-H} = 2.1 Hz, imidazole H), 6.54 (s, 2H, NCH$_2$N), 4.12 (t, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.73 (m, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.17 (m, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 0.77 (t, 6H, NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 137.31 (NCHN), 123.03, 122.83 (imidazole C), 56.81 (NCH$_2$N), 49.91 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.24 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.00 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.01 (NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. Anal. Calcd. for C$_{15}$H$_{26}$Cl$_2$N$_4$. 0.5 H$_2$O: C 52.63, N 16.37, H 7.95. Found: C 52.45, N 16.25, H 7.83. Mass (FAB): m/z 261(M$^+$ − 1).

4.3. Preparation of the complexes

4.3.1. [Ag$_2$($^{Bu}CC^{meth}$)$_2$][BF$_4$]$_2$

Ag$_2$O (0.58 g, 2.50 mmol) was added into an aqueous solution containing [($^{Bu}CC^{meth}$-H)$_2$]Cl$_2$ (0.33 g, 1.00 mmol) and the suspension was stirred at room temperature for 2 h in dark and filtered through Celite. NH$_4$BF$_4$ (0.21 g, 2.00 mmol) was added into the filtrate and stirred for 10 min, followed by filtration with a filter paper, air stable silver complex was isolated as a brown powder. Yield: 92% (0.42 g, 0.46 mmol). ^{1}H NMR (DMSO-d^6): δ 7.85 (s, 4H, imidazole H), 7.62 (s, 4H, imidazole H), 6.90 (br, s, 2H, N–CH$_2$–N), 6.36 (br, s, 2H, NCH$_2$N), 4.14 (t, J_{H-H} = 7.4 Hz, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.71 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.21 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 0.83 (t, J_{H-H} = 7.5 Hz, 12H, NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. ^{13}C NMR (DMSO-d^6): δ 123.57, 122.39 (imidazole C), 63.88 (NCH$_2$N), 51.71 (NCH$_2$CH$_2$CH$_2$CH$_3$), 33.55 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.64

(NCH$_2$CH$_2$CH$_2$CH$_3$), 13.91 (NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. Anal. Calcd. for Ag$_2$C$_{30}$H$_{48}$N$_8$B$_2$F$_8$. H$_2$O: C 38.84, N 12.09, H 5.44. Found: C 38.94, N 12.24, H 5.18. Mass (FAB): *m/z* 735 ($M^{2+} - 1$).

4.3.2. [($^{Bu}CC^{meth}$)$_2$Pd] [BF$_4$]$_2$

PdCl$_2$(CH$_3$CN)$_2$ (0.26 g, 1.00 mmol) was added into the acetonitrile solution containing [Ag$_2$($^{Bu}CC^{meth}$)$_2$][BF$_4$]$_2$ (0.91 g, 1.00 mmol) in dark condition and the mixture was allowed to stir for 24 h, followed by filtration giving a pale yellow clear filtrate. The solvent was removed in vacuo to yield a pale yellow powder. Yield: 86% (0.69 g, 0.86 mmol). ^{1}H NMR (acetone-d^6): δ 7.83 (s, 4H, imidazole H), 7.51 (s, 4H, imidazole H), 6.77 (d, $J_{H-H} = 13.6$ Hz, 2H, NCH$_2$N), 6.63 (d, $J_{H-H} = 13.6$ Hz, 2H, NCH$_2$N), 4.02 (m, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 3.55 (m, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.73 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.13 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 0.79 (t, $J_{H-H} = 7.5$ Hz, 12H, NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. ^{13}C NMR (acetone-d^6): δ 169.5 (carbene C), 123.03, 122.14 (imidazole C), 63.61 (NCH$_2$N), 50.46 (NCH$_2$CH$_2$CH$_2$CH$_3$), 33.09 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.50 (NCH$_2$CH$_2$CH$_2$CH$_3$), 12.94 (NCH$_2$CH$_2$CH$_2$CH$_3$) ppm. Anal. Calcd. for C$_{30}$H$_{48}$B$_2$F$_8$N$_8$Pd: C 45.00, N 13.99, H 6.04. Found: C 44.89, N 13.78, H 6.10. Mass (FAB): *m/z* 713 (PdL$_2$BF$_4^+$).

4.4. X-ray data collection and structure refinement

Single crystals of [($^{Bu}CC^{meth}$)$_2$Pd] [BF$_4$]$_2$ suitable for X-ray diffraction study were obtained by the diffusion of (CH$_3$CH$_2$)$_2$O into the CH$_3$CN solution of the complex. A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Bruker Smart APEXII CCD XRD. A crystal of the complex (0.2 mm × 0.2 mm × 0.1 mm) was selected for the structural analysis. The intensity data were collected at 273 K. All data were collected with ω scan technique using graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). All Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included at calculated positions. The structure was solved by direct methods using the SHELXS-97 computer program and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [54]. Complete structure data have been deposited. Salient crystal data are: C$_{30}$H$_{48}$B$_2$F$_8$N$_8$Pd: $M_f = 800.78$, triclinic, space group $P\bar{1}$, $a = 11.415(7)$ Å, $b = 11.525(7)$ Å, $c = 15.586(10)$ Å, $\alpha = 90.355(10)°$, $\beta = 92.798(10)°$, $\gamma = 112.270(10)°$, $V = 1894.7(2)$ Å^3, $Z = 2$, $D_{calc} = 1.404$ g cm^{-3}, $\mu = 0.561$ mm^{-1} and $\theta_{max} = 25.07°$. Of 18,550 reflections collected, 6729 were independent, $R_{int} = 0.0357$, and 4480 were observed ($I > 2\sigma(I)$); final R indices: GOF = 1.069, $R_1 = 0.0630$ ($I > 2\sigma(I)$) and $wR_2 = 0.1931$.

4.5. General procedure for the Heck reaction

A mixture of Pd(II) catalyst (10 mg, 1.2 mol%), NaOAc (270 mg, 2 mmol), TBAB (320 mg, 1 mmol), aryl bromide (157 mg, 1 mmol), styrene (156 mg, 1.5 mmol) and DMF (2.5 mL) was charged in a vial under air, locked up with a screw cap and then heated at 140 °C in an oil bath. After completion of the reaction (2 h), the mixture was extracted with diethyl ether or dichloromethane/H$_2$O (3 mL/2 mL) four times. The organic phase was separated and dried in vacuo. The crude product was purified with a fresh column.

5. Supporting information

CCDC 618499 contains the supplementary crystallographic data for this paper. These data can obtained free of charge from The Cambridge Crystallographic Center via http://www.ccdc.cam.ac.uk/data-request/cif.

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