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Synthesis and characterization of amide-functionalized N-heterocyclic carbene–Pd complexes

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ABSTRACT

Amide-functionalized N-heterocyclic carbene (NHC) precursors such as azolium compounds have been designed and synthesized. Reaction of $PdCl_2(CH_3CN)_2$ with the NHC–Ag complex derived from the azolium salt gave $[(NHC)PdCl_2]_2$ or $(NHC)_2PdCl_2$, whereas $PdCl_2(PPh_3)_2$ reacted with the Ag complex to afford a mixed carbene/phosphine complex such as $(NHC)(PPh_3)PdCl_2$ together with a cationic $[(NHC)(PPh_3)_2PdCl]^+Cl^-$ whose structure was characterized by X-ray crystallographic studies. Thus, the library of NHC–Pd complexes with a tethered amide group has been successfully expanded.

1. Introduction

In recent years, tremendous efforts have been made toward the synthesis of transition metal complexes bearing N-heterocyclic carbene (NHC) ligands [1]. Of particular interest is introduction of a pendent functional group to an NHC, since the functionalized NHC can anchor free carbene to a metal site, serve as a chelate ligand, control the stability of metal center, or introduce chirality [2]. In 2007, Lee and co-workers designed *amide-functionalized* NHC ligands and synthesized palladium(II) and nickel(II) complexes with chelating anionic amidate/NHC ligands [3]. Structurally similar anionic-tethered gold(I), silver(I) and nickel(II) complexes were introduced by Ghosh and co-workers [4]. More recently, Bouwman and co-workers subsequently reported on nickel(II) complexes bearing bidentate NHC ligands functionalized with anionic amidate moieties for the Kumada coupling reaction [5]. Gornitzka and Hemmert and co-workers introduced tetradentate NHC ligands and their palladium(II) and nickel(II) complexes [6]. Thus, anionic amidate/NHC ligands have received considerable attention.

In 2008, we synthesized a novel *hydroxyamide-functionalized* azolium salt derived from chiral β-amino alcohol [7]. By using the azolium salt, new tridentate anionic amidate/NHC–Pd(II) and dianionic alkoxy/amidate/NHC–Pd(II) complexes have been developed. Importantly, the Pd(II) complex catalyzes an asymmetric oxidative Heck-type reaction with excellent enantioselectivity [8]. The above-mentioned anionic amidate/NHC–Pd(II) complexes by Lee and Ghosh were synthesized from *amide-functionalized* azolium compounds in the presence of an appropriate base such as K_2CO_3 [3,4]. In contrast, synthesis of the Pd(II) complex from the *hydroxyamide-functionalized* azolium salt does not require such a base [7]. These facts prompted us to examine the preparation of NHC–Pd(II) complexes from *amide-functionalized* azolium compounds in the absence of a base. During the course of this study, we found that various palladium complexes were synthesized by using $PdCl_2(CH_3CN)_2$ or $PdCl_2(PPh_3)_2$ as a palladium precursor. Herein, a systematic study on the synthesis of the NHC–Pd(II) complexes with amide functionalities is described.

2. Results and discussion

2.1. Synthesis of $[(NHC)PdCl_2]_2$ complexes

The preparation of amide-functionalized NHC precursors such as 1-methyl-3-N-(propylacetoamido)benzimidazolium chloride (**1a**) and 1,3-N,N′-bis(propylacetoamido)benzimidazolium chloride (**2a**) is shown in Eq. (1). **1a** was prepared by reaction of 1-methylbenzimidazole with 2-chloro-N-propylacetamide in 1,4-dioxane under reflux. Similarly, **2a** was obtained in 73% yield.

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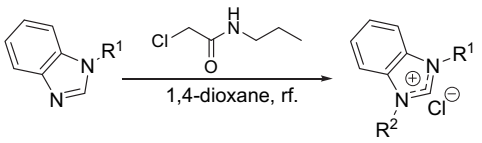
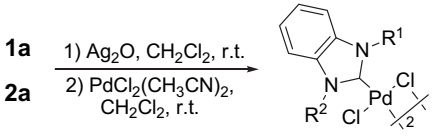


71% yield **1a** R^1 = -CH_3, R^2 = -$CH_2C(O)NHC_3H_7$

73% yield **2a** $R^1 = R^2$ = -$CH_2C(O)NHC_3H_7$ (1)

NHC complexes were successfully synthesized according to the Ag_2O method that was introduced by Lin et al. [9]. Ag_2O particularly serves as a mild base, reacting predominantly at the C_2 position of the azolium salt without deprotonation of other acidic protons. Treatment of **1a** with Ag_2O in CH_2Cl_2 at room temperature gave a white solid. The ^{1}H NMR spectrum of the solid without further purification suggests that NHC–Ag complex **1b** was obtained in almost pure form. The ^{13}C NMR spectrum of **1b** contains the characteristic carbene signal at δ 191.4 ppm. Since the silver complexes **1b** and **2b** have light-sensitive character, synthesis of NHC–Pd complexes **1c** and **2c** was carried out by a one-pot procedure without purification of the NHC–Ag intermediates from **1a** and **2a**, respectively (Eq. (2)). After treatment of **1a** with Ag_2O, the resulting silver complex **1b** was allowed to react with $PdCl_2(CH_3CN)_2$ at room temperature to give the corresponding neutral amide-functionalized NHC–Pd complex **1c** in good yield. NHC–Pd complex **2c** was obtained in 82% yield from the NHC precursor **2a**. Synthesis of a similar iodo-bridged dimeric monodentate NHC–Pd complex by reaction of $Pd(OAc)_2$ with an imidazolium salt in the presence of NaI and NaOEt has been reported [10]. It should be noted that no anionic amidate/NHC–Pd type complex was formed from the reaction with *amide-functionalized* azolium salts **1a** and **2a**. These facts would strongly indicate that the hydroxyl group on a *hydroxyamide-functionalized* azolium salt is crucial for the formation of an anionic palladium amidate complex [7].

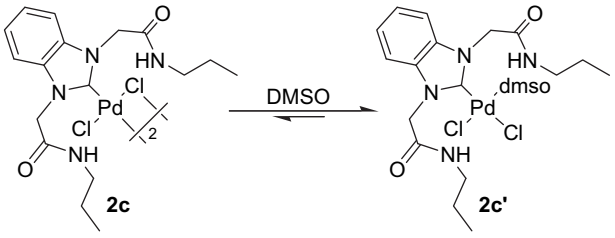


1a or **2a** : Ag_2O : $PdCl_2(CH_3CN)_2$ = 1.1 : 0.6 : 1 (2)

89% yield **1c** R^1 = -CH_3, R^2 = -$CH_2C(O)NHC_3H_7$

82% yield **2c** $R^1 = R^2$ = -$CH_2C(O)NHC_3H_7$

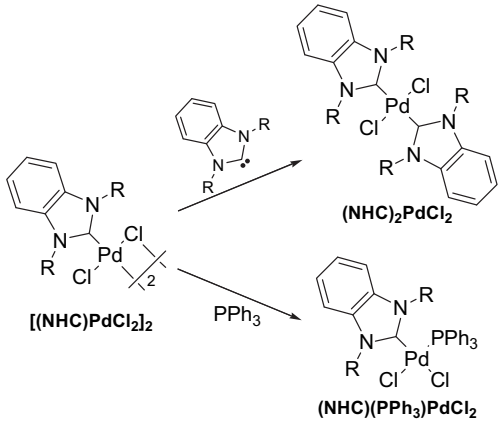
Interestingly, the ^{1}H NMR spectrum of **2c** in $(CD_3)_2SO$ indicates that it exists as a mixture of two NHC–Pd compounds, whereas the spectrum in CD_3OD indicates that it exists only a single compound (Fig. 1). Attention should be paid to the signal of the methylene proton adjacent to the carbonyl group. In CD_3OD, it appears as a singlet at δ 5.65 ppm. In $(CD_3)_2SO$, it appears as two kinds of signals: an A_2 system (δ 5.60 ppm) and an AX system [δ 5.62 and 5.33 ppm (J = 16.4 Hz)], in the ratio 17:83, as determined by integration. This might indicate that in $(CD_3)_2SO$ the major component (83%) is a new NHC–Pd complex **2c'** (Scheme 1). Indeed, it was reported that the donor numbers of $(CH_3)_2SO$, CH_3OH, H_2O, and CH_3CN are 30, 19, 18, and 14, respectively [11], indicating that $(CH_3)_2SO$ can strongly coordinate with a metal.



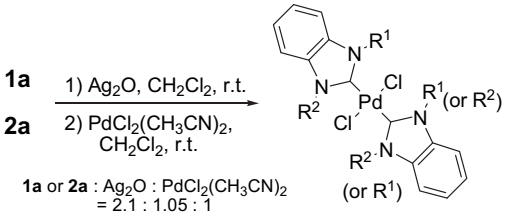
Scheme 1. Tentative structure of (NHC)(dmso)$PdCl_2$ **2c'** in DMSO.

2.2. Synthesis of $(NHC)_2PdCl_2$ and $(NHC)(PPh_3)PdCl_2$ complexes

Because the chloride-bridged dimeric monodentate NHC–Pd complex **2c** was found to vary in the presence of a strongly coordinating donor such as $(CH_3)_2SO$, we speculated that it might be possible to synthesize $(NHC)_2PdCl_2$ or $(NHC)(PPh_3)PdCl_2$, which is an analog of **2c'**, from $[(NHC)PdCl_2]_2$ **2c** in the presence of an additional NHC or PPh_3 ligand, respectively (Scheme 2).



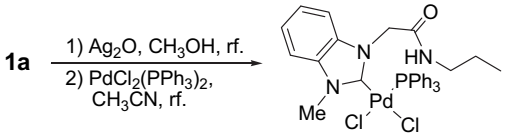
Scheme 2. Working hypothesis for conversion of dimeric NHC–Pd complex into $(NHC)_2PdCl_2$ or $(NHC)(PPh_3)PdCl_2$.



1a or **2a** : Ag_2O : $PdCl_2(CH_3CN)_2$ = 2.1 : 1.05 : 1 (3)

86% yield **1d** R^1 = -CH_3, R^2 = -$CH_2C(O)NHC_3H_7$

82% yield **2d** $R^1 = R^2$ = -$CH_2C(O)NHC_3H_7$



1a : Ag_2O : $PdCl_2(PPh_3)_2$ = 1.1 : 0.55 : 1 (4)

1e 86% yield

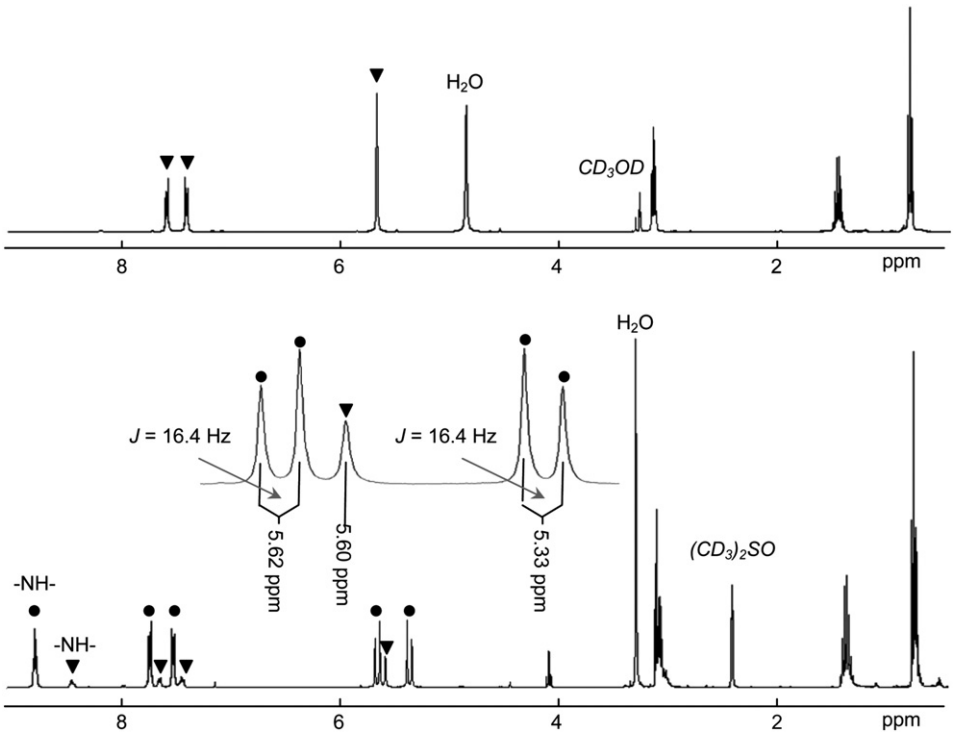
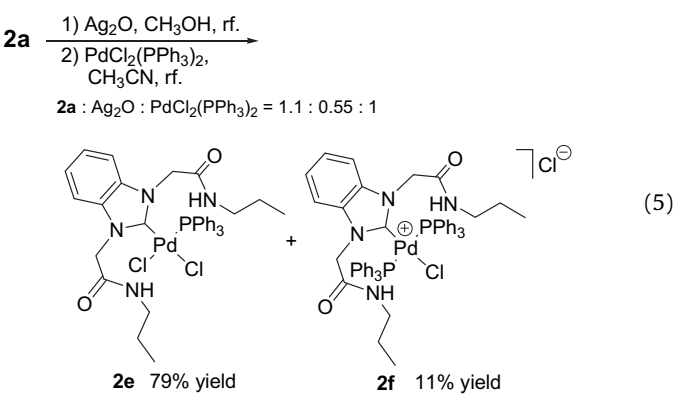


Fig. 1. ^{1}H NMR spectra of **2c** in CD_3OD (upper) and $(CD_3)_2SO$ (lower); signals for **2c** and **2c'** are represented by ▼ and ●, respectively.

The desired bis(NHC)–Pd(II) complexes **1d** and **2d** were successfully obtained by the same one-pot procedure as described for synthesis of **1c** and **2c** by simply changing the amount of NHC precursor used (Eq. (3)). During the course of this study, Ghosh and co-workers reported the synthesis of *trans*-[1-(*iso*-propyl)-3-{N-(benzylacetoamido)}imidazol-2-ylidene]$_2$PdCl$_2$, which is structurally similar to our complex **1d** [12]. Their asymmetrical amide-functionalized NHC–Pd complex, which was characterized by X-ray diffraction studies, was obtained as a single isomer in the solid state. However, the ^{1}H NMR spectrum of their complex indicates the existence of two isomers in solution, probably *trans-syn* and *trans-anti*. Although we did not succeed in the X-ray analysis of **1d**, the ^{1}H NMR spectrum of **1d** in $CDCl_3$ shows the existence of a 2:1 mixture probably due to the presence of two rotamers. In contrast, it should be noted that the symmetrical bis(NHC)–Pd complex **2d** exists in solution as a single form (See Supplementary data).

Attempts to obtain a mixed NHC/phosphine complex by the reaction of **1a** with PPh_3 were unsuccessful, giving a complex mixture of several unidentified products. After several trials, we eventually developed an efficient synthetic route to the desired (NHC)(PPh_3)$PdCl_2$ (**1e**) by using $PdCl_2(PPh_3)_2$ as a palladium precursor (Eq. (4)). Colorless crystals of **1e** were successfully grown from a saturated



(5)

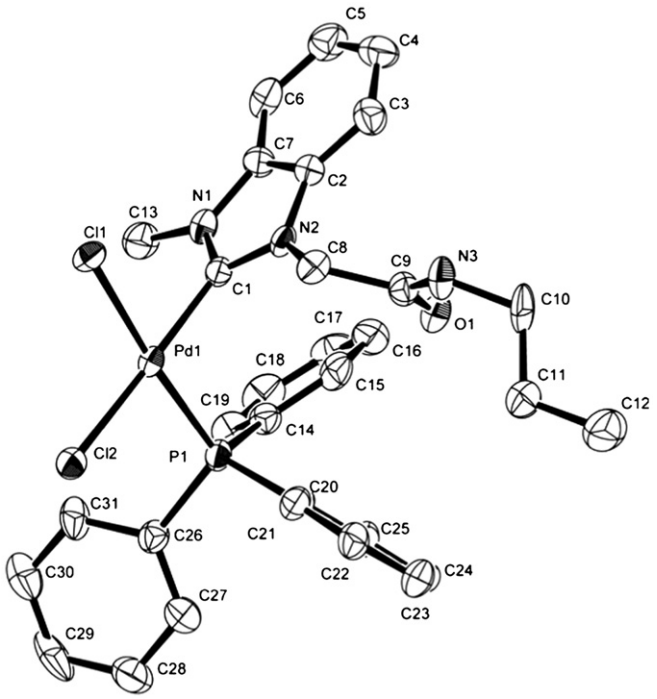


Fig. 2. Molecular structure of *cis*-(NHC)(PPh_3)$PdCl_2$ complex **1e** with the crystallographic numbering scheme; hydrogen atoms and $CHCl_3$ are omitted for clarity and selected lengths [Å] and angles [deg] are as follows: Pd1–C1 1.967(7), Pd1–P1 2.2535 (19), Pd1–Cl1 2.3562(17), Pd1–Cl2 2.365(2), C1–Pd1–P1 92.2(2), C1–Pd1–Cl1 83.6(2), P1–Pd1–Cl2 91.46(7), Cl1–Pd1–Cl2 92.74(6).

solution in chloroform by slow evaporation of the solvent at ambient temperature. The X-ray single-crystal diffraction study of **1e** revealed that the carbene and phosphine ligands are in a *cis* conformation (Fig. 2) [13]. The distance between the Pd and the Cl2 trans to carbene (d(Pd–Cl2) = 2.365(2) Å) is similar to the distance between the Pd and the Cl1 trans to the phosphine (d(Pd–Cl1) = 2.3562(17) Å). In ^{1}H NMR spectrum of *cis*-**1e** in $CDCl_3$, the signal of the methylene proton adjacent to the carbonyl group appears as an *AX* system [δ 5.63 and 4.07 ppm (J = 15.2 Hz)]. This might suggest that the NHC–Pd complex **2c'** derived from **2c** and DMSO involves *cis*-coordination of DMSO and NHC on a palladium(II) center (Scheme 1).

The mixed NHC/phosphine–Pd(II) (**2e**) was also synthesized from **2a** (Eq. (5)). Interestingly, a small amount of new mixed complex $[(NHC)(PPh_3)_2PdCl]^+Cl^-$ **2f** was isolated together with **2e**. The yields of **2e** and **2f** were 79% and 11%, respectively, based on the palladium precursor used. X-ray single-crystal diffraction study of **2f** shows that these two phosphine ligands are in a *trans* conformation (Fig. 3). The torsion angles for P1–Pd1–C1–N2 and P2–Pd1–C1–N1 are 99.3(2) and 96.6(2) degrees, respectively. The ^{1}H NMR spectrum of **2f** clearly indicates that it exists in solution as a C_2 symmetric form. Formation of the rare cationic complex **2f** is probably because of the strong donating capability of both NHC and PPh_3, which can stabilize the cationic metal center effectively. Quite recently, Hahn et al. reported that the similar $[(NHC)(PPh_3)_2PdCl]^+BF_4^-$ complex was synthesized by the oxidative addition of 2-chloro-N-methylbenzimidazole to $Pd(PPh_3)_4$ followed by protonation with NH_4BF_4 [14]. The bond lengths for the Pd–$C_{carbene}$ bond (2.000(3) Å) and the Pd–P bonds (Pd–P1 2.3587(9) Å, Pd–P2 2.3454(9) Å) of **2f** fall into the range reported for the $[(NHC)(PPh_3)_2PdCl]^+BF_4^-$ complex.

3. Conclusion

We have successfully expanded the collection of NHC–Pd(II) complexes bearing an amide functional group. Several distinct types of amide-functionalized NHC–Pd complexes such as $[(NHC)PdCl_2]_2$, $(NHC)_2PdCl_2$, $(NHC)(PPh_3)PdCl_2$, and $[(NHC)(PPh_3)_2PdCl]^+Cl^-$ were synthesized. Further studies focusing on design and synthesis of functionalized NHC precursors for development of efficient catalytic transformations are the subject of ongoing research in our laboratory.

4. Experimental

4.1. General procedures

All chemicals were obtained from commercial sources and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on spectrometers at 400 and 100 MHz, respectively. CD_3OD, $(CD_3)_2SO$ or $CDCl_3$ was used as the NMR solvent. Flash column chromatography was performed on silica gel 60 (Merck; mesh: 230–400; particle size: 0.040–0.063 nm). Elemental analyses were performed at Osaka University.

4.2. Synthesis of azolium salt **1a**

To 1,4-dioxane (20 mL) were added N-methylbenzimidazole (5.2 mmol, 687 mg) and 2-chloro-N-propylacetamide (5.0 mmol, 678 mg) derived from chloroacetyl chloride and propylamine. The reaction mixture was stirred at 110 °C for 2 days. The solvent was removed under reduced pressure, and the residue was dissolved in methanol. Activated carbon was added, and removed by filtration after 16 h. The filtrate was concentrated under reduced pressure to give a solid, which was purified by reprecipitation from ethyl acetate and methanol to give **1a** as a white solid (951 mg, 71% yield). ^{1}H NMR ($CDCl_3$): δ 10.70 (s, 1H), 9.35 (br, 1H), 8.03–7.64 (m, 4H), 5.69 (s, 2H), 4.20 (s, 3H), 3.18 (q, J = 6.4 Hz, 2H), 1.61–1.55 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 164.2, 143.3, 131.8, 131.5, 127.5, 127.2, 114.5, 112.1, 49.8, 41.6, 33.6, 22.4, 11.5. Anal. Calc. for $C_{13}H_{18}ClN_3O$: C, 58.31; H, 6.78; N, 15.69. Found: C, 57.71; H, 6.82; N, 15.62%.

4.3. Synthesis of azolium salt **2a**

To 1,4-dioxane (45 mL) were added N-propyl-1H-benzimidazole-1-acetamide (5.5 mmol, 1.19 g) and 2-chloro-N-propylacetamide (5.5 mmol, 0.74 g). The reaction mixture was stirred at 110 °C for 2 days. The isolation procedure described above was performed to give the desired product **2a** as a white solid (1.42 g, 73% yield). ^{1}H NMR (DMSO-d_6): δ 9.86 (s, 1H), 8.96 (br, 1H), 7.98–7.65 (m, 4H), 5.42 (s, 4H), 3.08 (q, J = 6.8 Hz, 4H), 1.50–1.41 (m, 4H), 0.86 (t, J = 7.2 Hz, 6H); ^{13}C NMR (DMSO-d_6): δ 164.4, 144.3, 131.3, 126.7, 113.7, 48.5, 40.8, 22.2, 11.5. Anal. Calc. for $C_{17}H_{25}ClN_4O_2\bullet1.5H_2O$: C, 53.75; H, 7.43; N, 14.74. Found: C, 53.71; H, 6.92; N, 14.71%.

4.4. One-pot synthesis of NHC–Pd complex **1c** via NHC–Ag complex **1b** from **1a**

A suspension of **1a** (0.11 mmol, 29 mg) and silver(I) oxide (0.06 mmol, 14 mg) in CH_2Cl_2 (10 mL) was stirred in the dark at room temperature. After 4 h, $PdCl_2(CH_3CN)_2$ (0.1 mmol, 26 mg) was added in the dark at room temperature. The resulting suspension was stirred for 16 h, filtered through a membrane filter (pore size: 0.2 μm), and evaporated to dryness in vacuo. The desired Pd complex was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 9/1) to give **1c** as a yellow solid (36 mg, 89% yield). **1b**: ^{1}H NMR ($CDCl_3$): δ 8.40 (s, 1H), 7.70–7.38 (m, 4H), 5.34 (s, 2H), 4.05 (s, 3H), 3.19 (q, J = 6.8 Hz, 2H), 1.59–1.49 (m, 2H), 0.85 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 191.4, 166.7, 134.4, 134.0, 124.3, 124.1, 112.5, 110.8, 52.1, 41.4, 35.9, 22.5, 11.5. **1c**: ^{1}H NMR (CD_3OD): δ 7.57–7.32 (m, 4H), 5.59 (s, 2H), 4.32 (s, 3H), 3.15 (t, J = 6.8 Hz, 2H), 1.53–1.44 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CD_3OD): δ 168.3, 136.1, 135.7, 124.9, 124.9, 111.9, 111.5, 52.1, 42.4, 35.3, 23.3, 11.7, the carbene ^{13}C NMR resonance was not observed. Anal. Calc. for $C_{26}H_{34}Cl_4N_6O_2Pd_2\bullet2H_2O$: C, 36.60; H, 4.49; N, 9.85. Found: C, 36.51; H, 4.46; N, 9.65%.

4.5. One-pot synthesis of NHC–Pd complex **2c** via NHC–Ag complex **2b** from **2a**

The reaction was performed as described above using **2a** (0.11 mmol, 39 mg) instead of **1a**. The desired Pd complex was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 9/1) to give **2c** as a yellow solid (40 mg, 82% yield). **2b**: ^{1}H NMR (DMSO-d_6): δ 8.40 (t, J = 5.6 Hz, 2H), 7.65–7.40 (m, 4H), 5.13 (s, 4H), 3.07 (q, J = 6.8 Hz, 4H), 1.49–1.40 (m, 4H), 0.85 (t, J = 7.2 Hz, 6H); ^{13}C NMR (DMSO-d_6): δ 165.9, 133.8, 123.9, 112.1, 51.0, 40.6, 22.3, 11.5, the carbene ^{13}C NMR resonance was not observed. **2c**: ^{1}H NMR (CD_3OD): δ 7.54–7.35 (m, 4H), 5.65 (s, 4H), 3.18 (t, J = 7.2 Hz, 4H), 1.57–1.48 (m, 4H), 0.88 (t, J = 7.6 Hz, 6H); ^{13}C NMR (CD_3OD): δ 168.4, 160.8, 136.1, 125.2, 112.1, 52.2, 42.5, 23.4, 11.8.

4.6. One-pot synthesis of $(NHC)_2PdCl_2$ complex **1d** from **1a**

A suspension of **1a** (0.21 mmol, 56 mg) and silver(I) oxide (0.105 mmol, 24 mg) in CH_2Cl_2 (10 mL) was stirred in the dark at room temperature. After 4 h, $PdCl_2(CH_3CN)_2$ (0.1 mmol, 26 mg) was added in the dark at room temperature. The resulting suspension was stirred for 16 h, filtered through a membrane filter (pore size: 0.2 μm), and evaporated to dryness in vacuo. The desired Pd complex was purified by column chromatography (SiO_2, $CHCl_3/CH_3OH$, 10/1) to give **1d** as a white solid (55 mg, 86% yield). **1d**

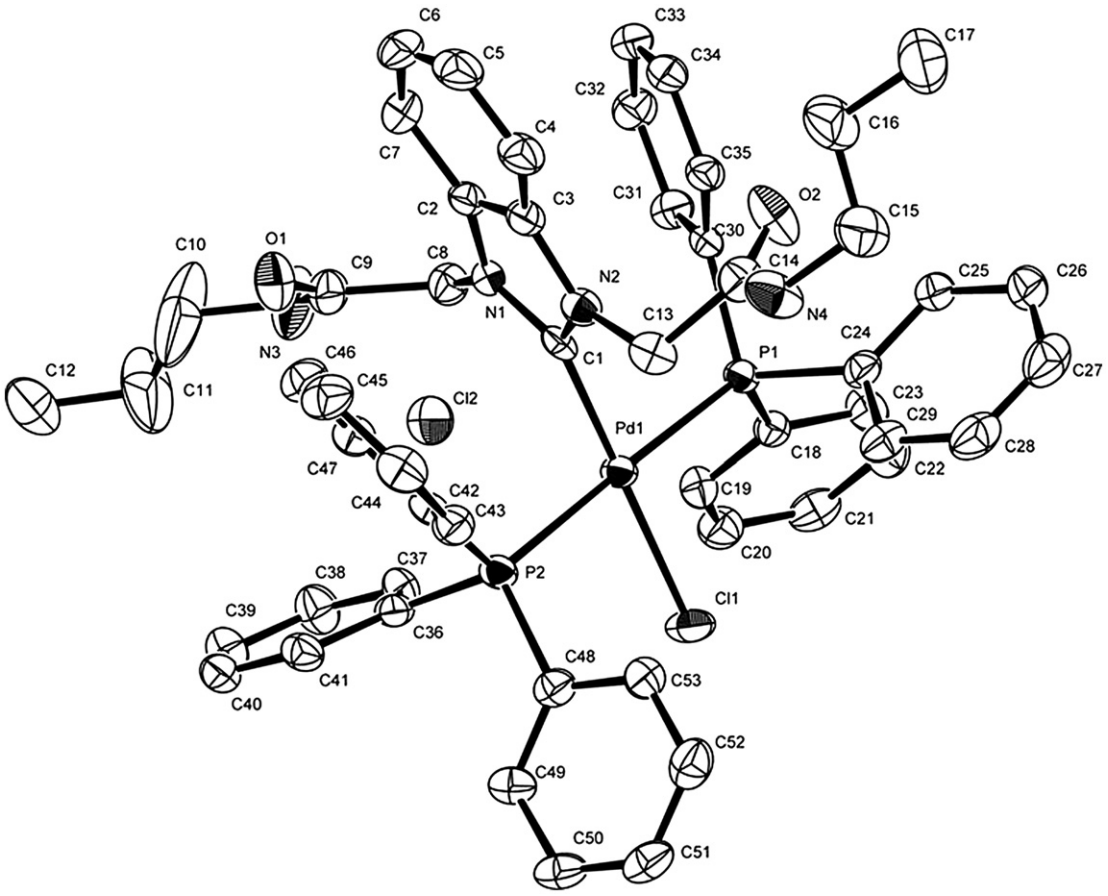


Fig. 3. Molecular structure of $[(NHC)(PPh_3)_2PdCl]^+Cl^-$ complex **2f** with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity and selected lengths [Å] and angles [deg] are as follows: Pd1–C1 2.000(3), Pd1–P1 2.3587(9), Pd1–P2 2.3454(9), Pd1–Cl1 2.3344(7), C1–Pd1–P1 91.99(9), C1–Pd1–P2 90.09(9), P1–Pd1–Cl1 90.21(2), P2–Pd1–Cl1 87.74(3).

(major): ^{1}H NMR ($CDCl_3$): δ 7.59–7.35 (m, 8H), 7.06–7.01 (m, 2H), 5.59 (s, 4H), 4.37 (s, 6H), 3.21–3.14 (m, 4H), 1.48–1.38 (m, 4H), 0.78–0.73 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 180.5, 166.5, 133.9, 133.8, 124.1, 124.0, 110.8, 110.4, 52.3, 41.5, 34.5, 22.3, 11.2. **1d** (minor): ^{1}H NMR ($CDCl_3$): δ 7.59–7.35 (m, 8H), 7.06–7.01 (m, 2H), 5.51 (s, 4H), 4.44 (s, 6H), 3.21–3.14 (m, 4H), 1.48–1.38 (m, 4H), 0.78–0.73 (m, 6H); ^{13}C NMR ($CDCl_3$) : δ 180.2, 166.2, 134.8, 133.8, 124.1, 124.0, 111.2, 110.3, 52.4, 41.5, 34.6, 22.3, 11.2. Anal. Calc. for $C_{26}H_{34}Cl_2N_6O_2Pd$: C, 48.80; H, 5.36; N, 13.13. Found: C, 48.69; H, 5.30; N, 13.00%.

4.7. One-pot synthesis of $(NHC)_2PdCl_2$ complex **2d** from **2a**

The reaction was performed as described above using **2a** (0.21 mmol, 74 mg) instead of **1a**. The desired Pd complex was purified by column chromatography (SiO_2, $CHCl_3/CH_3OH$, 9/1) to give **2d** as a white solid (68 mg, 82% yield). **2d**: ^{1}H NMR ($CDCl_3$): δ 7.63–7.42 (m, 8H), 6.90 (br, 4H), 5.51 (s, 8H), 3.21 (q, J = 6.0 Hz, 8H), 1.50–1.41 (m, 8H), 0.78 (t, J = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$): δ 165.9, 154.6, 124.9, 111.4, 104.4, 64.9, 41.6, 22.4, 11.2. Anal. Calc. for $C_{34}H_{48}Cl_2N_8O_4Pd$: C, 50.41; H, 5.97; N, 13.83. Found: C, 50.48; H, 5.73; N, 13.94%.

4.8. One-pot synthesis of $(NHC)(PPh_3)PdCl_2$ complex **1e** from **1a**

A mixture of **1a** (0.22 mmol, 55 mg) and silver(I) oxide (0.11 mmol, 26 mg) in CH_3OH (10 mL) was stirred in the dark at reflux temperature for 24 h, then concentrated under reduced pressure. To the resulting white solid, silver complex was added $PdCl_2(PPh_3)_2$ (0.2 mmol, 140 mg) in CH_3CN (10 mL). The mixture was stirred at reflux temperature in the dark for 24 h, filtered through a membrane filter (pore size: 0.2 μm), evaporated to dryness in vacuo. The desired Pd complex was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 9/1) to give **1e** as a white solid (115 mg, 86% yield). **1e**: ^{1}H NMR ($CDCl_3$): δ 7.70–7.17 (m, 19H), 5.63 (d, J = 15.2 Hz, 1H), 4.07 (d, J = 15.2 Hz, 1H), 3.93 (s, 3H), 3.06 (q, J = 6.4 Hz, 2H), 1.41–1.33 (m, 2H), 0.66 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 207.0, 165.3, 133.9, 133.8, 133.3, 132.1, 131.5, 129.3, 128.7, 128.5, 124.1, 124.1, 110.9, 110.0, 41.6, 34.5, 30.9, 22.0, 11.1. Anal. Calc. for $C_{31}H_{32}Cl_2N_3OPPd\bullet CHCl_3\bullet 0.5H_2O$: C, 48.09; H, 4.29; N, 5.26. Found: C, 47.78; H, 4.09; N, 5.17%. Crystallization of **1e** by slow evaporation from chloroform solution gave colorless crystals suitable for study by X-ray diffraction. Crystal data: $C_{31}H_{32}Cl_2N_3OPPd\bullet 2CHCl_3$, M = 909.60, monoclinic, a = 13.6410(12), b = 14.0267(14), c = 20.0749(18) Å, β = 93.534(3)°, U = 3833.8(6) Å^3, T = 123(2) K, space group $P2_1/c$ (no. 14), Z = 4, μ (Mo-Kα) = 10.321 cm^{-1}. The final Rw was 0.1382 ($I > 1\sigma(I)$).

4.9. One-pot synthesis of $(NHC)(PPh_3)PdCl_2$ complex **2e** and $[(NHC)(PPh_3)_2PdCl]^+Cl^-$ complex **2f** from **1a**

The reaction was performed as described above using **2a** (0.22 mmol, 77 mg) instead of **1a**. The desired Pd complexes were purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 9/1) to give **2e** (119 mg, 79% yield) and **2f** (22 mg, 11% yield) as white solids. **2e**: ^{1}H NMR (CD_3OD): δ 7.66–7.26 (m, 19H), 5.30 (d, J = 16.8 Hz, 2H), 4.77 (d, J = 16.8 Hz, 2H), 3.06–3.01 (m, 2H), 2.93–2.87 (m, 2H),

1.47–1.38 (m, 4H), 0.81 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (CD_3OD): δ 167.4, 153.9, 135.5, 135.4, 133.1, 133.0, 132.7, 130.0, 129.9, 129.8, 129.7, 125.3, 112.6, 52.2, 42.5, 23.3, 11.7. Anal. Calc. for $C_{35}H_{39}Cl_2N_4O_2PPd\bullet H_2O$: C, 54.31; H, 5.34; N, 7.24. Found: C, 54.29; H, 5.16; N, 7.19%. **2f**: ^{1}H NMR ($CDCl_3$): δ 7.64–7.26 (m, 36H), 5.59 (d, $J = 15.1$ Hz, 2H), 4.36 (d, $J = 15.1$ Hz, 2H), 3.16–3.11 (m, 2H), 3.01–2.98 (m, 2H), 1.41–1.33 (m, 4H), 0.66 (t, $J = 7.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 165.1, 137.1, 137.0, 134.0, 133.9, 133.8, 133.6, 133.6, 131.6, 131.6, 128.8, 128.7, 128.5, 128.4, 124.7, 111.2, 52.8, 41.5, 22.1, 11.2. Anal. Calc. for $C_{53}H_{54}Cl_2N_4O_2P_2Pd\bullet H_2O$: C, 61.43; H, 5.45; N, 5.41. Found: C, 61.85; H, 5.26; N, 5.51%. Crystallization of **2f** by slow evaporation from chloroform solution gave colorless crystals suitable for study by X-ray diffraction. Crystal data: $C_{53}H_{54}Cl_2N_4O_2P_2Pd$, $M = 1018.29$, monoclinic, $a = 12.4319(5)$, $b = 21.1834(9)$, $c = 18.5787(6)$ Å, $\beta = 95.0686(13)^\circ$, $U = 4873.6(3)$ Å^3, $T = 123(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, μ (Mo-Kα) = 3.005 cm^{-1}. The final wR^2 was 0.1247 (all data).

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Appendix A. Supplementary data

CCDC 799806 and 799807 contain the supplementary crystallographic data for **1e** and **2f**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.02.009.

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