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Article

A New Tridentate Pincer Phosphine/*N*-Heterocyclic Carbene Ligand: Palladium Complexes, Their Structures, and Catalytic Activities

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A new imidazolium salt, 1,3-bis(2-diphenylphosphanylethyl)-3*H*-imidazol-1-ium chloride (**2**), for the phosphine/*N*-heterocyclic carbene-based pincer ligand, PC^{NHC}P, and its palladium complexes were reported. The complex, [Pd(PC^{NHC}P)Cl]Cl (**4**), was prepared by the common route of silver carbene transfer reaction and a novel direct reaction between the ligand precursor, PC^{NHC}P·HCl and PdCl$_2$ without the need of a base. Metathesis reactions of **4** with AgBF$_4$ in acetonitrile produced [Pd(PC^{NHC}P)(CH$_3$CN)](BF$_4$)$_2$ (**5**). The same reaction in the presence of excess pyridine gave [Pd(PC^{NHC}P)(py)](BF$_4$)$_2$ (**6**). The X-ray structure determination on **4**–**6** revealed the chiral twisting of the central imidazole rings from the metal coordination plane. In solution, fast interconversion between left- and right-twisted forms occurs. The twisting reflects the weak π-accepting property of the central NHC in PC^{NHC}P. The uneven extent of twisting among the three complexes further implies the low rotational barrier about the Pd–NHC bond. Related theoretical computations confirm the small rotational energy barrier about the Pd–NHC bond (ca. 4 kcal/mol). Catalytic applications of **4** and **5** have shown that the complexes are modest catalysts in Suzuki coupling. The complexes were active catalysts in Heck coupling reactions with the dicationic complex **5** being more effective than the monocationic complex **4**.

Introduction

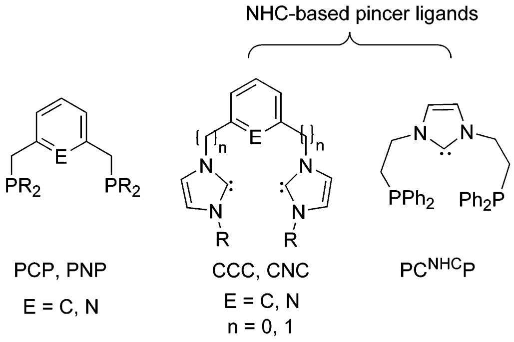

Figure 1. Pincer ligands.

Transition metal complexes with *N*-heterocyclic carbene (NHC) ligands have emerged as a hot research area.[1] Numerous publications related to their coordination chemistry and catalytic properties have been reported in the past 10 years.[1] On the other hand, metal complexes based on pincer framework (Figure 1) are continuously attracting attention because of their unique balance of stability vs reactivity which can provide enhanced metal complex reactivity and catalytic performances.[2] In this regard, transition metal complexes with phosphine-based pincer ligands have shown rich promise in bond activation, coordination chemistry, and catalysis.[2c] Recently, efforts have been made to prepare transition metal pincer complexes with NHC ligands.[3,4] For example, the palladium complexes of CCC and CNC pincer ligands have shown to be effective in catalyzing Heck coupling reaction.[3b−e] Since an earlier report on palladium complexes with mixed NHC-phosphine ligands[5a] and more

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recent articles on palladium complexes with bidentate phosphine/NHC ligands had demonstrated the effectiveness of phosphine/NHC combination in C−C coupling reactions,[5b−c] it would be of interest to explore whether the combinatory construction of phosphine and NHC into a pincer framework will result in new pincer complexes, which may display novel reactivity and enhanced catalytic activities.

Palladium complexes with NHC ligands were typically prepared from imidazolium salts via the palladium acetate protocol,[6] the silver carbene transfer reactions,[7] or the free carbene route.[8] In the first two methods, the carbenic proton of an imidazolium salt was deprotonated by basic ligands of the metal precursors, $Pd(OAc)_2$ and Ag_2O, respectively, while the latter method involves uses of inorganic or organic bases for the acidic proton abstraction with the generated free carbene then being trapped, after isolation or in situ, by a metal precursor. More recently, the oxidative addition of an imidazolium C−H bond by palladium(0) was shown to be a viable method for the preparation of palladium(II) NHC complexes.[9]

Here we report the synthesis of a new imidazolium salt for the pincer derivative, $PC^{NHC}P$, and the preparation of its palladium complexes. In contrast to the preparation of palladium NHC complexes reported in the literature, the pincer complex $[Pd(PC^{NHC}P)Cl]Cl$ was achieved by the metal-promoted C−H bond activation between the ligand precursor, $PC^{NHC}P{\cdot}HCl$, and $PdCl_2$ without the need of base. Crystallographic determinations on the palladium $PC^{NHC}P$ complexes prepared have shown that chiral twisting of the central imidazole rings from the metal coordination plane occurs. Two of the structures appear to have the highest degree of twisting among reported pincer complexes. Theoretical computations were performed to estimate the rotational energy barrier about the Pd−NHC bond. Catalytic applications of the new palladium(II) complexes in C−C coupling reactions were also reported.

Experimental Section

All reactions were performed under a dry nitrogen atmosphere using a Schlenk line and standard Schlenk technique. All solvents were distilled under nitrogen from the appropriate drying agent and stored in solvent reservoirs, which contained 4 Å molecular sieves, and purged with nitrogen. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13, 75.48, and 121.49 Hz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were in ppm relative to residual proton of $CDCl_3$ (^1H, δ 7.24; ^{13}C, δ 77.0) or DMSO-d_6 (^1H, δ 2.50; ^{13}C, δ 39.5). ^{31}P NMR chemical shifts were relative to 85% H_3PO_4 external standard (^{31}P: δ 0.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at Instrument Center, National Chung Hsing University, Taiwan. 1-(2-Chloroethyl)-1*H*-imidazole was prepared according to the literature procedure.[10]

Preparation of 1,3-Bis(2-chloroethyl)-3*H*-imidazol-1-ium chloride (1). A mixture of 1-(2-chloroethyl)-1*H*-imidazole (1.41 g, 10.78 mmol) in excess 1,2-dichloroethane was heated under reflux for 2 d. The solvent was then removed completely under vacuum. The viscous yellow oil remaining was washed with THF and dichloromethane, and then dried under vacuum. The compound could be used without further purification. Yield: 1.91 g (77%). ^1H NMR (DMSO-d_6): δ 4.10 (t, $^3J_{HH}$ = 5.4 Hz, 4H, $\mathrm{C}H_2$), 4.63 (t, $^3J_{HH}$ = 5.4 Hz, 4H, $\mathrm{C}H_2$), 7.94 (s, 2H, $\mathrm{C}H$), 9.48 (s, 1H, $\mathrm{NC}H\mathrm{N}$). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 43.6 (s, $C\mathrm{H}_2$), 50.7 (s, $C\mathrm{H}_2$), 123.2 (s, $C\mathrm{H}$), 137.9 (s, $\mathrm{N}C\mathrm{HN}$).

Preparation of 1,3-Bis(2-diphenylphosphanylethyl)-3H-imidazol-1-ium chloride (2). A mixture of $HPPh_2$ (0.17 mL, 0.40 mmol) and $KOBu^t$ (0.45 g, 0.40 mmol) in 2 mL of DMSO was stirred for about 20−30 min. The red solution was then added dropwise to a 2 mL DMSO solution of **1** **(**0.42 g, 1.83 mmol). After addition, the solution was allowed to react for 3 h. The solvent was removed completely under vacuum. Methanol (10 mL) was added and the white solid formed was filtered through a plug of Celite. The filtrate was pumped dry under vacuum. Upon addition of THF, a white solid formed which was then filtered, further washed with dried THF, and pumped dry under vacuum. Yield: 0.42 g (44%). Anal. Calcd for $C_{31}H_{31}N_2P_2Cl$: C, 70.39; H, 5.91; N, 5.30. Found: C, 70.02; H, 5.29; N, 5.63. mp 225−230 °C. ^1H NMR (DMSO-d_6): δ 2.75 (t, $^3J_{HH} = {}^2J_{HP}$ = 7.5 Hz, 2H, $\mathrm{PC}H_2$), 4.37 (q, $^3J_{HH} = {}^3J_{HP}$ = 7.5 Hz, 2H, $\mathrm{NC}H_2$), 7.02 (s, 2H, imi-*H*), 7.20−7.38 (m, 12H, Ph-*H*), 7.40−7.48 (m, 8H, Ph-*H*), 11.19 (s, 1H, $\mathrm{NC}H\mathrm{N}$). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 28.9 (d, $^1J_{CP}$ = 15.6 Hz, $\mathrm{P}C\mathrm{H}_2$), 47.8 (d, $^2J_{CP}$ = 22.0 Hz, $\mathrm{N}C\mathrm{H}_2$), 121.5 (imi-*C*), 128.8 (d, $^3J_{CP}$ = 7.1 Hz, Ph-*H*), 129.3 (s, Ph-*H*), 132.7 (d, $^2J_{CP}$ = 19.3 Hz, Ph-*H*), 135.8 (d, $^1J_{CP}$ = 11.2 Hz), 138.2 (s, $\mathrm{N}C\mathrm{HN}$). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −21.7 (s).

Preparation of $\mathbf{Ag(PC^{NHC}P)Cl}$ (3). To a 20 mL dichloromethane solution of **2** (0.41 g, 0.77 mmol) was added with solid Ag_2O (89 mg, 0.39 mmol). The mixture was allowed to stir in the dark overnight. A gray solid of AgCl was slowly precipitated from the solution and then removed by filtration. The filtrate was reduced to ca. $^1/_2$ of its original volume under vacuum. Upon addition of diethyl ether, a white solid was formed, which was filtered and dried under vacuum. Yield: 0.22 g (92%). Anal. Calcd for $C_{31}H_{30}N_2P_2AgCl$: C, 58.56; H, 4.76; N, 4.41. Found: C, 58.52; H, 4.80; N, 4.31. mp 165−170 °C. ^1H NMR (DMSO-d_6): δ 2.83 (br s, $\mathrm{PC}H_2$), 4.54 (br s, $\mathrm{NC}H_2$), 6.89 (br s, 2H, imi-*H*), 7.18−7.49 (m, 20H, Ph-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 30.2 (br s, $\mathrm{P}C\mathrm{H}_2$), 49.5 (br s, $\mathrm{N}C\mathrm{H}_2$), 121.2 (br s, imi-*C*), 128.8 (br s, Ph-*H*), 129.9 (br s, Ph-*H*), 132.8 (br s, Ph-*H*). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −10.0 (br s).

Preparation of $\mathbf{[Pd(PC^{NHC}P)Cl]Cl}$ (4). Method A. A 20 mL DMF solution of **3** (67 mg, 0.11 mmol) and $PdCl_2$ (19 mg, 0.11 mmol) was heated at 90 °C for 16 h. After cooling, the gray AgCl formed was filtered through a plug of Celite. The solvent of the filtrate was removed completely under vacuum. Upon addition of diethyl ether, a yellow solid was formed which was then filtered

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and dried under vacuum. Yield: 58 mg (83%). Anal. Calcd for $C_{31}H_{30}N_2Cl_2P_2Pd$: C, 55.58; H, 4.51; N, 4.18. Found: C, 55.44; H, 4.50; N, 4.20. mp 256−260 °C. ^{1}H NMR (DMSO-d_6): δ 2.73 (m, PCH_2), 4.49 (br m, NCH_2), 7.54 (m, 12H, Ph-H), 7.65 (s, 2H, imi-H), 7.82 (m, 8H, and Ph-H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 25.1 (t, $^1J_{CP}$ = 16.1 Hz, PCH$_2$), 47.0 (NCH$_2$), 124.2 (imi-C), 129.3 (t, $^2J_{CP}$ = 5.4 Hz, C_{ortho}), 129.7 (t, $^1J_{CP}$ = 25.6 Hz, P-C), 131.9 (C_{para}), 134.3 (t, $^3J_{CP}$ = 6.3 Hz, C_{meta}), 151.4 (t, $^1J_{CP}$ = 8.4 Hz, Pd-C). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 11.6 (s). **Method B.** A mixture of **2** (0.38 g, 0.72 mmol) and $PdCl_2$ (0.13 g, 0.72 mmol) in 15 mL of DMF was stirred at 90 °C overnight. The volatile was then removed completely under vacuum. The residue was dissolved with a minimum amount of dichloromethane. Upon addition of diethyl ether, a yellow solid was formed which was filtered and dried under vacuum. Yield: 0.46 g (94%). The spectroscopic and analytical data were identical to those from method A.

Preparation of [Pd(PC^{NHC}P)(CH$_3$CN)](BF$_4$)$_2$ (5). aA 10 mL acetonitrile solution of **4** (75 mg, 0.11 mmol) was treated with $AgBF_4$ (44 mg, 0.22 mmol) dissolved in 5 mL of the same solvent. The mixture was allowed to stir for 1 h. A gray solid of AgCl was slowly formed, which was filtered off through a plug of Celite. The solvent of the filtrate was removed completely under vacuum to give a brown solid. Yield: 71 mg (78%). Anal. Calcd for $C_{33}H_{33}B_2F_8N_3P_2Pd$: C, 48.72; H, 4.09; N, 5.16. Found: C, 48.90; H, 4.17; N, 5.23. mp 259−263 °C. ^{1}H NMR (DMSO-d_6): δ 2.03 (s, CH_3), 2.86 (br s, PCH_2), 4.75 (br s, NCH_2), 7.45−7.78 (m, 22H, imi-H and Ph-H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 1.56 (CH$_3$−C≡N), 25.4 (t, $^1J_{CP}$ = 16.8 Hz, PCH$_2$), 48.5 (NCH$_2$), 118.8 (CH$_3$-C≡N), 124.7 (imi-C), 128.7 (t, $^1J_{CP}$ = 25.1 Hz, P-C), 129.9 (t, $^2J_{CP}$ = 5.3 Hz, C_{ortho}), 132.6 (C_{para}), 134.1 (t, $^3J_{CP}$ = 6.7 Hz, C_{meta}), 144.3 (t, $^1J_{CP}$ = 10.0 Hz, Pd-C). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 15.5 (s).

Preparation of [Pd(PC^{NHC}P)(py)] (BF$_4$)$_2$ (6). To a 5 mL acetonitrile solution of **5** (55 mg, 0.068 mmol) was added excess pyridine (0.5 mL). The solution was allowed to stir overnight. The volume of the solution was reduced to about 1 mL under vacuum. Upon addition of diethyl ether, a white solid was formed which was then filtered and dried under vacuum. Yield: 44 mg (77%). Anal. Calcd for $C_{36}H_{35}B_2F_8N_3P_2Pd$: C, 50.77; H, 4.14; N, 4.93. Found: C, 50.67; H, 4.13; N, 4.91. mp 249−252 °C. ^{1}H NMR (DMSO-d_6): δ 3.01 (br s, PCH_2), 4.97 (br s, NCH_2), 6.97 (t, $^3J_{HH}$ = 6.5 Hz, 2H, py-H_{meta}), 7.36−7.63 (m, 23H, Ph-H, py-H), 8.14 (d, $^3J_{HH}$ = 4.8 Hz, 2H, py-H_{ortho}). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 24.7 (t, $^1J_{CP}$ = 16.8 Hz, PCH$_2$), 49.0 (NCH$_2$), 124.7 (imi-C), 126.4 (py-C_{meta}), 128.5 (t, $^1J_{CP}$ = 25.6 Hz, P-C), 129.6 (t, $^2J_{CP}$ = 5.2 Hz, Ph-C_{ortho}), 132.1 (Ph-C_{para}), 133.3 (t, $^3J_{CP}$ = 6.6 Hz, Ph-C_{meta}), 139.0 (py-C_{para}), 150.0 (t, $^1J_{CP}$ = 10.0 Hz, Pd-C), 150.1 (py-C_{ortho}). ^{31}P-{^{1}H} NMR (DMSO-d_6): δ 16.5 (s).

General Procedure for the Suzuki Coupling Reactions. In a typical run, a mixture of aryl bromides (1.0 mmol), phenylboronic acid (1.5 mmol), cesium carbonate (2.0 mmol), and 0.5 mol % of catalyst in 5 mL of 1,4-dioxane was stirred at 80 °C for an appropriate time under nitrogen. The solution was allowed to cool. A 1:1 mixture of diethyl ether/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL portion of diethyl ether, and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give a crude product which was subjected to column chromatography resulting in pure compounds.

General Procedure for the Heck Coupling Reactions. In a typical run, a 50 mL two-neck flask equipped with a reflux condenser was charged with aryl halides (1.0 mmol), styrene (1.4 mmol), anhydrous sodium acetate (1.1 mmol), and 0.5 mol % of catalyst. The flask was thoroughly degassed, 5 mL of *N*,*N*-dimethylacetamide was added via a syringe, and then the flask was placed in a preheated oil bath at 165−175 °C. In the cases of bromobenzene as substrate, after a fixed time, 10 mL of diethyl ether was added to the reaction mixture and the organic layer was washed 5× with water and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give the isolated product. With all the other substrates, aliquots (0.2 mL) were removed from the reaction after a fixed time and added to dichloromethane (10 mL). The organic portion was washed 5× with water and dried with anhydrous $MgSO_4$. The solution was filtered and the solvent was removed completely under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. For catalytic runs with low catalyst loading, stock solutions of appropriate concentration were prepared.

X-ray Data Collection. Crystals of **4** suitable for X-ray diffraction analysis were grown with slow diffusion of diethyl ether into a dichloromethane solution of **4**. Crystals of **5** and **6** were grown with the same procedure using the solvent combination of acetonitrile/diethyl ether. Typically, the crystal was removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a weighing paper. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 273(2) K. No decay was observed in 50 duplicate frames at the end of the data collection.

Solution and Structure Refinements. Calculations for the structures were performed using SHELXS-97 and SHELXL-97. Tables of neutral atom scattering factors, f' and f'', and absorption coefficient are from a standard source.[11] The structures were solved via Pattersons heavy-atom method. All atoms except hydrogen atoms were refined anisotropically. All hydrogen atoms were located in difference Fourier maps and included through the use of a riding model. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 235511−235513. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

Preparation of Imidazolium Salt. The preparation of ligand precursor, 1,3-bis(2-diphenylphosphanylethyl)-3*H*-imidazol-1-ium chloride, PC^{NHC}P·HCl **(2)** is shown in Scheme 1. The key intermediate 1,3-bis(2-chloroethyl)-3*H*-imidazol-1-ium chloride (**1**) had to be produced via a two-step procedure because attempts to carry out a one-pot reaction between imidazole and 1,2-dichloroethane always resulted in an impure mixture containing dehydrohalogenation products. Thus, the compound 1-(2-chloroethyl)-1*H*-imidazole was first synthesized by the reported phase-transfer catalytic approach.[10] The *N*-substituted imidazole was then heated in neat 1,2-dichloroethane to afford pure **1** in 77% yield. Further reaction of **1** with $KPPh_2$, in situ generated by $HPPh_2$ and KOBu^t, in DMSO produced **2** as a white solid in 44% yield. The organic salt, which is stable under nitrogen protection but slowly oxidized in the air, was characterized

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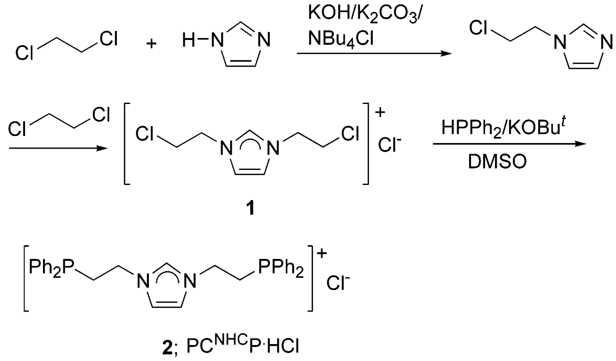
Scheme 1

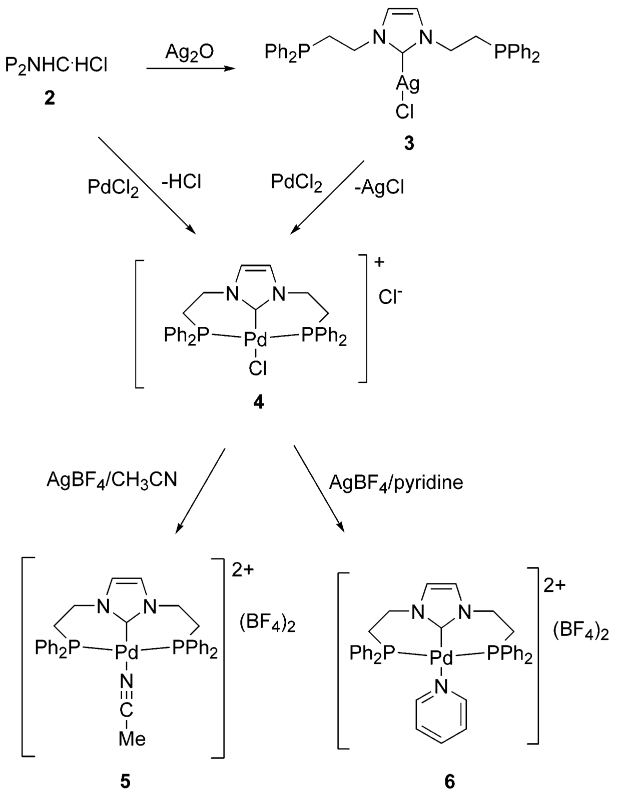


by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies and elemental analysis. As expected, a single $^{31}P\{^1H\}$ NMR resonance was observed at δ −21.7. The carbenic hydrogen was observed at δ 11.19 which is close to the upper limit of related imidazolium halides (δ 9.0−12.0),[3c−g] suggesting a high acidity of this proton.

Preparation of Silver Complex. Treating $PC^{NHC}P{\cdot}HCl$ with 0.5 equiv of Ag_2O in dichloromethane readily produced a white solid. The ^1H NMR of **3** clearly shows that the downfield signal at about δ 11 was absent, indicating the successful deprotonation of $PC^{NHC}P{\cdot}HCl$ and hence, the coordination of NHC, instead of the phosphine moieties, to the Ag(I) center. Also, in the $^{31}P\{^1H\}$ NMR spectrum, the upfield resonance observed at δ −10.0 indicates the presence of free phosphine groups. It should be noted that all the NMR signals of **3** are broad which can be attributed to the fluxionality of the dangling phosphanylethyl moieties. It has been shown that the formation of $[Ag(NHC)_2]X$ with two NHC ligands coordinated to the silver center was possible if an excess amount of Ag_2O was employed.[12] However, the analytical data of **3** suggest that only one $PC^{NHC}P$ ligand is coordinated to the silver center and agrees with the molecular formula being $Ag(PC^{NHC}P)Cl$.

Preparation of Palladium Complexes (4−6). The palladium complex $[Pd(PC^{NHC}P)Cl]Cl$ (**4**) was successfully prepared via the silver carbene transfer reaction by stirring a mixture $PdCl_2$ and **3** in dichloromethane for 16 h with 83% yield (Scheme 2). The yellow solid obtained was air stable and thermally robust. The$^{31}P\{^1H\}$ NMR resonance was downfield shifted to δ 11.6 upon metal coordination. In the ^1H NMR spectrum, the presence of only one set of signals for the ethyl protons suggests that the molecule is symmetry-related. Interestingly, these ethylene protons appear as two broad singlets, suggesting the involvement of a dynamic process. The broadening of these signals can be attributed to the interconversion between the left- and right-twisted forms (atropisomers) in solution (see structure description below), similar to what had observed in the related complexes [Pd(CNC)Cl]X and [Pd(CCC)Br].[3a,3c] The interconversion is faster than the ^1H NMR time scale as decoalescence of the ethylene signals was not observed even at −60 °C. This rapid interconversion is sharply different from those in [Pd(CNC)Cl]X and [Pd(CCC)Cl] in which conformations are rigid at either room temperature or −50 °C. The low rotational barrier about the Pd−NHC bond and the flexibility of the ethylene spacer can account for the differences. The $^{13}C\{^1H\}$ NMR spectra of **4** clearly indicate the successful formation of chelating Pd−NHC complex and trans disposition of phosphine groups. The carbenic carbon of $PC^{NHC}P$ was observed at δ 151.4 as a triplet with $^2J_{CP} = 8.4$ Hz, the magnitude of which corresponds to the cis coupling of two phosphine groups. Consistently, the methylene carbon (at δ 25.1) and the ortho-, ipso-, and meta-carbons of the phenyl groups (at δ 129.3, 129.7 and 134.3, respectively) appear as triplets because of virtual coupling,[13] which also indicates unambiguously the trans disposition of the two phosphine groups.

Scheme 2



We also followed the routine procedure of employing NaOAc as base for the generation of free carbene, which was then trapped by $PdCl_2$ in situ affording **4** in 50% of yield. One of the key features of pincer ligands is the metal-promoted C−R (R = H or C) bond activation in their corresponding ligand precursors due to steric requirement, which results in the production of tridentate cyclometalated pincer complexes.[14] Therefore, we anticipated that a similar metal-promoted C−H bond activation in $PC^{NHC}P{\cdot}HCl$ would occur and so a direct reaction between the ligand precursor

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Table 1. Crystallographic Data for **4**, **5**, and **6**

	4	**5**	**6**
empirical formula	$C_{31}H_{30}Cl_2N_2P_2Pd$	$C_{33}H_{33}B_2F_8N_3P_2Pd$	$C_{36}H_{35}B_2F_8N_3P_2Pd$
formula weight	669.85	813.58	851.63
color and habit	colorless prism	colorless prism	colorless prism
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$C2/c$
a, Å	50.480(16)	13.749(3)	17.598(7)
b, Å	11.333(3)	12.538(2)	13.394(5)
c, Å	24.738(7)	20.682(4)	17.272(7)
α, deg	90	90	90
β, deg	114.119(11)	96.412(4)	107.512(12)
γ, deg	90	90	90
V, Å^3	12917(7)	3543.2(12)	3883(3)
T, K	273(2)	273(2)	273(2)
Z	16	4	4
D_{calcd}, mg/m^3	1.378	1.525	1.457
μ, mm^{-1}	0.861	0.685	0.628
range of transm. factor	0.85−0.81	0.88−0.85	0.90−0.86
no. of unique data	12706	6945	4592
no. of parameters refined	705	443	237
R_1 [$I > 2\sigma I$]	0.0648	0.0445	0.0494
wR_2 (all data)	0.2293	0.1232	0.1509

2 and $PdCl_2$ would afford **4** without the requirement of a base. Remarkably, it was proven to be the case, as the reaction between **2** and $PdCl_2$ in the absence of base cleanly reacted to produce **4** in 94% of yield. This reaction represents the first example of formation of palladium(II) NHC complex from *N*-substituted imidazolium salts and $PdCl_2$ directly without the need of base. The feasibility of this reaction can be attributed to the intrinsic high acidity of **3** and the chelating requirement of the pincer ligand resulting in facile elimination of hydrogen chloride from the imidazolium chloride. Metathesis reaction of **3** with $AgBF_4$ in acetonitrile produced the ionic complex $[Pd(PC^{NHC}P)(CH_3CN)](BF_4)_2$ (**5**). The pyridine adduct $[Pd(PC^{NHC}P)(py)](BF_4)_2$ (**6**) was obtained by a similar reaction in the presence of excess pyridine. Both **4** and **5** are stable in air. Like **4**, **5** and **6** also exhibit broad ethylene signals, which are not resolved even at −60 °C in their ^{1}H NMR spectra. Thus, the rapid chiral conformational change also occurs in them. The^{31}P{^{1}H} NMR resonances in **5** (δ 15.5) and **6** (δ 16.5) were observed downfield to that of **4** (δ 11.6**)**, which can be attributed to the dicationic nature of the complexes.

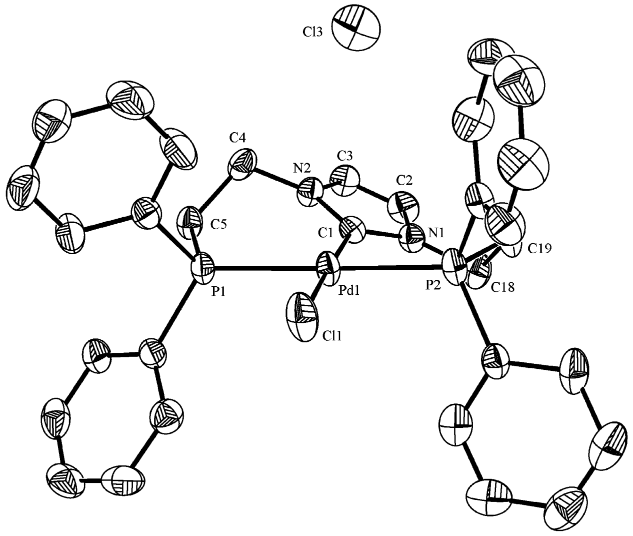

Figure 2. Molecular structure of **4** with thermal ellipsoids depicted at 35% probability level. Only one independent molecule in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity. Selected bond distances: Pd(1)−C(1), 1.983(7); Pd(1)−P(1), 2.3248(19); Pd(1)−P(2), 2.297(2); Pd(1)−Cl(1), 2.333(2) Å. Selected bond angles: C(1)−Pd(1)−P(2), 91.4(2); C(1)−Pd(1)−P(1), 91.7(2); P(2)−Pd(1)−Cl(1), 85.96(7); P(1)−Pd(1)−Cl(1), 90.88(7); P(2)−Pd(1)−P(1), 176.22(7); C(1)−Pd(1)−Cl(1), 177.1(2) deg.

Structure Description of 4−6. The molecular structures of **4**−**6** were determined (Table 1) and their selected bond distances and angles are given in Figures 2−4, respectively. In the structure of **4**, there are two independent molecules in the asymmetric unit of the *C*2/*c* unit cell (only one of the molecules is used for structural analysis below). One of the counter chloride anions is disordered with partial occupancy in 6 different locations. In contrast, in the structure of **6**, there is only a half of the molecule present in the asymmetric unit of the *C*2/*c* unit cell. The full molecule is generated by a crystallographic C_2 rotation axis along the Pd−C(1) bond, while in the structure of **4** and **5** the complex molecules also possess a noncrystallographic C_2 rotation axis along the same bond. In each of the structures, the palladium center adopts a square planar geometry and the imidazole ring is twisted making an angle with the metal coordination plane. For example, in the structure of **4**, the angle between the imidazole ring and the plane defined by Pd(1)−Cl(1)−C(1)−P(1)−P(2) (the twist angle) is 27.1°. Interestingly, in comparison with **4**, the central imidazole rings in **5** and **6** are highly twisted. In fact, the twist angles of **5** and **6** (48.7° and 48.9°) are significantly bigger than that of **4**. It is conceived from the figures that the twisting of the imidazole ring from the metal coordination plane and the flexibility of the ethylene spacer are essential for the palladium center to accommodate the bulky pincer ligand in the square planar coordination geometry. The direction of twist determines the chirality generated. **4-6** crystallized in centrosymmetric space group so that both the left- and right-twisted forms were present and related by the centers of symmetry in the unit cell. It is the interconversion between left- and right-twisted forms in solution leading to the broadening of ethylene protons in **4**−**6**. The twisting also means that the overlapping

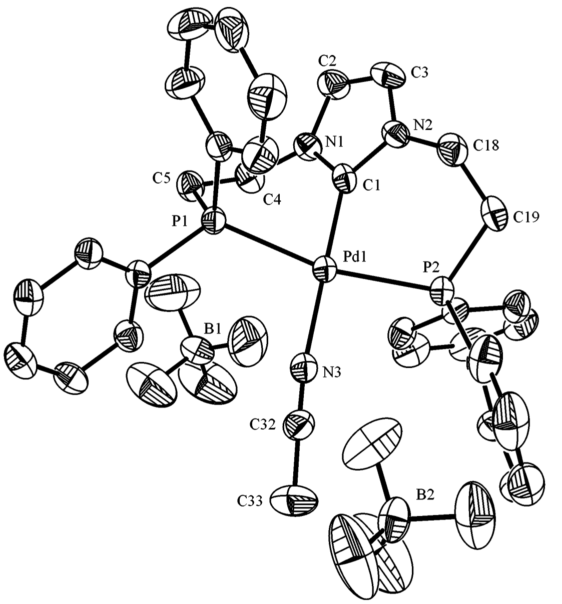

Figure 3. Molecular structure of **5** with thermal ellipsoids depicted at 35% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Pd(1)−C(1), 1.961(4); Pd(1)−P(1), 2.3276(11); Pd(1)−P(2), 2.3200(12); Pd(1)−N(3), 2.052(4); N(3)−C(32), 1.125(5) Å. Selected bond angles: C(1)−Pd(1)−P(2), 85.71(12); C(1)−Pd(1)−P(1), 81.86(12); P(2)−Pd(1)−N(3), 93.89(10); P(1)−Pd(1)−N(3), 98.57(10); P(2)−Pd(1)−P(1), 166.87(4); C(1)−Pd(1)−N(3), 179.39(16); N(3)−C(32)−C(33), 178.4(5) deg.

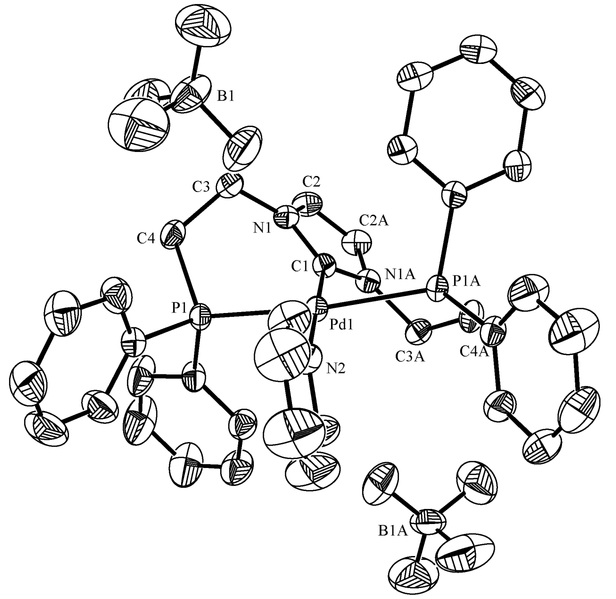

Figure 4. Molecular structure of **6** with thermal ellipsoids depicted at 35% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Pd(1)−C(1), 1.985(4); Pd(1)−P(1), 2.3300(11); Pd(1)−N(2), 2.086(4) Å. Selected bond angles: C(1)−Pd(1)−P(1), 83.32(2); P(1)−Pd(1)−N(2), 96.68(2); P(1)−Pd(1)−P(1A), 166.65(5); C(1)−Pd(1)−N(2), 180.000(2) deg.

of metal d_π orbital with the p_z orbital of the carbenic carbon is inefficient, which confirms the negligible π-accepting property of NHC ligand.[15] Further evidence came from the great variation in the twist angle, implying the low rotation barrier about the Pd−NHC bond (see theoretical computations below). The degree of twisting in the structures can also be quantified by the dihedral angles (P−Pd(1)−C(1)−N), which are 25.25°, 29.02° in **4**, 48.18°, 49.10° in **5**, and 49.02° in **6**, respectively. Both **5** and **6** appear to have the highest degree of twisting among reported pincer complexes as the corresponding dihedral angle in similar Pd(II) pincer complexes of CCC and CNC[3a,3c] and Pt(II) pyrazolyl complexes is in the range of 38.5−45.5°.[16] The smaller Pd−C(1) bond distance in **5** (1.961(4) Å) compared with those in **4** (1.983(7) Å) and **6** (1.985 (4) Å) is due to the smaller trans influence of the acetonitrile ligand. The shortening of Pd(1)−C(1) distance in **5** does not warrant the high extent of twisting, as the twist angle of **5** is the same as that of **6**. The question whether the twisting is trans ligand dependent remains to be explored.

Theoretical Computations. To explore the Pd−NHC bonding feature, we performed theoretical computations of several related species. The three-parameter hybrid of exact exchange and Becke's exchange energy,[17] and of Lee, Yang, and Parr's nonlocal correlation energy[18] (B3LYP) has been applied. We used the 6-31G(d) basis sets for H, C, N, P, and Cl and the LANL2DZ effective core potential plus basis functions for Pd.[19] The Gaussian03 suite of programs has been used in these computations.[20] First, the geometries of the cations **4**−**6** were obtained, and the optimized geometrical parameters are in excellent agreement with the X-ray data. The computed dihedral angles (P−Pd−C−N) (**4** 27.6°, 30.5°; **5** 42.7°, 43.1°; **6** 40.3°) differ only by a few degrees from the diffraction data. We have further studied two species in which the ethylene connection in the pincer ligand is removed (Scheme 3). A constrained search on the potential energy surfaces of **7** and **8** shows that the rotational energy barriers of the imidazole rings are rather small. The geometrical parameters are not very different during the rotation, the most noticeable change being Pd−C(NHC) of **7**, which is lengthened from 2.017 Å (90.0°) to 2.048 Å (0°). The minima of both species occur at dihedral angle = 90.0°, corresponding to structures having the imidazole ring orthogonal to the metal coordination plane, while their maxima occur at 0°, corresponding to the coplanar structures. The rotational

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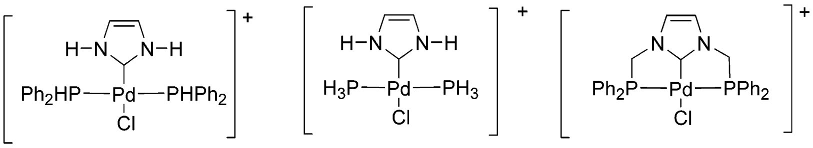
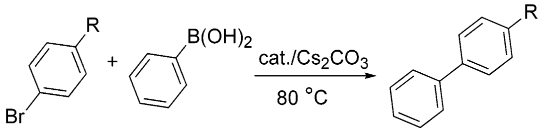
Scheme 3



7 **8** **9**

Table 2. Pd-Catalyzed Suzuki Coupling Reaction between Phenylboronic Acid and Aryl Bromides[a]



entry	catalyst	R	time, h	yield, %[b]
1	4	COMe	2	99
2	5	COMe	2	72
3	4	H	16	90
4	5	H	16	82
5	4	OMe	16	38
6	5	OMe	16	34

[a] Reaction condition: 1 mmol of aryl halide, 1.5 mmol of phenylboronic acid, 2.0 mmol of Cs_2CO_3, 0.5 mol % of Pd catalyst, 5 mL of 1,4-dioxane. [b] Isolated yield.

Table 3. Pd-Catalyzed Heck Coupling Reaction of 4-Bromoacetophenone and Styrene[a]

entry	catalyst	R′	yield, % (trans/gem)	TOF (h^{-1})
1	4	15 min	36 (97:3)	288
2	4	30 min	46 (96:4)	184
3	4	1 h	89 (96:4)	174
4	5	15 min	71[b] (100:0)	568
5	5	30 min	80 (94:6)	320
6	5	1 h	100 (95:5)	200

[a] Reaction condition: 1 mmol of aryl halides, 1.4 mmol of styrene, 1.1 mmol of NaOAc, 0.5 mol % of Pd catalyst, 5 mL of DMA. [b] Yield and trans/gem ratio are determined by ^{1}H NMR.

energy barrier is 3.0 kcal/mol for **7** and 4.9 kcal/mol for **8**, respectively. Thus, the Pd−NHC bond can be readily rotated in order to minimize the ring strain and steric repulsion. Interestingly, we found that when the ethylene is replaced by methylene spacer, the pincer ligand in **9** is planar.

Catalytic Reactions. The catalytic applicability of **4** and **5** in C−C coupling reactions was investigated. As seen in Table 2, **4** and **5** were effective in the Suzuki coupling of phenylboronic acid with activated aryl bromides. However, prolonged reaction time was needed for unactivated substrates. Only poor yields were obtained with deactivated 4-bromoanisole as substrates. The monocationic complex **4** is slightly more active than the dicationic complex **5**.

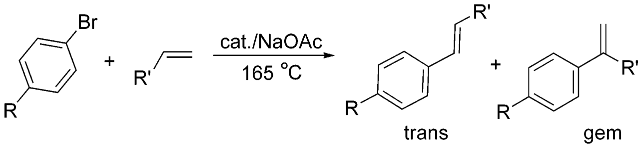
Complexes **4** and **5** are more efficient in Heck coupling reactions. Table 3 gives the comparative results between **4** and **5** from the standard coupling between 4-bromoacetophenone and styrene. In contrast to the catalytic results from Suzuki reaction, **5** is found to be more reactive than **4** in Heck reaction. In fact, as seen in Table 4 (entry 3), **5** with an amount as low as 1.25×10^{-6} mol % exhibits a TON of 56 000 000 in the Heck coupling reaction between the reactive phenyl iodide and styrene. This level of activity is significantly higher than those obtained by palladium complexes of phosphine-based pincer (PCP)[21] and bis-carbene CNC pincer,[3b] and comparable to that reported by palladium complexes with amido-based pincer.[22] In general, good yields of coupled products could be obtained from the reactions between aryl bromides derivatives and styrene (Table 5). The corresponding reactions with *n*-butyl acrylate as olefin partner gave slightly lower yields. Longer reaction times were required for unactivated and deactivated aryl bromides. The trans/gem ratio of the stibene products obtained compares well with those of similar pincer complexes.[3b−e] Only trans products were obtained with *n*-butyl acrylate as substrate. However, both **4** and **5** gave poor yields in reactions with activated aryl chlorides as substrates. For example, under the same catalytic condition, **5** affords a 27% of yield in 24 h for the reaction between 4-chloroacetophenone and styrene.

Table 4. Pd-Catalyzed Heck Coupling Reaction of Phenyl Iodide and Styrene Catalyzed by **5**[a]

entry	mole %	time	yield,[c] %(trans/gem)[b]	TON
1	5×10^{-5}	48 h	100 (90:10)	2 000 000
2	5×10^{-6}	48 h	100 (89:11)	20 000 000
3	1.25×10^{-6}	48 h	70 (89:11)	56 000 000

[a] Reaction condition: 1 mmol of aryl halides, 1.4 mmol of styrene, 1.1 mmol of NaOAc, complex **5**, 5 mL of DMA. [b] Determined by ^{1}H NMR. [c] Isolated yield.

Table 5. Pd-Catalyzed Heck Coupling Reaction[a]



entry	catalyst	R′	R	time, h	yield, % (trans/gem)
1	4	Ph	COMe	1	89[b] (96:4)
2	5	Ph	COMe	1	100[b](95:5)
3	4	Ph	H	4	81[c] (93:7)
4	5	Ph	H	4	94[c] (93:7)
5	4	Ph	OMe	20	80[b] (95:5)
6	5	Ph	OMe	20	100[b] (93:7)
7	4	*n*-BuO−CO	COMe	2	72[b] (100:0)
8	5	*n*-BuO−CO	COMe	2	100[b] (100:0)
9	4	*n*-BuO−CO	H	4	75[c] (100:0)
10	5	*n*-BuO−CO	H	4	82[c] (100:0)
11	4	*n*-BuO−CO	OMe	20	78[b] (100:0)
12	5	*n*-BuO−CO	OMe	20	87[b] (100:0)

[a] Reaction condition: 1 mmol of aryl halides, 1.4 mmol of styrene, 1.1 mmol of NaOAc, 0.5 mol % of Pd catalyst, 5 mL of DMA. Yield and trans/gem ratio are the average of two runs. [b] Determined by ^{1}H NMR. [c] Isolated yield.

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In this regard, **4** and **5** are inferior to palladium complexes with phosphinito PCP pincer ligand[23] and bis-carbene CNC pincer ligand containing methylene spacers, which are more effective with aryl chlorides.[3c,3d]

Conclusion

We report the preparation of a new imidazolium salt, 1,3-bis(2-diphenylphosphanylethyl)-3*H*-imidazol-1-ium chloride, for the pincer ligand $PC^{NHC}P$. The palladium complex **4** can be prepared by the routine procedure of silver carbene transfer reaction or by a novel metal-promoted direct reaction between the imidazolium salt with $PdCl_2$. The intrinsic high acidity and steric requirement of the ligand favors the successful deprotonation of the imidazolium salt and facile elimination of HCl without the need of a base. The X-ray structures of **4**−**6** have shown that, in each case, the central imidazole ring is twisted from the palladium coordination plane producing pairs of atropisomers in the crystal lattice. **5** and **6** are highly twisted. The uneven extent of twisting among **4**−**6** implies the weak π-accepting property of the NHC and the low rotational barrier about the Pd−NHC bond. In solution, rapid atropisomerization occurred, which is faster than the NMR time scale even at −60 °C. Related theoretical computations on **7** and **8** with no spacer between the imidazole ring and phosphorus atoms confirmed that the rotational energy barrier about the Pd−NHC bond is small (ca. 4 kcal/mol), indeed. The preferred structures of **7** and **8** are with the imidazole ring orthogonal to the metal coordination plane, whereas in the computed structure **9** the one-carbon connection does not allow the imidazole ring to turn but locks it in coplanar position. The two-carbon spacer in **4**−**6** imposes extra steric bulkiness and its flexibility coupled with the low rotation barrier about the Pd−NHC bond lead to the square planar coordination of the $PC^{NHC}P$ ligand around the metal center with significant twisting of the central imidazole ring. Catalytic applications of **4** and **5** have shown that the complexes were modest catalysts in Suzuki coupling. The complexes were efficient in Heck coupling reactions with aryl bromide as substrates. The dicationic complex **5** with a coordinated acetonitrile ligand is more efficient than the monocationic complex **4** bearing a chloride ligand. Complex **5** exhibited a TON as high as 56 000 000 in the reaction between phenyl iodide and styrene. However, both **4** and **5** were ineffective with aryl chlorides.

Acknowledgment. We are grateful to the National Science Council of Taiwan for financial support of this work (Grant NSC 92-2113-M-018-005-).

Supporting Information Available: Crystallographic data of **4**, **5**, and **6** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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