



Synthesis and structural characterization of metal complexes based on pyrazole/imidazolium chlorides

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Abstract

A series of imidzoalium salt, $L \cdot HCl$, for the potentially bidentate pyrazole/*N*-heterocyclic carbene was synthesized. Reactions of a 2:1 mixture between $L \cdot HCl$ bearing bulky *N*-substitution and Ag_2O produced $Ag(L)Cl$, whereas a novel compound with unique stoichiometry $AgL_2(AgCl)_{0.5}Cl$ was produced from $L \cdot HCl$ bearing *N*-methyl group under identical condition. Reactions of $L \cdot HCl$ with $PdCl_2$ produced zwitterionic $Pd^{II}Cl_3L \cdot H$. Selected structural determinations on $L \cdot HCl$, $Ag(L)Cl$, $AgL_2(AgCl)_{0.5}Cl$, and $Pd^{II}Cl_3L \cdot H$ revealed intriguing crystal chemistry in which the less-stable *gauche* rotamers were obtained exclusively. A preliminary application of the zwitterionic complexes, $Pd^{II}Cl_3L \cdot H$, in Heck coupling reaction of aryl bromide with *n*-butyl acrylate shows effective activity.

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Keywords: Pyrazole; Imidazolium chlorides; *Gauche* preference; Palladium complex; X-ray determination; Heck reaction

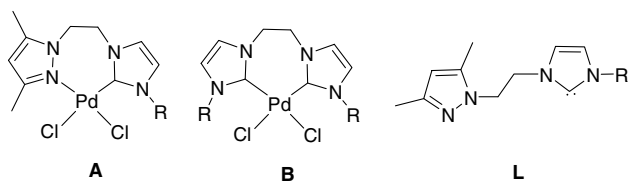
1. Introduction

In the past 10 years, *N*-heterocyclic carbenes (NHC) are receiving much attention for their wide applicability in coordination chemistry and catalysis [1]. They are generally accessible via deprotonation of imidazolium salts. Recently, research efforts have also been devoted for the synthesis of functionalized *N*-heterocyclic carbene ligands [2,3]. Incorporation of the carbene functionality into ligand systems containing other ‘classical’ donor groups offers vast opportunities for ligand design which may lead to the discovery of new efficient catalysts. Along this direction, we started out a project to explore if the new seven-member palladacycle **A** with a pyrazole-functionalized NHC carbene **L** is a more effective catalyst than the structurally similar palladium bis(NHC) compound **B** (Scheme 1) [4].

In this paper, we report the synthesis of imidazolium chloride $L \cdot HCl$ with pyrazole/NHC precursor functionality and its metal complexes. Interesting, in the course of our investigation, we structurally characterized selected examples of the ligand precursor $L \cdot HCl$, their silver NHC complexes AgL , and a zwitterionic palladium compound $Pd^{II}Cl_3L \cdot H$, which display intriguing crystal chemistry. Most importantly, the ethylene spacer in **L** has a high preference to adopt the less stable *gauche* conformation as revealed by X-ray structural analysis. The anomalous *gauche* effect in 1,2-difluoroethane, with the *gauche* rotamer being more stable than its *anti* rotamer, has been widely reported and can be attributed to a stereo-electronic nature [5]. Alternatively, the energetic *gauche* rotamer can be stabilized by intermolecular forces such as hydrogen bonds in the crystal lattice [6]. Although, a DFT theoretical computation on the silver and palladium complexes indicates that the *anti* conformations are more stable in the gas phase, the structural analysis of a variety of compounds strongly indicate a *gauche* preference in the solid state.

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Scheme 1.

This *gauche* preference provides a potential utility of compounds based on $L \cdot HCl$ in the construction of novel supramolecular solids for materials and bio-organic applications.

Neutral and cationic palladium(II) complexes are widely used as catalyst precursors in $C_{sp^2}-C_{sp^2}$ coupling reactions [7]. However, zwitterionic palladium complexes with different electrophilicities and donor ligand lability in comparison with the neutral and cationic complexes have not previously been employed. To understand the utility of the zwitterionic system in C–C coupling reactions, a preliminary application of $Pd^{II}Cl_2L \cdot H$ in Heck coupling reaction of aryl bromide with *n*-butyl acrylate is also reported, which shows effective activity.

2. Experimental

2.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using a Schlenk line with 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 and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 and 75.48 MHz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for 1H and ^{13}C spectra were recorded in ppm relative to residual proton of $CDCl_3$ (1H : δ 7.24; ^{13}C : δ 77.0) and $DMSO-d_6$ (1H : δ 2.50; ^{13}C : δ 39.5). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at Instrument Center, National Chung Hsing University, Taiwan. 1-Naphthalen-1-ylmethyl-1*H*-imidazole [4], 1-(4-fluorobenzyl)-1*H*-imidazole [4], and 1-(2,4,6-trimethylphenyl)-1*H*-imidazole [8] were synthesized according to the literature procedures.

2.2. 1-(2-Chloroethyl)-3,5-dimethyl-1*H*-pyrazole

A 50 mL 1,2-dichloroethane solution of KOH (15.57 g, 0.28 mol), K_2CO_3 (12.16, 0.09 mol), tetrabutylammonium chloride (0.24 g, 0.88 mmol), and 3,5-dimethylpyrazole (4.00 g, 0.04 mmol) was heated at

45 °C for 3.5 h. The solution was filtered, washed with water, and dried with anhydrous $MgSO_4$. Removal of the solvent under vacuum gave a yellow liquid as pure product. Yield: 4.7 g (71%). 1H NMR ($CDCl_3$): δ 2.11 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.74 (t, $^3J_{HH} = 6.3$ Hz, 2H, CH_2), 4.13 (t, $^3J_{HH} = 6.3$ Hz, 2H, CH_2), 5.69 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.7 (C_3), 13.2 (C_3), 42.7 (C_2), 49.4 (C_2), 104.8 (py-CH), 139.4 (quaternary C), 147.9 (quaternary C).

2.3. General procedure for the preparation of 1a–1d

A mixture of 1-(2-chloroethyl)-3,5-dimethyl-1*H*-pyrazole and an appropriate *N*-substituted imidazole with mole ratio of ca. 1:2–4 in 10–30 mL of DMF was heated at 120 °C for 1 day. The solvent was allowed to remove completely under vacuum. Upon addition of diethylether, the solid formed was filtered, washed with more diethylether, and dried under vacuum.

2.4. 1-[2-(3,5-Dimethylpyrazol-1-yl)ethyl]-3-(4-fluorobenzyl)-3*H*-imidazol-1-ium chloride (1a)

1-(2-Chloroethyl)-3,5-dimethyl-1*H*-pyrazole (1.00 g, 6.30 mmol) and 1-(4-fluorobenzyl)-1*H*-imidazole (4.44 g, 25.22 mmol) were used. A cream-white solid was obtained. Yield: 2.09 g (96%). Anal. Calc. for $C_{17}H_{20}ClFN_4$: C, 60.98; H, 6.02; N, 16.73. Found: C, 60.87; H, 6.10; N, 16.71%. m.p. 180–185 °C. 1H NMR ($CDCl_3$): δ 1.90 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 4.42 (d, $^3J_{HH} = 5.4$ Hz, 2H, CH_2), 4.86 (d, $^3J_{HH} = 5.4$ Hz, 2H, CH_2), 5.48 (s, 2H, CH_2), 5.62 (s, 1H, CH), 6.88 (s, 1H, imi-*H*), 7.00 (t, $^3J_{HH} = ^3J_{HF} = 8.7$ Hz, 2H, Ar-*H*), 7.24 (s, 1H, imi-*H*), 7.43 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 5.1$ Hz, 2H, Ar-*H*), 10.30 (s, 1H, NCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.6 (C_3), 13.3 (C_3), 47.8 (C_2), 49.2 (C_2), 52.6 (C_2), 105.6 (py-CH), 116.4 (d, $^2J_{CF} = 21.8$ Hz, C_{meta}), 121.2 (imi-CH), 122.9 (imi-CH), 129.0 (C_{ipso}), 135.7 (d, $^3J_{CF} = 8.4$ Hz, C_{ortho}), 137.6 (py-C), 140.4 (py-C), 148.7 (NCHN), 163.1 (d, $^1J_{HF} = 250.0$ Hz, C-F).

2.5. 1-[2-(3,5-Dimethylpyrazol-1-yl)ethyl]-3-(2,4,6-trimethylbenzyl)-3*H*-imidazol-1-ium chloride (1b)

1-(2-Chloroethyl)-3,5-dimethyl-1*H*-pyrazole (0.54 g, 3.39 mmol) and 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (1.26 g, 6.78 mmol) were used. An off-white solid was obtained. Yield: 0.68 g (58%). Anal. Calc. for $C_{19}H_{25}ClN_4$: C, 50.77; H, 4.14; N, 4.93. Found: C, 50.67; H, 4.13; N, 4.91%. m.p. 203–205 °C. 1H NMR ($CDCl_3$): δ 1.93 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 4.57 (m, 2H, CH_2), 5.18 (m, 2H, CH_2), 5.68 (s, 1H, CH), 6.91 (s, 2H, Ar-*H*), 7.04 (s, 1H, imi-*H*), 7.51 (s, 1H, imi-*H*), 10.00 (s, 1H, NCHN).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 11.1 (C_3), 13.4 (C_3), 17.3 (C_3), 21.0 (C_3), 48.0 (C_2), 49.5 (C_2), 105.6 (py-CH), 122.5 (imi-CH), 123.7 (imi-CH), 129.8 (Ar-CH), 130.5 (quaternary C), 134.0 (quaternary C), 138.3 (quaternary C), 140.5 (quaternary C), 141.3 (quaternary C), 148.6 (NCHN).

2.6. 1-[2-(3,5-Dimethylpyrazol-1-yl)ethyl]-3-naphthalen-1-ylmethyl-3H-imidazol-1-ium chloride (**1c**)

1-(2-Chloroethyl)-3,5-dimethyl-1H-pyrazole (2.35 g, 14.80 mmol) and 1-naphthalen-1-ylmethyl-1H-imidazole (9.16 g, 43.90 mmol) were used. A white solid was obtained. Yield: 4.09 g (75%). Anal. Calc. for $\text{C}_{21}\text{H}_{23}\text{ClN}_4$: C, 68.74; H, 6.32; N, 15.27. Found: C, 68.69; H, 6.23; N, 15.18%. m.p. 115–120 °C. ^1H NMR (CDCl_3): δ 1.85 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 4.45 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 4.95 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 5.50 (s, 1H, CH), 5.93 (s, 2H, CH_2), 6.94 (s, 1H, imi-H), 7.14 (s, 1H, imi-H), 7.47–7.62 (m, 4H, Ar-H), 7.85–7.98 (m, 3H, Ar-H), 10.48 (s, 1H, NCHN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.6 (C_3), 13.3 (C_3), 47.8 (C_2), 49.2 (C_2), 51.4 (C_2), 105.4 (py-CH); 121.3, 122.5, 122.8, 125.4, 126.7, 127.9, 129.1, 130.8, 133.4, 137.5, 140.5, (py-C, Ar-C, Ar-CH, imi-CH); 148.7 (NCHN).

2.7. 1-[2-(3,5-Dimethylpyrazol-1-yl)ethyl]-3-methyl-3H-imidazol-1-ium chloride (**1d**)

1-(2-Chloroethyl)-3,5-dimethyl-1H-pyrazole (2.01 g, 12.60 mmol) and 1-methylimidazole (4.0 mL, 50.40 mmol) were used. A white solid was obtained. Yield: 2.40 g (80%). Anal. Calc. for $\text{C}_{11}\text{H}_{17}\text{ClN}_4$: C, 54.88; H, 7.12; N, 23.27. Found: C, 54.77; H, 7.13; N, 23.25%. m.p. 198–202 °C. ^1H NMR (CDCl_3): δ 1.93 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.94 (s, 3H, NCH₃), 4.36 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 4.84 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 5.64 (s, 1H, CH), 6.79 (s, 1H, imi-H), 7.43 (s, 1H, imi-H), 10.22 (s, 1H, NCHN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.8 (C_3), 13.4 (C_3), 36.6 (C_3), 47.9 (C_2), 48.9 (C_2), 105.7 (py-CH), 123.0 (imi-CH), 122.7 (imi-CH), 138.0 (py-C), 140.4 (py-C), 148.7 (NCHN).

2.8. General procedure for the preparation of **2a–2d**

A mixture of **1** and Ag_2O (2:1) was stirred in ca. 20 mL of dichloromethane in the dark overnight. The solution was then filtered through a small pad of Celite. The solvent was removed completely under vacuum. Upon addition of diethylether, the solid formed was filtered, washed with more diethylether and dried under vacuum.

2.9. Preparation of **2a**

Complex **1a** (0.83 g, 2.47 mmol) and Ag_2O (0.29 g, 1.24 mmol) were used. A yellow solid was obtained.

Yield: 0.83 g (76%). Anal. Calc. for $\text{C}_{17}\text{H}_{19}\text{AgClF}_1\text{N}_4$: C, 46.23; H, 4.34; N, 12.68. Found: C, 46.20; H, 4.31; N, 12.65%. m.p. 60–65 °C. ^1H NMR (CDCl_3): δ 1.80 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 4.32 (t, $^3J_{\text{HH}} = 5.4$ Hz, 4H, CH_2), 4.59 (t, $^3J_{\text{HH}} = 5.4$ Hz, 4H, CH_2), 5.26 (s, 2H, CH_2), 5.70 (s, 1H, CH), 6.46 (s, 2H, imi-H), 6.84 (s, 2H, imi-H), 7.03 (t, $^3J_{\text{HH}} = 3J_{\text{HF}} = 8.3$ Hz, 2H, Ar-H), 7.25 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 5.4$ Hz, 2H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 15.1 (C_3), 18.7 (C_3), 53.6 (C_2), 56.4 (C_2), 58.5 (C_2), 109.7 (py-CH), 120.6 (d, $^2J_{\text{CF}} = 21.6$ Hz, C_{meta}), 127.4 (imi-CH), 127.5 (imi-CH), 134.7 (d, $^3J_{\text{CF}} = 8.4$ Hz, C_{ortho}), 138.5 (C_{ipso}), 144.6 (py-C), 152.2 (py-C), 166.9 (d, $^1J_{\text{HC}} = 244.1$ Hz, CF), 184.5 (Ag-C).

2.10. Preparation of **2b**

Complex **1b** (0.19 g, 0.55 mmol) and Ag_2O (63 mg, 0.27 mmol) were used. A grey-white solid was obtained. Yield: 0.19 g (75%). Anal. Calc. for $\text{C}_{19}\text{H}_{24}\text{AgClN}_4$: C, 50.52; H, 5.36; N, 12.40. Found: C, 50.48; H, 5.30; N, 12.51%. m.p. 175–180 °C. ^1H NMR (CDCl_3): δ 1.93 (s, 6H, CH_3), 2.02 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.36 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 4.69 (t, $^3J_{\text{HH}} = 4.8$ Hz, 2H, CH_2), 5.77 (s, 1H, CH), 6.64 (s, 1H, imi-H), 6.81 (s, 1H, imi-H), 6.94, (s, 2H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.9 (C_3), 13.5 (C_3), 17.6 (C_3), 21.0 (C_3), 49.0 (C_2), 51.6 (C_2), 105.5 (py-CH), 121.6 (imi-C), 122.6 (imi-C), 129.5 (Ar-CH), 134.4 (quaternary C), 135.1 (quaternary C), 139.6 (quaternary C), 139.8 (quaternary C), 148.7 (quaternary C), signal for Ag-C was not observed.

2.11. Preparation of **2c**

Complex **1c** (0.49 g, 1.33 mmol) and Ag_2O (0.16 g, 0.66 mmol) were used. A white solid was obtained. Yield: 0.45 g (72%). Anal. Calc. for $\text{C}_{21}\text{H}_{22}\text{AgClN}_4$: C, 53.24; H, 4.68; N, 11.83. Found: C, 53.29; H, 4.62; N, 11.83%. m.p. 90–92 °C. ^1H NMR (CDCl_3): δ 1.75 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 4.29 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 4.58 (t, $^3J_{\text{HH}} = 5.4$ Hz, 2H, CH_2), 5.66 (s, 1H, CH), 5.70 (s, 2H, CH_2), 6.31 (s, 1H, imi-H), 6.68 (s, 1H, imi-H), 7.32–7.54 (m, 4H, Ar-H), 7.85–7.90 (m, 3H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.6 (C_3), 13.5 (C_3), 49.1 (C_2), 51.8 (C_2), 53.7 (C_2), 105.2 (py-CH), 120.8, 121.8, 122.7, 125.3, 126.3, 127.1, 127.5, 127.9, 129.0, 130.3, 130.8, 133.8, 140.0, 148.7 (py-C, Ar-C, Ar-CH, imi-CH), 180.6 (Ag-C).

2.12. Preparation of **2d**

Complex **1d** (0.33 g, 1.38 mmol) and Ag_2O (0.16 g, 0.69 mmol) were used. A white solid was obtained. Yield: 0.42 g (88%). Anal. Calc. for $\text{C}_{22}\text{H}_{32}\text{Ag}_{1.5}\text{Cl}_{1.5}\text{N}_8$: C, 42.38; H, 5.17; N, 17.97. Found: C, 42.41; H, 5.13; N,

17.90%. m.p. 98–100 °C. ^1H NMR (CDCl_3): δ 1.81 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 3.76 (s, 3H, CH_3), 4.23 (t, $^3J_{\text{HH}} = 5.4$ Hz, 4H, CH_2), 4.49 (t, $^3J_{\text{HH}} = 5.4$ Hz, 4H, CH_2), 5.66 (s, 2H, CH), 6.34 (s, 2H, imi-*H*), 6.80 (s, 2H, imi-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 10.6 (C_3), 13.5 (C_3), 38.8 (C_3), 49.2 (C_2), 51.4 (C_2), 105.2 (py-CH), 121.8 (imi-CH), 121.9 (imi-CH), 140.0 (py-C), 148.6 (py-C), 180.5 (Ag-C).

2.13. General procedure for the preparation of **3a–3d**

A mixture of **1** and PdCl_2 (2:1) was stirred in ca. 10 mL of DMF at room temperature for 4 h. The solvent was removed completely under vacuum. The solid, formed upon addition of THF, was filtered, washed with more THF, and dried under vacuum.

2.14. Preparation of **3a**

Complex **1a** (0.27 g, 0.78 mmol) and PdCl_2 (69 mg, 0.39 mmol) were used. An orange solid was obtained. Yield: 0.20 g (100%). Anal. Calc. for $\text{C}_{17}\text{H}_{20}\text{Cl}_3\text{FN}_4\text{Pd}$: C, 39.87; H, 3.94; N, 10.94. Found: C, 39.98; H, 3.83; N, 10.91%. m.p. 201 °C. ^1H NMR (DMSO-d_6): δ 1.95 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 4.38 (t, $^3J_{\text{HH}} = 5.7$ Hz, 2H, CH_2), 4.56 (t, $^3J_{\text{HH}} = 5.7$ Hz, 2H, CH_2), 5.38 (s, 2H, CH_2), 5.74 (s, 1H, CH), 7.27 (t, $^3J_{\text{HH}} = ^3J_{\text{HF}} = 8.4$ Hz, 2H, Ar-*H*), 7.41 (virtual t, $^3J_{\text{HH}} = ^4J_{\text{HH}} = 5.4$ Hz, 2H, Ar-*H*), 7.62 (s, 2H, imi-*H*), 7.78 (s, 2H, imi-*H*), 8.94 (s, 1H, NCH N). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6): δ 15.3 (C_3), 18.4 (C_3), 52.3 (C_2), 54.0 (C_2), 56.1 (C_2), 110.1 (py-CH), 120.6 (d, $^2J_{\text{CF}} = 21.8$ Hz, C_{meta}), 127.5 (imi-CH), 128.2 (imi-CH), 135.7 (d, $^3J_{\text{CF}} = 8.7$ Hz, C_{ortho}), 136.3 (C_{ipso} py-C), 141.7 (py-C), 143.0 (d, $^1J_{\text{HC}} = 210.4$ Hz, CF), 152.0 (NCHN).

2.15. Preparation of **3b**

Complex **1b** (81 mg, 0.23 mmol) and PdCl_2 (21 mg, 0.12 mmol) were used. A dark brown solid was obtained. Yield: 42 mg (70%). Anal. Calc. for $\text{C}_{19}\text{H}_{25}\text{Cl}_3\text{N}_4\text{Pd}$: C, 43.70; H, 4.83; N, 10.73. Found: C, 43.38; H, 4.92; N, 10.63%. m.p. >280 °C. ^1H NMR (DMSO-d_6): δ 1.95 (s, 6H, CH_3), 2.00 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.51 (br s, 2H, CH_2), 4.67 (br s, 2H, CH_2), 5.79 (s, 1H, CH), 7.13 (s, 2H, Ar-*H*), 7.97 (s, 1H, imi-*H*), 7.87 (s, 1H, imi-*H*), 9.23 (s, 1H, NCHN). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6): δ 10.8 (C_3), 13.7 (C_3), 17.2 (C_3), 21.0 (C_3), 47.5 (C_2), 49.6 (C_2), 105.5 (py-CH), 123.7 (imi-CH), 124.3 (imi-CH), 129.6 (Ar-CH), 131.4 (quaternary C), 134.6 (quaternary C), 138.1 (quaternary C), 139.7 (quaternary C), 140.7 (quaternary C), 147.2 (NCHN).

2.16. Preparation of **3c**

Complex **1c** (0.30 g, 0.82 mmol) and PdCl_2 (73 mg, 0.41 mmol) were used. An orange solid was obtained. Yield: 0.18 g (82%). Anal. Calc. for $\text{C}_{21}\text{H}_{23}\text{Cl}_3\text{N}_4\text{Pd}$: C, 46.35; H, 4.26; N, 10.29. Found: C, 46.68; H, 4.64; N, 10.25%. m.p. 155–160 °C. ^1H NMR (DMSO-d_6): δ 1.85 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 4.32 (t, 2H, $^3J_{\text{HH}} = 5.1$ Hz, 2H, CH_2), 4.56 (t, 2H, $^3J_{\text{HH}} = 5.1$ Hz, CH_2), 5.54 (s, 1H, CH), 5.89 (s, 2H, CH_2), 7.38–7.63 (m, 5H, imi-*H*, Ar-*H*), 7.81 (s, 1H, imi-*H*), 8.00–8.10 (m, 3H, Ar-*H*), 8.81 (s, 1H, NCHN). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6): δ 10.5 (C_3), 13.6 (C_3), 47.5 (C_2), 49.3 (C_2), 50.2 (C_2), 105.2 (py-CH), 123.3, 126.0, 126.9, 127.6, 127.8, 129.3, 130.0, 130.5, 130.8, 133.8, 137.1, 139.7, 140.0 (py-C, Ar-C, Ar-CH, imi-CH), 147.3 (NCHN).

2.17. Preparation of **3d**

Complex **1d** (0.50 g, 2.08 mmol) and PdCl_2 (0.18 g, 1.04 mmol) were used. An orange solid was obtained. Yield: 0.38 g (86%). Anal. Calc. for $\text{C}_{11}\text{H}_{17}\text{Cl}_3\text{N}_4\text{Pd}$: C, 31.60; H, 4.10; N, 13.40. Found: C, 31.55; H, 4.08; N, 13.37%. m.p. 258–260 °C. ^1H NMR (DMSO-d_6): δ 2.05 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 3.83 (s, 3H, CH_3), 4.39 (t, $^3J_{\text{HH}} = 5.7$ Hz, 2H, CH_2), 4.55 (t, $^3J_{\text{HH}} = 5.7$ Hz, 2H, CH_2), 5.79 (s, 1H, CH), 7.53 (s, 1H, imi-*H*), 7.69 (s, 1H, imi-*H*), 9.02 (s, 1H, NCH N). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6): δ 10.7 (C_3), 13.7 (C_3), 36.2 (C_2), 47.6 (C_2), 49.3 (C_2), 105.5 (py-CH), 123.0 (imi-C), 123.9 (imi-C), 137.4 (py-C), 139.8 (py-C), 147.2 (NCHN).

2.18. 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 4-bromoacetophenone (1.0 mmol), *n*-butyl acrylate (1.4 mmol), anhydrous sodium acetate (1.1 mmol) and 0.5 mol% of catalyst. The flask was thoroughly degassed, added with 5 mL of *N,N*-dimethylacetamide via a syringe, and then placed in a preheated oil bath at 170–175 °C. After 6 h, 10 mL of dichloromethane was added to the reaction mixture and the organic layer was washed with five times of 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. The residue was dissolved in CDCl_3 and analyzed by ^1H NMR.

2.19. X-ray data collection

Crystal of **1a**, **2b**, **2d**, and **3a** were obtained by vapor diffusion of diethylether into its corresponding acetonitrile solution. Typically, the crystal was removed from

the vial with a small amount of mother liquor and immediately coated with silicon grease on a weighting paper. A suitable crystal was mounted on a glass fiber with silicon grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 273(2) K. No decay was observed in 50 duplicate frames at the end of the data collection. Crystallographic data of **1a**, **2b**, **2d**, and **3a** are listed in Table 1.

2.20. 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 [9]. 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.

3. Results

3.1. Synthesis of ligand precursors **1a–1d**

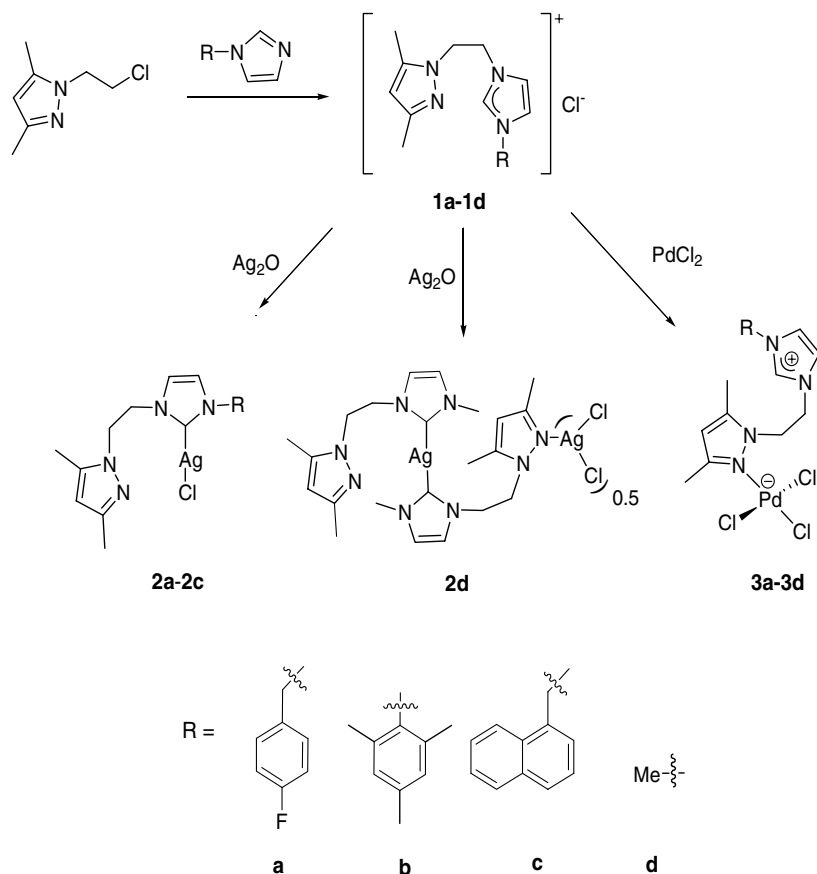
The key intermediate 1-(2-chloroethyl)-3,5-dimethyl-1*H*-pyrazole was first prepared following a published procedure of phase-transfer catalytic approach in 71% yield [10]. The pyrazole/imidazolium chlorides **1a–1d** were then obtained by quaternization reaction of an appropriate *N*-substituted imidazole with the pyrazole derivative in DMF at 120 °C for 1 day (Scheme 2). Excess amount of *N*-substituted imidazoles (2–4 times)

were needed to speed up the reaction and afford better yields. Subsequent removal of solvent and precipitation with diethylether produced **1a–1d** as white solids in good yields (58–96%). All the new imidazolium chlorides obtained dissolve readily in dichloromethane and chloroform. They were characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies as well as elemental analyses. The carbenic hydrogen in **1a–1d** observed at δ 10.00–10.48 is in the usual range of related imidazolium halides (δ 9.0–12.0) [4].

For a representative example of **1**, an X-ray structural determination on a crystal of **1a**, obtained by vapor diffusion of diethylether into an acetonitrile solution, was performed. The molecular structure and its selected bond distances and angles are shown in Fig. 1. The structure of **1a** includes a water molecule in the asymmetric unit, conceivably coming from the wet re-crystallization solvents used. Interestingly, **1a** adopts a less stable *gauche* form instead of its more stable staggered conformation, with a N(2)–C(4)–C(5)–N(3) dihedral angle of 56.71°. Also, the 4-fluorobenzyl group is disposed on the same side of the pyrazolyethyl group across the imidazole ring. To obtain a rationale for this apparent unstable conformation, the packing of the structure was examined carefully. In fact, the solid of **1a** · H₂O forms an intriguing layer structure. In the crystal lattice, each water molecule forms O–H···Cl hydrogen bridges with two chloride anions ($d(\text{H}\cdots\text{Cl}) = 2.556 \text{ \AA}$, $d(\text{O}\cdots\text{Cl}) = 3.236 \text{ \AA}$, and $\angle(\text{OHCl}) = 170.16^\circ$; $d(\text{H}\cdots\text{Cl}) = 2.506 \text{ \AA}$, $d(\text{O}\cdots\text{Cl}) = 3.196 \text{ \AA}$, and $\angle(\text{OHCl}) = 151.92^\circ$) linking an inversion related water molecule together into a cyclic network (Fig. 2). This cyclic network further links up two inversion-related molecules of **1a** through an unconventional

Table 1
Crystallographic data of **1a**, **2b**, **2d**, and **3a**

	1a · H ₂ O	2b	2d · H ₂ O	3a
Empirical formula	C ₁₇ H ₂₀ ClFN ₄ · H ₂ O	C ₁₉ H ₂₄ AgClN ₄	C ₂₂ H ₃₂ Ag _{1.5} Cl _{1.5} N ₈ · H ₂ O	C ₁₇ H ₂₀ Cl ₃ F ₄ N ₄
Formula weight	352.84	451.74	641.55	512.12
Color and Habit	Colorless prism	Colorless prism	Colorless prism	Orange prism
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> <i>c</i>
<i>a</i> (Å)	15.192(9)	7.522(2)	10.707(3)	19.73(5)
<i>b</i> (Å)	14.130(9)	18.098(5)	10.813(3)	9.76(2)
<i>c</i> (Å)	8.558(5)	15.066(5)	14.121(4)	13.19(3)
α (°)	90	90	72.255(10)	90
β (°)	93.94(3)	101.94(3)	89.616(12)	127.20(5)
γ (°)	90	90	64.814(13)	90
<i>V</i> (Å ³)	1832.7(19)	2006.6(11)	1394.7(7)	2024(8)
<i>T</i> (K)	273(2)	273(2)	273(2)	273(2)
<i>Z</i>	4	4	2	4
<i>D</i> _{calcd} (Mg/m ³)	1.279	1.495	1.528	1.680
μ (mm ⁻¹)	0.229	1.146	1.236	1.330
Range of transmission factor	0.96–0.47	0.83–0.76	0.81–0.78	0.90–0.87
Number of unique data	4310	4727	5400	2851
Number of parameters refined	218	226	316	224
<i>R</i> ₁ [<i>I</i> > 2 σ <i>I</i>]	0.0547	0.0410	0.0865	0.0930
<i>WR</i> ₂ (all data)	0.1822	0.1174	0.2509	0.2558



Scheme 2.

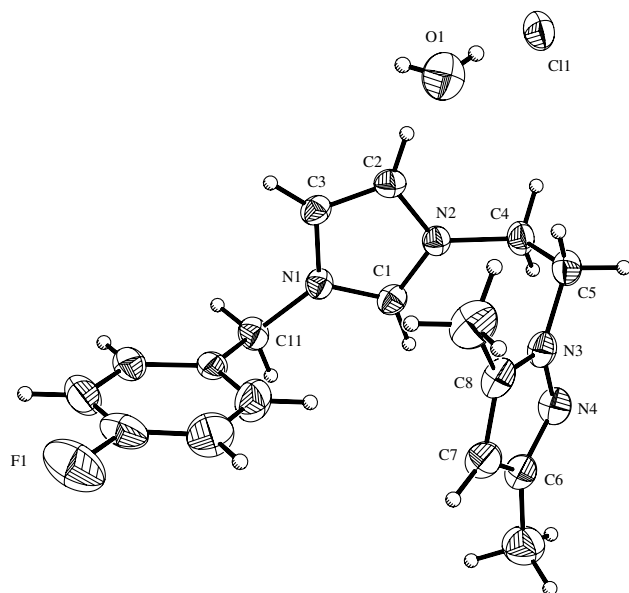


Fig. 1. Molecular structure of **1a** · H₂O. Selected bond distances (Å): N(1)–C(1), 1.327(3); N(2)–C(1), 1.320(3); N(3)–N(4), 1.356(3); Selected bond angles (°): C(1)–N(1)–C(3), 108.1(2); C(1)–N(2)–C(2), 108.2(2); N(1)–C(1)–N(2), 109.1(2); C(6)–N(4)–N(3), 104.9(2).

hydrogen contact between the oxygen and hydrogen atom upon C(7) ($d(\text{H}\cdots\text{O}) = 2.395 \text{ \AA}$, $d(\text{O}\cdots\text{C}) = 3.174 \text{ \AA}$, and $\angle(\text{OHC}) = 141.2^\circ$). This supramolecular hydrogen network together with π – π stacking of imidazole and phenyl rings generate a layer structure in which the chloride anions and water molecules are concentrated in the central hydrophilic portions of each layer. The organic portions with all the fluorine atoms pointing away from the central portions form the fluororous layers that sandwich the ionic portions. It is reasonable to suggest that the more energetic *gauche* conformation in **1a** is stabilized by the formation of such layer packing structure.

3.2. Synthesis of silver complexes **2a–2c**

By stirring a dichloromethane solution of the ligand precursors **1a–1c** and Ag₂O in a molar ratio of 2:1 overnight, white solids of **2a–2c** were formed after simple work-up procedure. The compounds are air-stable and soluble readily in dichloromethane and chloroform. The ¹H NMR spectra of **2a–2c** clearly show that the carbenic protons of **1a–1c** were absent, indicating the successful deprotonation and formation of Ag(NHC) moiety. It has been shown that reactions of imidazolium salts with Ag₂O can afford silver NHC compounds with

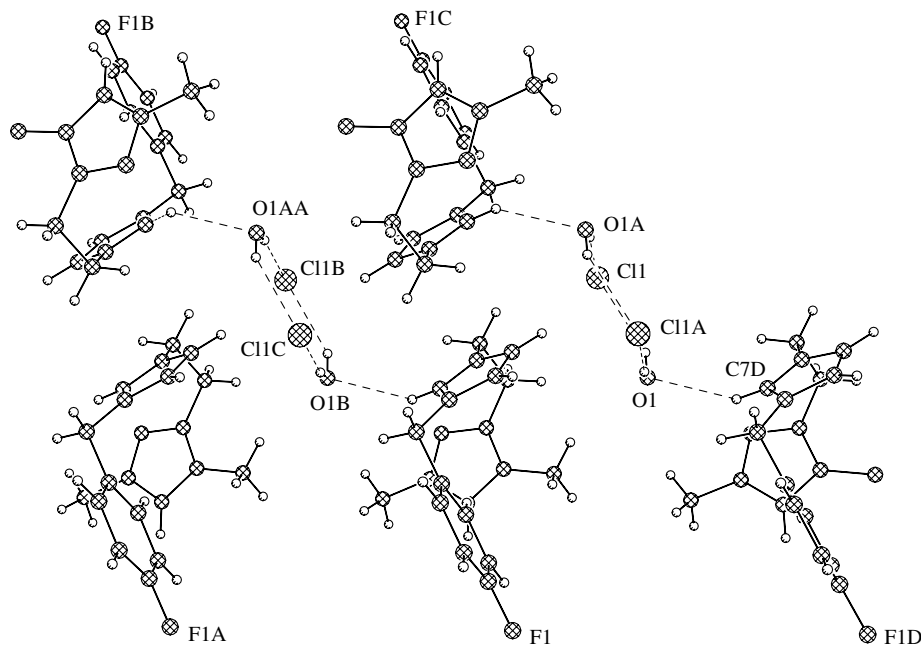


Fig. 2. A view of the layer structure in **1a** along *a*-axis showing the hydrogen contacts between the water molecules, chloride anions, and organic cations.

a wide range of stoichiometry, including 1:1 or 2:1 Ag/NHC adducts [11]. In order to confirm the stoichiometry of the white products formed, an X-ray structural analysis on a crystal of **2b** was performed. The molecular structure and its selected bond distances and angles are shown in Fig. 3. The structure confirms that **2b** was Ag(L)Cl with 1:1 L:Ag(I) stoichiometry. The

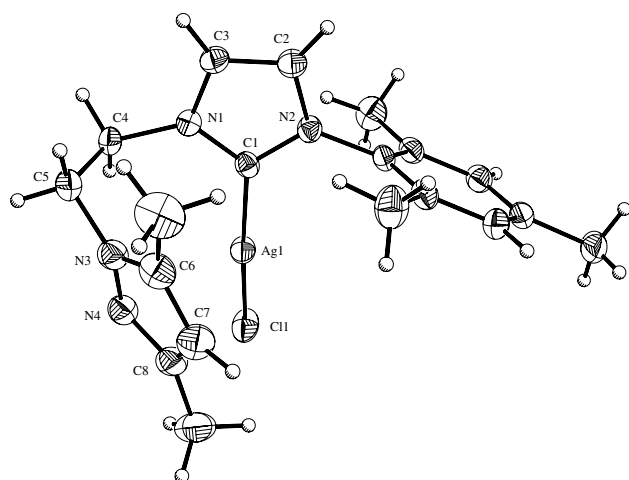


Fig. 3. Thermal ellipsoid plot of **2b** at the 30% probability level. Selected bond distances (Å): Ag(1)–Cl(1), 2.083(4); Ag(1)–C(1), 2.3375(12); N(1)–C(1), 1.355(5); N(2)–C(1), 1.352(5); N(3)–N(4), 1.364(5); Selected bond angles (°): C(1)–Ag(1)–Cl(1), 171.71(11); N(1)–C(1)–Ag(1), 128.1(3); N(2)–C(1)–Ag(1), 127.2(3); C(1)–N(1)–C(3), 110.9(3); C(1)–N(2)–C(2), 111.2(3); N(1)–C(1)–N(2), 104.3(3); C(8)–N(4)–N(3), 105.1(4).

Ag(I) center adopts a distorted linear coordination geometry with a bond angle of 171.71(11)°. The Ag(1)–C(1) distance of 2.083(4) Å and Ag(1)–Cl(1) distance of 2.436(8) Å are within expected values.

Our previous structural studies on several bis(imidazolium) salts indicated that different *N*-substitutions have little effect on structural dimensions of the imidazole rings [4,12]. Therefore, even though crystal structures of **1b** and **2a** were not obtained, it would be still of significant interest to compare the structures of **1a** and **2b** for the dimensional change of the imidazole ring upon deprotonation and coordination to the silver(I) center. The structural change of the imidazole ring is best visualized by turning to Fig. 4, which compares the bond lengths and angles in **1a** and **2b**. It clearly

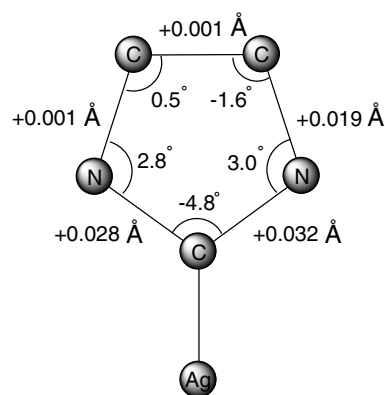


Fig. 4. A schematic diagram showing the dimensional change of the imidazole ring upon deprotonation and coordination of Ag(I) center in **2b**.

shows that the two C–N bonds at the carbenic carbon C(1) were lengthened resulting in a significant decrease of 4.8° for the N(1)–C(1)–N(2) bond angle.

Remarkably, like **1a**, **2b** also adopts a *gauche* conformation such that the pyrazolylethyl group is folded and disposed above the metal center. The N(1)–C(4)–C(5)–N(3) dihedral angle is 52.81° . However, examination of the packing in **2b** did not reveal any significant intra- and intermolecular forces in this case. Because of the similar bulky *N*-substitution on the imidazole rings, **2a** and **2c** presumably have the same molecular structure. Satisfactory elemental analyses for **2a–2c** were obtained and their yields were in the range 72–76%.

3.3. Synthesis of silver complexes **2d**

In remarkable contrast to **2a–2c**, reactions of **1d** with Ag_2O under *identical* condition produced instead of 1:1 NHC/Ag complex like **2a–2c**, a 2:1 complex **2d** as revealed by the X-ray structural determination. The white solid obtained is also air-stable and dissolve readily in chlorinated solvent. Likewise, in its ^1H NMR spectrum, the absence of downfield resonance at δ 10.22 suggested the successful formation of the $\text{Ag}(\text{NHC})$ moiety.

Crystals of **2d** were grown by vapor diffusion of diethylether into an acetonitrile solution. Complex **2d** also incorporates a water molecule its asymmetric unit of the triclinic space group $P\bar{1}$. Surprisingly, one of the pyrazole rings was coordinated to a AgCl_2 unit, which was formed from the associated counter chloride anion and an additional AgCl fragment refined best to have a 50% site of occupancy. This occupancy factor appears to be reliable as the equivalent isotropic thermal displacement parameters of the two independent silver atoms in **2d** were almost equal. Therefore, the overall stoichiometry of the reaction between a 2:1 mixture of **1d** and Ag_2O is the formation of $\text{AgL}_2(\text{AgCl})_{0.5}\text{Cl} \cdot \text{H}_2\text{O}$ and 0.5 equiv of AgCl , which was filtered during the work-up procedure. This composition of **2d** was confirmed by the elemental analysis of the bulk sample and the X-ray structural analysis of a crystal from an independent preparation. An unusual stoichiometry was also proposed in a closely related $\text{Ag}(\text{NHC})_2\text{I} \cdot x\text{AgI}$ compound, in which the value $x = 0.3$ to 0.4 was estimated based on elemental analysis [13]. The $[\text{Ag}(\text{NHC})_2][\text{AgBr}_2]$ reported is another closely related compound [11].

As seen in Fig. 5, the less bulky *N*-methyl group favors the formation of a coplanar $\text{Ag}(\text{I})$ bis(NHC) complex with a dihedral angle of 2.1° between the imidazole rings. The Ag(1) center adopts a linear coordination geometry (\angle at Ag(1) = $179.5(4)^\circ$) with two Ag–C bonds (2.088(11) and 2.092(10) Å) similar to that in **2b**. The second Ag center adopts a trigonal planar coordination geometry (\angle at Ag(2) = 359.6°) with two significantly unequal Ag–Cl distances (2.630(4) and 2.354(9)

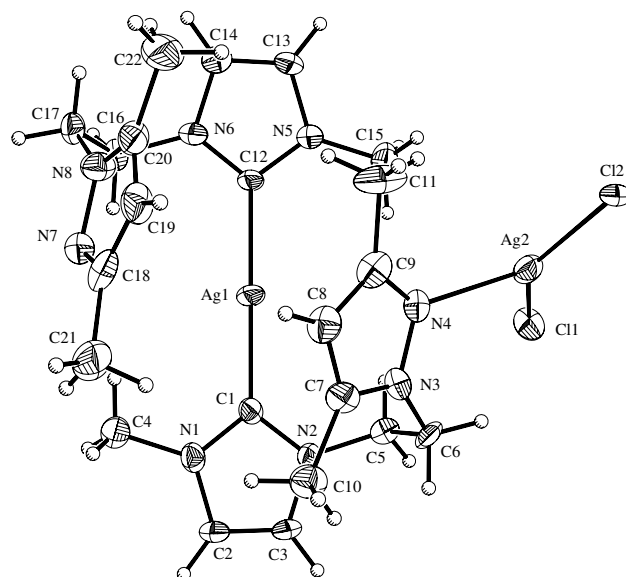


Fig. 5. Thermal ellipsoid plot of **2d** at the 30% probability level. The fragment Ag(2)–Cl(2) is of 50% occupancy. Selected bond distances (Å): N(1)–C(1), 1.338(12); N(2)–C(1), 1.346(13); N(3)–N(4), 1.373(12); N(6)–C(12), 1.333(13); N(5)–C(12), 1.352(12); N(7)–N(8), 1.419(13); Ag(1)–C(1), 2.088(11); Ag(1)–C(12), 2.092(10); Ag(2)–Cl(1), 2.630(4); Ag(2)–Cl(2), 2.436(8); Ag(2)–N(4), 2.354(9). Selected bond angles ($^\circ$): Ag(1)–C(1)–N(1), 128.5(8); Ag(1)–C(1)–N(2), 127.6(7); C(1)–N(1)–C(2), 112.3(9); C(1)–N(2)–C(3), 110.4(9); N(1)–C(1)–N(2), 103.9(9); C(12)–N(6)–C(14), 111.1(9); C(12)–N(5)–C(13), 110.2(9); N(6)–C(12)–N(5), 105.0(9); Ag(1)–C(12)–N(5), 126.6(8); Ag(1)–C(12)–N(6), 128.5(8); C(9)–N(4)–N(3), 105.4(9); N(3)–N(4)–Ag(2), 119.9(7); N(4)–Ag(2)–Cl(1), 113.4(3); N(4)–Ag(2)–Cl(2), 106.4(3); Cl(1)–Ag(2)–Cl(2), 139.8(2).

Å). Similar to **2b**, upon deprotonation and coordination to the silver center, a significant reduction of bond angles at the carbenic carbons C(1) (-5.2°) and C(12) (-4.1°) were observed. Most remarkably, the two organic ancillaries also adopt a *gauche* conformation with two dihedral angles of 66.81° (N(6)–C(16)–C(17)–N(8)) and 63.13° (N(2)–C(5)–C(6)–N(3)), respectively. Again, we examined the possible intermolecular forces that can stabilize this less stable conformation in the crystal lattice. As seen in Fig. 6, two molecules of **2d** indeed pack about a center of symmetry making face-to-face contact with a mean plane separation of 3.407 Å into a supramolecular pair. The non-bonded Ag \cdots Ag interaction is 3.798 Å. The Ag centers also interact with N(2) atoms forming a pair-wise centrosymmetric non-bonded interactions of 3.739 Å. Within each pair, the 3,5-dimethylpyrazolylethyl groups on each imidazole ring are directed away from the adjacent molecule. The incorporated water molecule also plays a significant role in pairing **2d** by forming hydrogen bonds via the hydrogen atoms on O(1) with N(7) ($d(\text{H}\cdots\text{N}) = 1.941$ Å, $\angle(\text{OHN}) = 169.25^\circ$), and with Cl(1) ($d(\text{H}\cdots\text{Cl}) = 2.371$ Å, $\angle(\text{OHC1}) = 154.09^\circ$), respectively. Further non-conventional hydrogen contacts of oxygen atoms link up

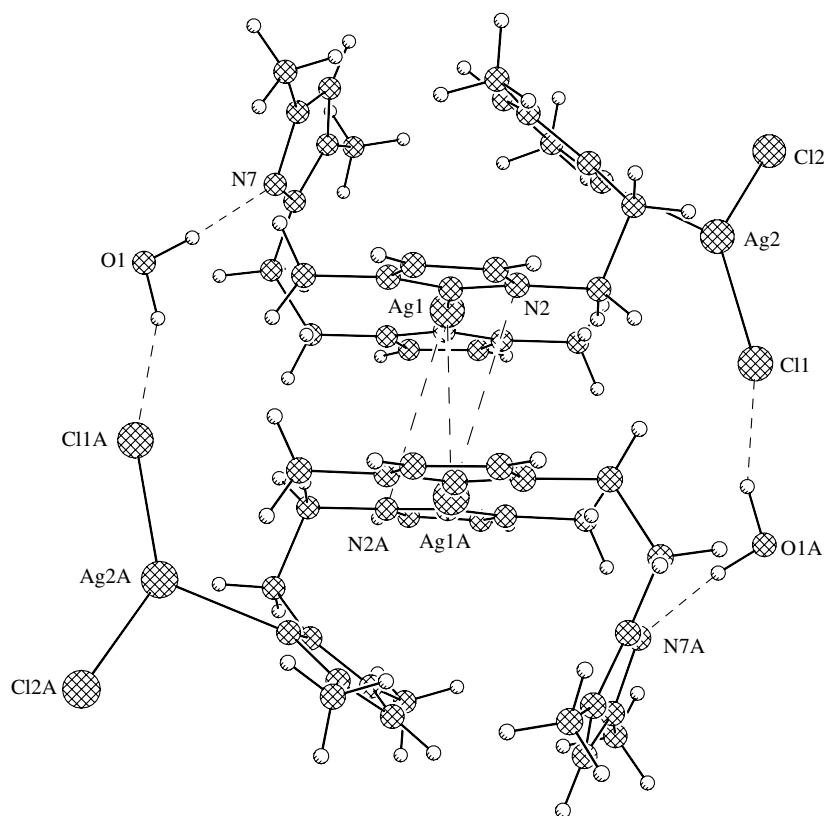


Fig. 6. A view of the face-to-face contact between a pair of **2d** molecules. Hydrogen atoms are omitted for clarity.

pairs of **2d** into a network structure (see [supplementary material](#)). It is obvious that the *gauche* conformation in **2d** further enhances such supramolecular interactions by folding the dangling organic fragments inwards (see [Fig. 5](#)) such that the occupied volume and intermolecular repulsions among pairs in the crystal lattice are minimized. Notably, the present model for **2d** · H₂O implies that there is a full AgCl portion scrambled within each pair.

3.4. Synthesis of zwitterionic palladium complexes **3a–3d**

The silver carbene transfer reaction is a general protocol for the preparation of palladium NHC compounds [14]. We anticipated that reactions between the silver carbene complexes **2a–2d** and PdCl₂ would afford palladium complexes of chelating pyrazole/NHC ligand. However, to our surprise, the reactions of **2a–2d** with PdCl₂ did not afford the anticipated palladium complexes of pyrazole/NHC ligand. This is rather unexpected, as reactions of excess **1a–1d** with PdCl₂ cleanly produced the zwitterionic palladium pyrazole complexes **3a–3d**, Pd^{II}Cl₃L · H in excellent yields. The yellow-orange compounds are stable in the solid state. They are insoluble in THF and partly soluble in dichloromethane and DMF. The carbenic proton in L · HCl is upfield shifted upon coordination with PdCl₂, reflecting the

reduction of charge density on the imidazole rings due to the zwitterionic nature. For example, the carbenic proton in **1d** observed at δ 10.0 (in CDCl₃) was upfield shifted in **3d** to δ 9.00 (in DMSO-d₆).

For a representative example, crystals of **3a** suitable for X-ray structural determination were grown by vapor diffusion of diethylether in an acetonitrile solution. Complex **3a** was successfully solved in the non-centrosymmetric space group *Cc*, despite the moderate quality of the crystal. Unlike **1a**, **2b**, and **2d** which crystallized with pairs of enantiomers in the crystal lattices, **3a** crystallized with only a single enantiomer in a chiral pseudo-helical conformation (*C*₁ symmetry). [Fig. 7](#) shows that the palladium center adopts a square planar coordination environment with a dihedral angle between the pyrazole ring and metal coordination plane being 72.3°. Surprisingly, the dangling imidazolium group is again locked in a *gauche* conformation with a N(2)–C(4)–C(5)–N(3) dihedral angle of 59.88°. No significant short intra- or intermolecular interactions were observed in this case.

3.5. Theoretical computation on **2b** and **3a**

In order to explore if the *gauche* conformations in **2b** and **3a** are stereo-electronic in nature, we perform theoretical computation on these two compounds. The three-

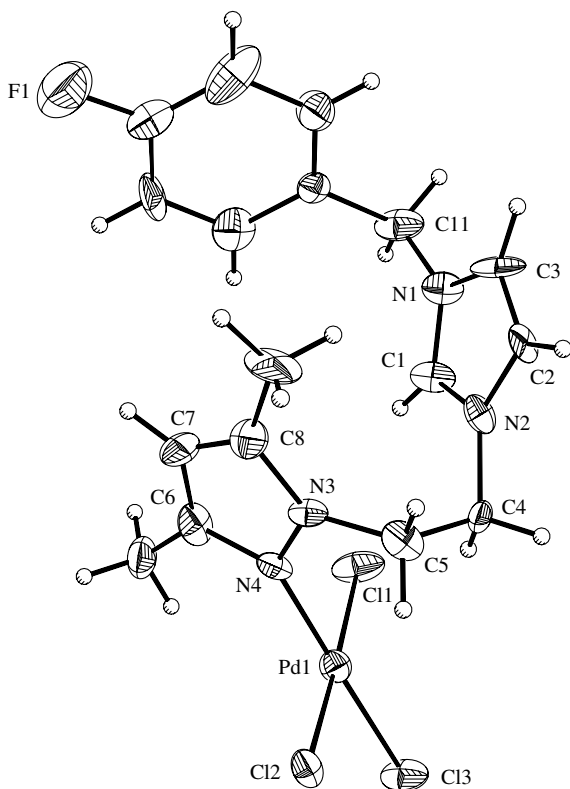


Fig. 7. Thermal ellipsoid plot of **3a** at the 30% probability level. Selected bond distances (Å): Pd(1)–N(4), 1.97(2); Pd(1)–Cl(1), 2.288(9); Pd(1)–Cl(2), 2.294(8); Pd(1)–Cl(3), 2.301(9); N(1)–C(1), 1.33(3); N(2)–C(1), 1.32(3); N(3)–N(4), 1.41(3); Selected bond angles (°): C(1)–N(1)–C(3), 106.9(19); C(1)–N(2)–C(2), 109(2); N(1)–C(1)–N(2), 108(2); C(6)–N(4)–N(3), 102(2); N(4)–Pd(1)–Cl(1), 86.2(7); N(4)–Pd(1)–Cl(2), 90.2(7); Cl(1)–Pd(1)–Cl(3), 176.3(3); Cl(2)–Pd(1)–Cl(3), 91.1(4).

parameter hybrid of exact exchange and Becke's exchange energy [15], and of Lee, Yang, and Parr's non-local correlation energy [16] (B3LYP) has been applied. We used the 6-31G(d) basis sets for H, C, N, Cl and the LANL2DZ effective core potential plus basis functions for Pd and Ag [17]. The GAUSSIAN03 suite of programs has been used in these computations [18]. The energetic difference between *gauchelanti* conformations in **2b** and **3a** were estimated to be 1.9 and 0.9 kcal mol⁻¹, respectively, with the *anti* conformation being more stable in both cases.

3.6. Heck coupling

Even though, chelating palladium complexes **A** have not been prepared yet, we were interested to see if zwitterionic Pd(II) complexes **3a–3d** are effective catalysts in Heck reaction. We employ the reaction between 4-bromoacetophenone and *n*-butyl acrylate with sodium acetate as base at 173 °C as a standard test (Table 2). Our preliminary investigation shows that catalysts **3a–3d**, in regardless of the *N*-substitutions, are equally effective in the production of *trans n*-butyl cinnamate quantita-

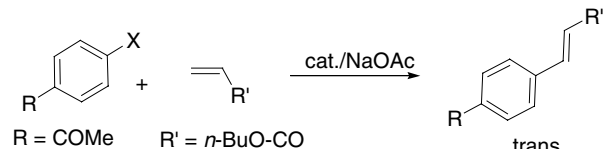
tively in 6 h (entries 1–4). To gauge the effectiveness of **3a–3d** in comparison with simple phosphine-based catalytic systems of Pd(OAc)₂/2PPh₃ and Pd(PPh₃)₄, we carried out the standard catalytic reaction with the latter two systems under identical conditions (entries 5–6). The results clearly indicate that **3a–3d** and the phosphine-based systems are equally effective. In order to differentiate their catalytic performance, we lowered the reaction temperature to 120 °C in entries 7–8. Consequently, **3a** became less effective than Pd(OAc)₂/2PPh₃. The catalytic performance of **3a–3d** is also probed by using the much less reactive 4-chloroacetophenone as substrate, entry 9 shows that **3a** can produce a 37% of the coupled product with a prolonged reaction time of 24 h at 173 °C, whereas the simple phosphine systems are totally ineffective under the same condition (entries 11–12). Increasing the catalyst loading of **3a** to 3 mol% does not improve the yield, however (entry 10).

4. Discussion

A series of novel imidazolium salts (L · HCl) for the potentially bidentate ligand based on pyrazole/*N*-heterocyclic carbene (L) was synthesized by reacting 1-(2-chloroethyl)-3,5-dimethyl-1*H*-pyrazole with an appropriate *N*-substituted imidazole. The X-ray structural analysis of the fluorine-containing **1a** reveals the formation of an intriguing layer structure in which the hydrophilic layer is sandwiched between the fluororous hydrophobic layers. The hydrogen bonding and π – π stacking play a crucial role in this overall layer structure.

Silver(I) NHC complexes are generally accessible by reacting the basic Ag₂O with the imidazolium salts in the dark [14]. Silver complexes **2a–2c** of 1:1 Ag:L stoichiometry were produced by reactions of L · HCl with Ag₂O. However, reactions of **1d** with Ag₂O under identical synthetic conditions produced a novel solid **2d** which identified to be AgL₂(AgCl)_{0.5}Cl · H₂O by X-ray structural analysis. Molecules of **2d** are aligned in supramolecular pairs via face-to-face contacts in the crystal lattice. A silver center is coordinated to two L via the NHC functionality with an additional pyrazole-bound AgCl fragment scramble among the pair. It is obvious that the bulkiness of the *N*-substitution on the imidazole ring has a profound effect on the formation of different adducts with the smaller *N*-methyl group favors the formation of a 1:2 Ag:NHC compound, whereas bulky *N*-substitution leads to a neutral 1:1 Ag:NHC compound.

Preparation of Pd(II) NHC complexes via the silver carbene transfer reactions is becoming a general protocol [14]. It is rather surprising that anticipated reactions between **2a–2d** and PdCl₂ failed to produce the chelating palladium complexes, Pd^{II}LCl₂. Indeed, reactions of L · HCl with PdCl₂ produce readily the zwitterionic

Table 2
Catalytic Heck reactions^a


Entry	Catalyst	X	Temperature (°C)	Time	Yield ^b (%)
1	3a	Br	173	6	100
2	3b	Br	173	6	100
3	3c	Br	173	6	100
4	3d	Br	173	6	100
5	Pd(OAc) ₂ /2PPh ₃	Br	173	6	100
6	Pd(PPh ₃) ₄	Br	173	6	100
7	3a	Br	120	6	69
8	Pd(OAc) ₂ /2PPh ₃	Br	120	6	100
9	3a	Cl	173	24	37
10	3a	Cl	173	24	36 ^c
11	Pd(OAc) ₂ /2PPh ₃	Cl	173	24	0
12	Pd(PPh ₃) ₄	Cl	173	24	0

^a Reaction condition: 1 mmol of aryl bromide, 1.4 mmol of *n*-butyl acrylate, 1.1 mmol of NaOAc, 0.5 mol% of Pd catalyst, 5 mL of DMA, an average of two runs.

^b Determined by ¹H NMR.

^c 3 mol% of Pd catalyst.

Pd^{II}Cl₃L · H which, in **3a** crystallizes into a chiral atropisomer with pseudo-helical conformation. We sought to prepare the target compound **A** by the routine protocol of trapping the free carbene, generated in situ by deprotonation of L · HCl, with PdCl₂ as well as direct reactions of Pd^{II}Cl₃L · H with a suitable base. However, both of these procedures resulted in decomposition products only. Notably, a similar silver complex of pyridine/NHC ligand with an ethylene spacer also failed to produce a chelating palladium complex [13]. These results suggest that seven-member palladacycles, such as **A**, containing NHC and nitrogen donor ligands may be intrinsically unstable in comparison with the seven-member palladacycles of bis(NHC) **B** [4].

Most interestingly, in each of the four X-ray structures of compounds based on L · HCl determined, the ethylene spacer in L is in the less stable *gauche* conformation. In case of **1a** and **2d**, close examination of the crystal packing revealed the involvements of intermolecular hydrogen bonds and face-to-face contacts which provide the stabilization forces in the crystal lattices. However, in **2b** and **3a**, the apparent lack of such stabilizing intermolecular forces makes the *gauche* conformations very peculiar. In fact, the energy difference in the gas phase between the staggered and the *gauche* conformations in **2b** and **3a** was estimated by DFT to be as high as 1.9 and 0.9 kcal mol⁻¹, respectively, with the *anti* conformation being more stable in both cases. This theoretical computation suggested that the *gauche* rotamers in **2b** and **3a** are not stereo-electronic in nature as in 1,2-difluoroethane [5] and the prevailing *gauche* rotamers in crystals of **2b** and **3a** can only be attributed to the crystal packing effect in the solid

state. In **1a** and **2d**, extra stabilization of *gauche* rotamers by intermolecular forces exists. It seems likely that compounds based on pyrazole/imidazolium chloride L · HCl have a general preference for the less-stable *gauche* forms in solid states. This unique *gauche* preference in L · HCl may provide potential applicability in crystal engineering for the construction of novel supramolecular molecules for materials and bio-organic applications.

Our preliminarily application of **3a–3d** in the Heck reaction of 4-bromoacetophenone and *n*-butyl acrylate shows that the zwitterionic **3a–3d** are also active catalysts. In comparison with simple phosphine-based Pd catalytic systems, **3a–3d** are equally efficient at high temperature. However, at a milder reaction temperature, **3a** is less efficient than Pd(OAc)₂/2PPh₃. Interestingly, **3a** is able to mediate the much less reactive 4-chloroacetophenone as substrate, whereas the phosphine-based systems are totally ineffective. This difference in reactivity can be attributed to the better thermal stability of **3a** supported by L · HCl than Pd(OAc)₂/2PPh₃ under harsh reaction conditions. It should be noted that the active catalyst of **3a–3d** might be a monodentate Pd(II) species bearing a pyrazolyl ligand or an effective amount of species **A** produced under catalytic conditions. Recently, the use of ionic liquid in organometallic catalysis is receiving much attention [19]. **3a–3d** with the pendent imidazolium groups contain the favorable structural element for their immobilization in ionic liquids of 1,3-dialkylimidazolium salts. The catalytic application of **3a–3d** in C–C coupling reactions with ionic liquid as solvent is currently under investigation.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 238528–238531. 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; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.09.053.

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