# Complexes of palladium(II) with N-heterocyclic carbenes from adamantylimidazole as precatalysts for thiophene and imidazole arylation*

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Complexes of palladium(II) with N-heterocyclic carbenes of the PEPPSI-type were synthesized by the reaction of $PdCl_2$ with 1-adamantyl-3-(R-methyl)-1*H*-imidazolium salts. These complexes were used as productive precatalysts for substituted thiophene and imidazole arylation by C—H-activation.

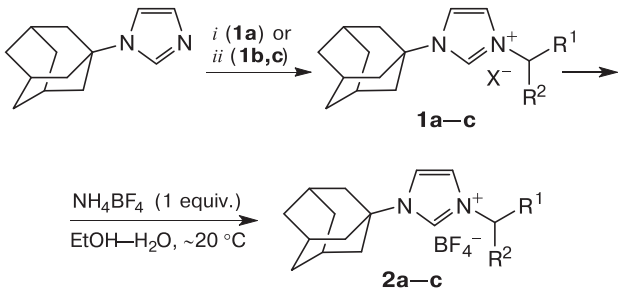
**Key words:** N-heterocyclic carbenes, palladium, C—H-activation, arylation, imidazole, thiophene.

N-Heterocyclic carbenes (NHC) and their metal complexes occupy one of pivotal positions in the contemporary organometallic chemistry.[1—4] Although in many cases NHC are not inferior to phosphine ligands, they still have not found wide practical application in cross coupling reactions. A reason for this could probably be a relative hydrolytic instability of NHC complexes.[5] This problem can be approached with the aid of a specific class of NHC—Pd complexes, namely, so called PEPPSI complexes (PEPPSI is Pyridine Enhanced Precatalysts: Preparation, Stabilisation and Initiation).[6—9] The latter are used as precatalysts for various cross coupling reactions including those of Suzuki[10—12], Negishi[13,14], Sonogashira[15], as well as amination,[16,17] and sulfenylation[18] reactions. Studies have been reported on application of these complexes in the reactions of C—H-activation such as synthesis of heterocycles[19,20], arylation of phenols[21], thiophenes[22,23], pyrazoles[24], oxazoles[25], imidazoles[26—29], and also benzyl group activation[30]. Recently, we have synthesized novel unsymmetrically substituted PEPPSI-type palladium(II) complexes and showed their possible use as precatalysts in the reaction of C—H-activation/arylation of substituted thiophenes.[23]

The present work is aimed at the synthesis of novel unsymmetrically substituted PEPPSI palladium(II) complexes based on 1-adamantyl-1*H*-imidazole and study of their catalytic activity in arylation of thiophenes and imidazoles. Introduction of a bulky hydrophobic moiety (adamantyl, naphthyl, benzhydryl) improves the hydrolytic stability of such complexes that can further withstand extraction in methylene chloride—water system during their isolation.

The parent imidazolium salts were obtained by quaternization of 1-adamantylimidazole with alkylation agents such as iodomethane, 1-(chloromethyl)naphthalene, and chlorodiphenylmethane (Scheme 1). Salts of 1-adamantylimidazolium bearing methyl (**1a**), 1-naphthyl (**1b**), or diphenylmethyl (**1c**) groups at the C(3) atom were synthesized. The halide counterion was then replaced with tetrafluoroborate one since the latter is not capable of forming complexes with palladium atom.

**Scheme 1**




*i*. MeI (2 equiv.), $PhCH_3$, ~20 °C, 24 h; *ii*. $XCHR^1R^2$ (1 equiv.), MeCN, reflux, 4 h.

| Compound | X | $R^1$ | $R^2$ | Yield (%) |
|---|---|---|---|---|
| **1a** | I | H | H | 95 |
| **1b** | Cl | 1-Naphthyl | H | 57 |
| **1c** | Br | Ph | Ph | 79 |
| **2a** | — | H | H | 100 |
| **2b** | — | 1-Naphthyl | H | 81 |
| **2c** | — | Ph | Ph | 73 |

* Based on the materials of the V International Scientific Conference "Advances in Synthesis and Complexing" (April 22—26, 2019, Moscow, Russia).

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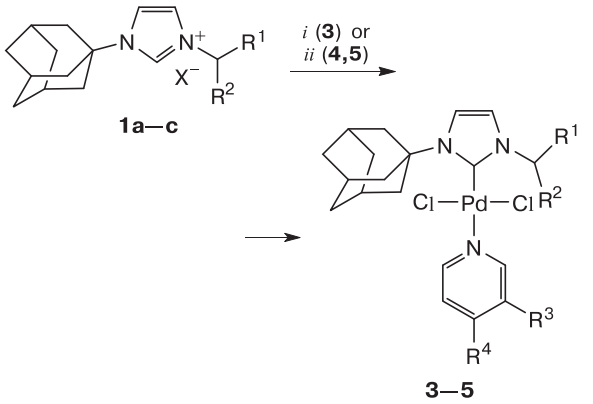
PEPPSI complexes were synthesized according to the known procedure[23,31] comprising the one-pot NHC formation from imidazolium salt followed by coordination of the former with the solvated palladium(II). As auxiliary ligands, pyridine, 3-methylpyridine and 4-methylpyridine were used (Scheme 2). Unfortunately, we failed to obtain complexes with 2-methylpyridine. This was probably caused by steric hindrances as the reaction was terminated at the step of formation of *trans*-dichlorobis(2-methylpyridine)palladium(II) complex.[32]

**Scheme 2**




*i*. $PdCl_2$ (1 equiv.), $K_2CO_3$ (5 equiv.), pyridine; *ii*. Picoline (2 equiv.), MeCN.

| Compound | $R^1$ | $R^2$ | $R^3$ | $R^4$ | *t* | *T*/°C | Yield (%) |
|---|---|---|---|---|---|---|---|
| **3a** | H | H | H | H | 5 h | 65 | 51 |
| **3b** | 1-Naphthyl | H | H | H | 5 h | 80 | 63 |
| **3c** | Ph | Ph | H | H | 5 h | 80 | 34 |
| **4b** | 1-Naphthyl | H | Me | H | 50 min | 65 | 77 |
| **4c** | Ph | Ph | Me | H | 5 h | 65 | 27 |
| **5a** | H | H | H | Me | 5 h | 65 | 41 |
| **5b** | 1-Naphthyl | H | H | Me | 5 h | 80 | 39 |
| **5c** | Ph | Ph | H | Me | 5 h | 80 | 46 |

We failed to develop reaction conditions to obtain PEPPSI complex from compound **1a** and 3-methylpyridine. The known procedure[33] to synthesize PEPPSI complexes with bromide and iodide ligands starting from palladium(II) acetate and excess of potassium halide proved to be inapplicable for salts **1a** and **1c** since only the formation of bispyridine complex was observed. During the reaction progress, in some experiments palladium black was formed; in this case the process was terminated prior to the standard time (5 h). Control of temperature (from 65 to 80 °C) and reaction time (from 50 min to 5 h) based on the appearance of palladium black serves to rise significantly the yields of the complexes and decrease the duration of the synthesis (as in the case of compound **4b**, obtained in 50 min).

Composition and structure of complexes **3**—**5** were confirmed by elemental analysis, $^1H$ and $^{13}C$ NMR spectroscopy and X-ray diffraction data. Signals of the C(2) atom of imidazolium ring in the $^{13}C$ NMR spectra, disappearing in DEPT spectra, are found in the range of δ 145—151 corresponding to the literature data[23] for such complexes (δ 143—146).

Complex **3a** crystallizes in the centrosymmetric space group of monoclinic syngony (Fig. 1). Adamantyl substituent in the molecule is disordered on two positions with an occupancy of 0.61(2) : 0.39(2); minor disorder component has been omitted in the Figure. In the crystal molecules are connected in one-dimentional chains extended along the axis *b*, due to a nonclassical intermolecular hydrogen bond C(2)—H(2)···Cl(2) [$1-x$, $-0.5+y$, $1.5-z$]. Two crystallographically independent molecules of complex **5c** crystallize in the centrosymmetric space group $P\bar{1}$ as a solvate with one molecule of acetonitrile (Fig. 2 shows only one of the molecules). Independent molecules of the complex are linked to each other *via* intermolecular hydrogen bond C(2A)—H(2A)···Cl(2) [$1-x$, $1-y$, $1-z$] (indices "A" designate atoms of the second independent molecule).

Using arylation of 2,3-diphenylthiophene with iodobenzene as an example, catalytic activity of complexes **3a**—**c** was studied (Scheme 3). Results of this study are given in Table 1. Reported data[23] for complex **3d** with benzyl substituent and PEPPSI-IPr are given for comparison.[6] Catalytic activity of palladium compounds $Pd[P(Ph)_3]_4$ (see Ref. 34) and $PdCl_2$ was tested for comparison under the same conditions. As illustrated in Table 1, in the model reaction complex with naphthylmethyl substituent (**3b**) is more active whereas complexes bearing methyl (**3a**) and diphenylmethyl (**3c**) substituents demonstrate lower catalytic activity compared to that found

**Table 1.** Catalytic activity of palladium compounds in arylation of 2,3-diphenylthiophene with iodobenzene

| Precatalyst | Conversion of 2,3-diphenylthiophene* | Yield of **6*** |
|---|---|---|
| | % | |
| **3a** | 97 | 55 |
| **3b** | 99 | 84 |
| **3c** | 99 | 46 |
| **3d** | 98 | 59 |
| **4b** | 97 | 43 |
| **4c** | 83 | 36 |
| **5a** | 96 | 46 |
| **5b** | 94 | 62 |
| **5c** | 95 | 39 |
| PEPPSI-IPr | 100 | 69 |
| $Pd[P(Ph)_3]_4$ | 96 | 58 |
| $PdCl_2$ | 95 | 41 |
| **3b** (PhBr in place of PhI) | 45 | 0 |
| **3b** (PhCl in place of PhI) | 14 | 0 |

* GC-MS data.

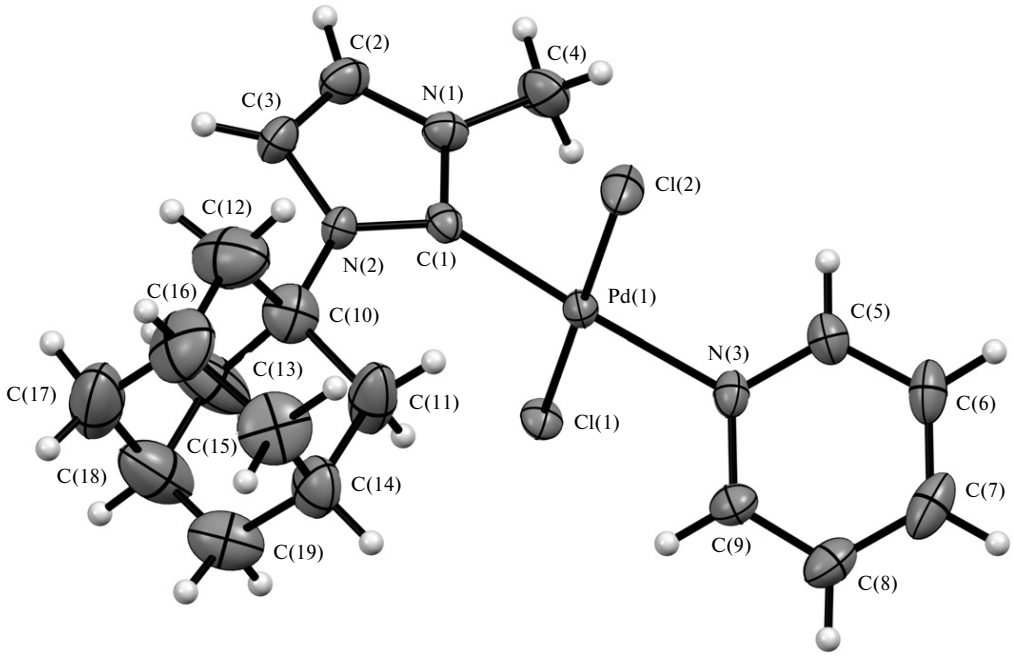



**Fig. 1.** Molecular structure of complex **3a**. Thermal ellipsoids are set at the 30% probability level.

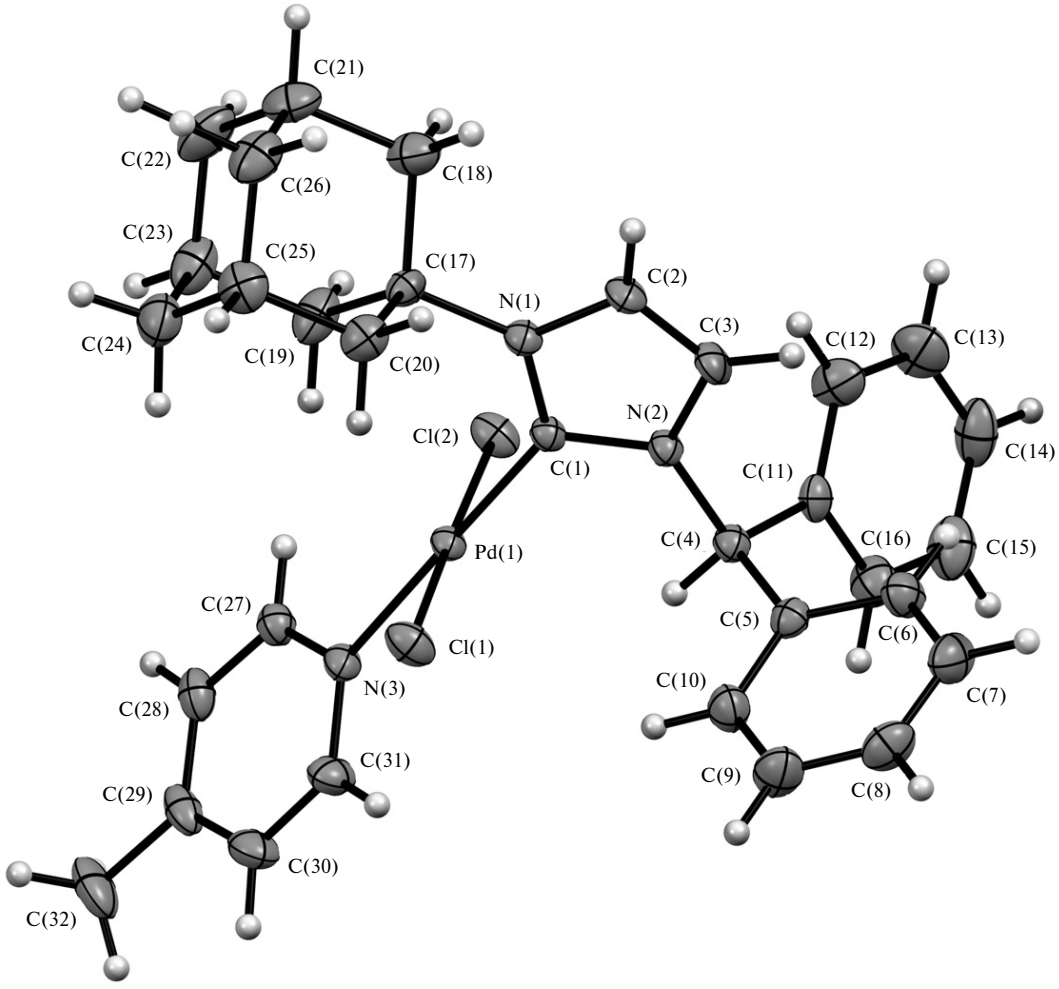
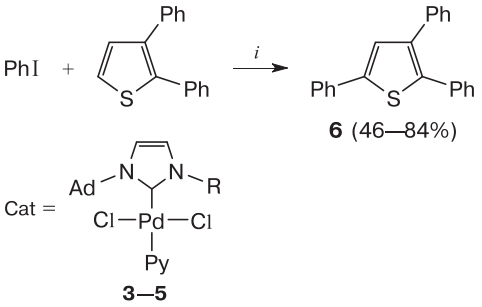



**Fig. 2**. Molecular structure of complex **5c**. Thermal ellipsoids are set at the 30% probability level.

for benzyl substituent (**3d**). The features described are also observed for picolinic complexes **4b**,**c** and **5a**—**c**. In our earlier study negligible response of the catalytic behavior of complexes to the transfer from pyridine to picoline was noted.[23] By contrast, in the present study a decrease in activity was observed. When passing to 3-methylpyridine, this decrease was much more pronounced than in the case of 4-methylpyridine. Complex **3b** was superior in activity to the known catalysts such as PEPPSI-IPr,[6] $Pd[P(Ph)_3]_4$ (see Ref. 34), and $PdCl_2$. Using catalytic reactions with complex **3b** as an example, it was demonstrated that chlorobenzene and bromobenzene are unsuitable as arylating agents — these substrates do not enter arylation reaction.

**Scheme 3**




Ad is 1-adamantyl.

*i*. Cat (2 mol.%), pivalic acid (30 mol.%), $Cs_2CO_3$ (2.5 equiv.), dimethylacetamide (DMA), reflux, 3 h.

Table 2 shows data obtained in arylation of 1-methylimidazole with *p*-bromobenzonitrile proceeding with as low as 0.5 mol.% of palladium **3a**—**d** (Scheme 4). Since at 110 °C conversion was ~50%, all experiments were also performed at 130 °C. Arylation proceeded involving C(5) atom of 1-methylimidazole similar to the previously reported process.[35] In contrast to the literature data,

**Table 2.** Catalytic activity of complexes **3a**—**d** in combination of *p*-bromobenzonitrile with 1-methyl-1*H*-imidazole

| Precatalyst | *T*/°C | Conversion of *p*-bromobenzonitrile* | Yield of **7*** |
|---|---|---|---|
| | | % | |
| **3a** | 110 | 58 | 27 |
| | 130 | 87 | 41 |
| **3b** | 110 | 30 | 15 |
| | 130 | 91 | 87 |
| **3c** | 110 | 55 | 20 |
| | 130 | 78 | 40 |
| **3d** | 110 | 39 | 16 |
| | 130 | 55 | 25 |

* GC-MS date.

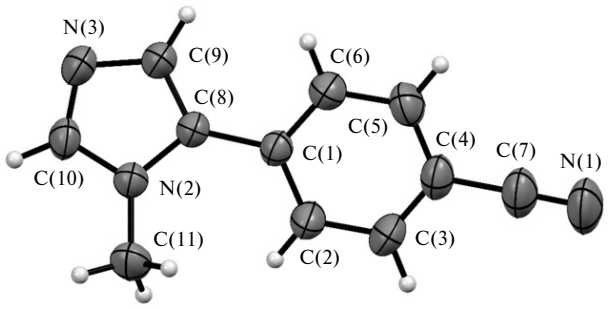
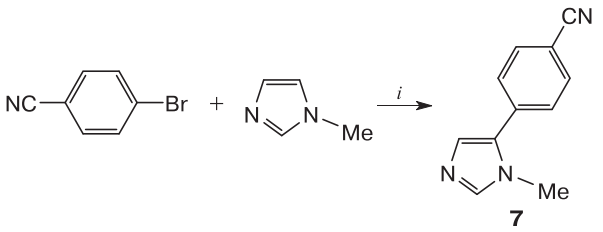



**Fig. 3.** Molecular structure of compound **7**. Thermal ellipsoids are set at the 50% probability level.

compound **7** was the single arylation product.[36] These experiments revealed that 2-methylimidazole did not undergo arylation under given conditions. Structure of compound **7** (Fig. 3) is identical to the previously published one.[35] Similar to arylation of 2,3-diphenylthiophene, PEPPSI complex with naphthylmethyl substituent (**3b**) was high active catalyst at 130 °C.

**Scheme 4**




*i*. Cat (0.5 mol.%), pivalic acid (30 mol.%), $K_2CO_3$ (2 equiv.), DMA, 110—130 °C, 10 h.

Although studying the nature of the catalyst was not among the purposes of our work, taking into account the literature data[37—40] and the reaction conditions, it can be assumed that catalysts represent nanoparticles of palladium(0) or their clusters stabilized by N-heterocyclic carbene ligands.

To summarize, the procedure to obtain adamantyl-substituted Pd-PEPPSI complexes through the reaction between $PdCl_2$ and 1-adamantyl-3-methyl-1*H*-imidazolium salts and pyridine (or picolines) has been improved. Complexes of Pd-PEPPSI with imidazole NHC-ligands were for the first time studied as precatalysts in arylation of 1-methyl-1*H*-imidazole *via* C—H-activation. By the example of catalytic arylation of 2,3-diphenylthiophene with complex **3b** it has been demonstrated that novel complexes Pd-PEPPSI bearing adamantyl-substituted ligands can be superior to their known[23] analogs in catalytic activity. Ease of synthesis and high catalytic activity (in terms of C—H-activation) of Pd-PEPPSI complexes with 1-adamantyl-3-methyl(1-naphthyl)-substituted li-

gand enable their application in catalytic arylation *via* C—H-activation of substituted thiophenes and imidazoles to be considered.

## Experimental

$^1$H and $^{13}$C spectra were recorded in $CDCl_3$ on a Bruker Avance Neo 400 (400 and 100 MHz) spectrometer; chemical shifts are given relatively to an internal standard: for $^1$H NMR spectra HMDS was used, for $^{13}$C NMR spectra the residual proton signals of deuterated solvent were used as references (δ 77.0). IR spectra were obtained on a Bruker FT-IR VERTEX 80v Fourier spectrometer (in a thin film obtained by evaporation of a substance solution in chloroform directly on the NaCl glass (hereinafter, $CHCl_3$) or in suspension in paraffin oil). The electron impact mass spectra (70 eV) were recorded on an Agilent Technologies 6890N/5975B apparatus, capillary column HP-5ms, 30000×0.25 mm, 0.25 μm, vaporization temperature 260—290 °C, temperature programming in the range 20—40 °C min$^{-1}$, helium as a carrier-gas, 1 mL min$^{-1}$. Melting points were determined on a PTP-2 instrument. Elemental analysis (C, H, N) was performed on a CHNS VARIO EL CUBE apparatus (Germany). Silicagel 60 (Alfa Aesar, 0.032—0.070 mm) was used for column chromatography. Benzhydryl bromide, $PdCl_2$, 1-chloromethylnaphthalene, 3-picoline, 4-picoline, 1-methylimidazole, and 2-methylimidazole (Alfa Aesar, Great Britain); pyridine (reagent grade), acetonitrile (extra pure), rectified ethanol, $K_2CO_3$ (reagent grade), petroleum ether (40—70 °C), iodomethane (reagent grade), ethyl acetate (reagent grade), acetone (reagent grade), methylene chloride (reagent grade, stabilized with 0.5% methanol), 2,3-diphenylthiophene (reagent grade), *p*-bromobenzonitrile (reagent grade), chlorobenzene (reagent grade), bromobenzene (reagent grade), iodobenzene (reagent grade), and phenanthrene (reagent grade) of domestic production were used. 1-Adamantyl-1*H*-imidazole[41] and $Pd[P(Ph)_3]_4$ (see Ref. 42) were obtained according to the previously reported procedures.

**1-Adamantyl-3-methyl-1*H*-imidazolium iodide (1a)[43].** To a solution of 1-adamantyl-1*H*-imidazolium (607 mg, 3 mmol) in toluene (30 mL) iodomethane (0.37 mL, 6 mmol) was added, and the reaction mixture was stirred for 1 day. The precipitate was filtered off and washed with cold ethyl acetate. Yield 1.032 g (95%), grey powder. $^1$H NMR, δ: 1.80 (t, 6 H, 3 4-$CH_2$ of adamantane, $J$ = 3.2 Hz); 2.25 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 3.2 Hz); 2.33 (s, 3 H, 3 3-CH of adamantane); 4.21 (s, 3 H, Me); 7.47 (t, 1 H, CH of imidazole, $J$ = 1.8 Hz); 7.50 (t, 1 H, CH of imidazole, $J$ = 1.8 Hz); 10.11 (td, 1 H, 2-CH of imidazole, $J_1$ = 1.6 Hz, $J_2$ = 0.4 Hz). $^{13}$C NMR, δ: 28.9; 34.8; 36.8; 42.5; 60.4; 117.8; 123.0; 135.0.

**Synthesis of compounds 1b,c (general procedure).** A solution of 1-adamantylimidazole (0.45 g, 2.25 mmol) and arylhalide (2.25 mmol) in acetonitrile (5 mL) was heated under reflux for 4 h. Then, the solvent was distilled off. The solid residue was washed with a small amount of ethyl acetate and dried.

**1-Adamantyl-3-(1-naphtylmethyl)-1*H*-imidazolium chloride monohydrate (1b).** Yield 0.488 g (57%), white powder, m.p. 166—168 °C (EtOAc). Found (%): C, 73.16; H, 7.00; N, 6.87. $C_{24}H_{27}ClN_2 \cdot H_2O$. Calculated (%): C, 72.62; H, 7.36; N, 7.06. IR (suspension in paraffin oil), ν/cm$^{-1}$: 3391; 3046; 2915; 2854; 2464; 1598; 1545; 1513; 1451; 1360; 1308; 1253; 1152; 1104; 1053; 810; 785; 751; 660. $^1$H NMR, δ: 1.70 (s, 6 H, 3 4-$CH_2$ of adamantane); 2.15 (s, 6 H, 3 2-$CH_2$ of adamantane); 2.22 (br.s, 3 H, 3 3-CH of adamantane); 6.16 (s, 2 H, $CH_2$); 7.11 (t, 1 H, CH of imidazole, $J$ = 1.6 Hz); 7.40—7.49 (m, 3 H, 2 3,6-CH of naphthalene, CH of imidazole); 7.55 (ddd, 1 H, 7-CH of naphthalene, $J_1$ = 8.2 Hz, $J_2$ = 7.2 Hz, $J_3$ = 1.4 Hz); 7.69 (d, 1 H, 2-CH of naphthalene, $J$ = 6.8 Hz); 7.83 (d, 1 H, 4-CH of naphthalene, $J$ = 4.4 Hz); 7.83 (d, 1 H, 5-CH of naphthalene, $J$ = 4.8 Hz); 8.24 (d, 1 H, 8-CH of naphthalene, $J$ = 8.0 Hz); 11.10 (s, 1 H, 2-CH of imidazole). $^{13}$C NMR, δ: 29.3; 35.10; 42.6; 50.7; 60.4; 118.3; 121.3; 123.0; 125.3; 126.3; 127.5; 128.8; 128.8; 129.2; 130.3; 131.1; 133.8; 135.8.

**1-Adamantyl-3-(diphenylmethyl)-1*H*-imidazolium bromide monohydrate (1c).** Yield 0.83 g (79%), pale-yellow powder, m.p. 255—257 °C (EtOAc). Found (%): C, 66.06; H, 6.10; N, 6.79. $C_{26}H_{29}BrN_2 \cdot H_2O$. Calculated (%): C, 66.81; H, 6.68; N, 5.99. IR (suspension in paraffin oil), ν/cm$^{-1}$: 3182; 3162; 3142; 3089; 3050; 2787; 2745; 2718; 2686; 2611; 1584; 1567; 1538; 1498; 1345; 1311; 1273; 1252; 1204; 1181; 1168; 1147; 1114; 1103; 1084; 1029; 1002; 996; 880; 859; 828; 801; 761; 705; 654; 643; 637; 621; 614; 593; 519. $^1$H NMR, δ: 1.74 (br.s, 6 H, 3 4-$CH_2$ of adamantane); 2.23 (br.s, 6 H, 3 2-$CH_2$ of adamantane); 2.26 (br.s, 3 H, 3 3-CH of adamantane); 7.14 (s, 1 H, CH of imidazole); 7.25—7.30 (m, 4 H, 4 CH, *m*-Ph); 7.31—7.34 (m, 6 H, 4 CH, *o*-Ph, 2 CH, *p*-Ph); 7.58 (br.s, 1 H, CH); 8.02 (s, 1 H, CH of imidazole); 10.59 (s, 1 H, 2-CH Ar). $^{13}$C NMR, δ: 29.3; 35.1; 42.6; 60.8; 65.8; 119.0; 120.9; 128.3; 128.9; 129.0; 135.5; 136.9.

**Synthesis of tetrafluoroborates 2a—c (general procedure).** A suspension of an imidazolium salt (2.25 mmol) in ethanol (10 mL) was heated until complete dissolution. To a clear solution, a solution of ammonium tetrafluoroborate (2.5 mmol) in water (5 mL) was added and the resulting solution was left for evaporation in a fume hood. Crystals of salts **2a—c** precipitated were filtered off and dried.

**1-Adamantyl-3-methyl-1*H*-imidazolium tetrafluoroborate semihydrate (2a).** Yield 0.705 g (quantitative), white or pale-yellow crystals, m.p. 171—172 °C. Found (%): C, 53.91; H, 6.22; N, 8.76. $C_{14}H_{21}BF_4N_2 \cdot 0.5H_2O$. Calculated (%): C, 53.70; H, 7.08; N, 8.59. IR ($CHCl_3$), ν/cm$^{-1}$: 3425; 3382; 3166; 3113; 3069; 2915; 2864; 1570; 1558; 1451; 1368; 1345; 1312; 1284; 1261; 1245; 1191; 1166; 1106; 1070; 1045; 1034; 998; 841; 829; 815; 772; 750; 659; 638; 618; 521; 419. $^1$H NMR, δ: 1.78 (t, 6 H, 3 4-$CH_2$ of adamantane, $J$ = 2.8 Hz); 2.17 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 3.2 Hz); 2.29 (s, 3 H, 3 3-CH of adamantane); 4.01 (s, 3 H, $CH_3$); 7.45 (t, 1 H, CH of imidazole, $J$ = 1.8 Hz); 7.49 (t, 1 H, CH of imidazole, $J$ = 2.0 Hz); 8.99 (s, 1 H, 2-CH of imidazole). $^{13}$C NMR, δ: 28.9; 34.8; 35.91; 42.0; 59.9; 118.2; 123.3; 133.7.

**1-Adamantyl-3-(1-naphthylmethyl)-1*H*-imidazolium tetrafluoroborate monohydrate (2b).** Yield 0.817 g (81%), colorless crystals, m.p. 220—221 °C. Found (%): C, 64.42; H, 5.96; N, 6.27. $C_{24}H_{27}BF_4N_2 \cdot H_2O$. Calculated (%): C, 64.30; H, 6.52; N, 6.25. *И* IR (suspension in paraffin oil), ν/cm$^{-1}$: 1552; 1423; 1364; 1172; 1149; 1067; 1053; 815; 794; 786; 616. $^1$H NMR, δ: 1.67 (s, 6 H, 3 4-$CH_2$ of adamantane); 2.07 (s, 6 H, 3 2-$CH_2$ of adamantane); 2.17 (s, 3 H, 3-CH of adamantane); 5.83 (s, 2 H, $CH_2$); 7.07 (s, 1 H, CH of imidazole); 7.30 (s, 1 H, CH of imidazole); 7.40—7.48 (m, 2 H, 2 3,6-CH of naphthalene); 7.53 (t, 1 H, 7-CH of naphthalene, $J$ = 7.2 Hz); 7.58 (d, 1 H, 2-CH of naphthalene, $J$ = 7.2 Hz); 7.83 (d, 1 H, 4-CH of naphthalene, $J$ = 6.8 Hz); 7.85 (d, 1 H, 2-CH of naphthalene, $J$ = 7.2 Hz); 7.97 (d, 1 H, 8-CH of naphthalene, $J$ = 8.4 Hz); 9.04 (s, 1 H,

2-CH of imidazole). $^{13}$C NMR, δ: 29.4; 35.2; 42.3; 50.9; 60.6; 118.4; 121.9; 122.5, 125.6; 126.5; 127.8; 128.3; 129.0; 129.4; 130.5; 131.1; 133,6; 133.9.

**1-Adamantyl-3-(diphenylmethyl)-1*H*-imidazolium tetrafluoroborate (2c).** Yield 0.739 g (73%), small colorless needle-shaped crystals, m.p. 197—198 °C. Found (%): C, 68.32; H, 5.90; N, 5.53. $C_{26}H_{29}BF_4N_2$. Calculated (%): C, 68.43; H, 6.41; N, 6.14. IR (suspension in paraffin oil), ν/cm$^{-1}$: 3163; 3141; 3103; 3065; 3054; 3035; 1562; 1546; 1494; 1365; 1347; 1313; 1287; 1260; 1191; 1154; 1115; 1065; 1047; 1033; 927; 855; 755; 698; 658; 648. $^1$H NMR, δ: 1.76 (t, 6 H, 3 4-$CH_2$ of adamantane, $J$ = 3.0 Hz); 2.18 (t, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 3.2 Hz); 2.28 (br.s, 3 H, 3 3-CH of adamantane); 7.13 (t, 1 H, CH of imidazole, $J$ = 2.0 Hz); 7.22—7.27 (m, 4 H, 4 *m*-$CH_{Ar}$); 7.28 (br.s, 1 H, CH); 7.33—7.42 (m, 6 H, 6 *o*,*p*-$CH_{Ar}$); 7.57 (t, 1 H, CH of imidazole, $J$ = 1.8 Hz); 9.03 (t, 1 H, 2-CH of imidazole, $J$ = 1.6 Hz). $^{13}$C NMR, δ: 29.0; 34.7; 41.9; 60.5; 66.4; 118.4; 121.0; 127.8; 128.7; 128.8; 133.7; 136.2.

***trans*-Dichloro(1-adamantyl-3-methylimidazol-2-yliden)(pyridin)palladium(II) semihydrate (3a).** Palladium(II) chloride (177 mg, 1 mmol), compound **2a** (304 mg, 1 mmol), and potassium carbonate (415 mg, 3 mmol) were suspended in pyridine (10 mL). The reaction mass was stirred for 5 h at 65 °C. Pyridine was evaporated *in vacuo*. Bottom residue was dissolved in dichloromethane (25 mL), washed with saturated NaCl solution (50 mL), and dried over $MgSO_4$. The product was isolated by column chromatography on silica gel (dichloromethane—methanol, 9 : 1), and crystallized from acetonitrile. Yield 0.244 g (51%), yellow crystals, m.p. 248—249 °C (MeCN). Found (%): C, 47.43, H, 5.21, N, 8.33. $C_{19}H_{25}Cl_2N_3Pd \cdot 0.5H_2O$. Calculated (%): C, 47.37; H, 5.44; N, 8.72. IR ($CHCl_3$), ν/cm$^{-1}$: 3134; 3097; 3070; 2977; 2909; 2854; 1606; 1487; 1449; 1402; 1361; 1346; 1306; 1260; 1238; 1208; 1181; 1105; 1079; 1047; 1019; 830; 756; 731; 709; 691; 665. $^1$H NMR, δ: 1.81 (q, 6 H, 3 4-$CH_2$ of adamantane, $J$ = 9.8 Hz); 2.32 (s, 3 H, 3 3-CH of adamantane); 2.81 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 2.4 Hz); 4.32 (s, 3 H, $CH_3$); 6.91 (d, 1 H, CH of imidazole, $J$ = 2.0 Hz); 7.11 (d, 1 H, CH of imidazole, $J$ = 2.4 Hz); 7.32 (t, 2 H, 2 3,5-CH of pyridine, $J$ = 6.8 Hz); 7.73 (t, 1 H, 4-CH of pyridine, $J$ = 7.6 Hz); 9.00 (d, 2 H, 2 2,6-CH of pyridine, $J$ = 4.8 Hz). $^{13}$C NMR, δ: 30.1; 36.0; 39.3; 44.52; 59.8; 119.0; 122.2; 124.4; 137.8; 151.5; 153.3.

***trans*-Dichloro(1-adamantyl-3-(1-naphthylmethyl)imidazol-2-yliden)(pyridin)palladium(II) (3b).** A solution of palladium(II) chloride (127 mg, 0.72 mmol) in boiling pyridine (5 mL) was cooled to 80 °C, and compound **1b** (273 mg, 0.72 mmol), and then potassium carbonate (279 mg, 2.15 mmol) were added thereto. The reaction mixture was stirred for 5 h at 80 °C. Pyridine was evaporated *in vacuo*, the bottom residue was dissolved in THF (200 mL), and passed through the layer of silica gel. Yield 272 mg (63%), yellow powder, m.p. 145—149 °C. Found (%): C, 58.31; H, 5.26; N, 6.47. $C_{29}H_{31}Cl_2N_3Pd$. Calculated (%): C, 58.16; H, 5.22; N, 7.02. IR (suspension in paraffin oil), ν/cm$^{-1}$: 3047; 2983; 2908; 2852; 1604; 1566; 1511; 1448; 1422; 1397; 1359; 1306; 1216; 1172; 1104; 1071; 808; 792; 783; 756; 688; 665. $^1$H NMR, δ: 1.77—1.90 (m, 6 H, 3 4-$CH_2$ of adamantane); 2.35 (s, 3 H, 3 3-CH of adamantane); 2.85 (br.s, 6 H, 3 2-$CH_2$ of adamantane); 6.36 (d, 1 H, CH of imidazole, $J$ = 2.1 Hz); 6.53 (s, 2 H, $CH_2$); 6.97 (d, 1 H, CH of imidazole, $J$ = 2.1 Hz); 7.33 (m, 2 H, 2 3,5-CH of pyridine); 7.47—7.55 (m, 3 H, 3 3,6,7-CH of naphthalene); 7.63 (d, 1 H, 2-CH of naphthalene, $J$ = 5.7 Hz); 7.78 (br.s, 1 H, 4-CH of pyridine); 7.88 (dd, 1 H, 4-CH of naphthalene, $J_1$ = 7.2 Hz, $J_2$ = 1.8 Hz); 7.91 (d, 1 H, 5-CH of naphthalene, $J$ = 7.5 Hz); 8.28 (d, 1 H, 8-CH of naphthalene, $J$ = 7.5 Hz); 9.04 (br.s, 2 H, 2 2,6-CH of pyridine). $^{13}$C NMR, δ: 29.6; 35.5; 37.7; 42.2; 43.9; 118.3; 119.5; 123.9; 124.0; 124.2; 124.4; 125.7; 126.8; 128.9; 129.3; 130.6; 127.4; 138.0; 148.7; 149.0; 151.0.

***trans*-Dichloro(1-adamantyl-3-(diphenylmethyl)imidazol-2-yliden)(pyridin)palladium(II) (3c).** To a solution of palladium(II) chloride (127 mg, 0.72 mmol) in boiling pyridine (5 mL) cooled to 80 °C, compound **2c** (329 mg, 0.72 mmol), and then potassium carbonate (279 mg, 2.15 mmol) were added. The reaction mixture was stirred for 5 h at 80 °C. Pyridine was evaporated *in vacuo*, the bottom residue was washed with water and recrystallized from acetonitrile. Yield 0.165 mg (34%), yellow crystals, m.p. 208—210 °C (MeCN). Found (%): C, 59.85; H, 4.82; N, 7.15. $C_{31}H_{33}Cl_2N_3Pd$. Calculated (%): C, 59.58; H, 5.32; N, 6.72. IR ($CHCl_3$), ν/cm$^{-1}$: 3063; 3030; 2984; 2911; 2853; 1605; 1496; 1485; 1449; 1419; 1405; 1360; 1343; 1307; 1256; 1218; 1200; 1180; 1165; 1104; 1072; 1046; 1032; 841; 827; 813; 753; 727; 693; 666; 649. $^1$H NMR, δ: 1.85 (qd, 6 H, 3 4-$CH_2$ of adamantane, $J_1$ = 17.2 Hz, $J_2$ = 0.8 Hz); 2.37 (s, 3 H, 3 3-CH of adamantane); 2.91 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 2.8 Hz); 6.86 (d, 1 H, CH of imidazole, $J$ = 2.4 Hz); 7.18 (d, 1 H, CH of imidazole, $J$ = 2.4 Hz); 7.30—7.40 (m, 12 H, 10 CH Ar 2 3,5-CH of pyridine); 7.74 (tt, 1 H, 4-CH of pyridine, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz); 8.67 (s, 1 H, CH); 8.95 (dt, 2 H, 2 2,6-CH of pyridine, $J_1$ = 4.8, $J_2$ = 1.6 Hz). $^{13}$C NMR, δ: 29.6; 35.5; 43.9; 59.6; 68.6; 118.8; 119.7; 123.9; 127.5; 127.9; 127.9; 128.6; 137.2; 138.6; 147.1; 151.1.

***trans*-Dichloro[1-adamantyl-3-(1-naphthylmethyl)imidazol-2-yliden](3-methylpyridin)palladium(II) polyhydrate (4b).** Palladium(II) chloride (177 mg, 1 mmol), 3-methylpyridine (0.178 mL, 2 mmol), imidazolium salt **2b** (379 mg, 1 mmol), and potassium carbonate (415 mg, 3 mmol) were suspended in acetonitrile (10 mL). The reaction mixture was stirred for 50 min at 65 °C. The solvent was distilled off *in vacuo*. The bottom residue was dissolven in dichloromethane (25 mL), the resulting suspension was washed with saturated NaCl solution (50 mL). Organic layer was separated, dried over $MgSO_4$, and purified by column chromatography on silica gel, eluting with dichloromethane. Dichloromethane was evaporated to a final volume of 10 mL, and the product was precipitated with petroleum ether. Yield 509 mg (77%), yellow powder, m.p. 139—140 °C. Found (%): C, 54.64; H, 5.09; N, 5.54. $C_{30}H_{33}Cl_2N_3Pd \cdot 2.5H_2O$. Calculated (%): C, 54.76; H, 5.82; N, 6.39. IR ($CHCl_3$), ν/cm$^{-1}$: 3140; 3106; 2985; 2910; 2853; 1608; 1599; 1583; 1512; 1483; 1454; 1422; 1398; 1373; 1360; 1339; 1325; 1306; 1256; 1242; 1213; 1198; 1172; 1130; 1106; 1063; 1030; 829; 809; 793; 785; 755; 722; 699; 688; 666; 544; 419. $^1$H NMR, δ: 1.82 (q, 6 H, 3 4-$CH_2$ of adamantane, $J$ = 10.6 Hz); 2.34 (br.s, 6 H, 3-$CH_3$ of picoline + 3 3-CH of adamantane); 2.84 (s, 6H, 3 2-$CH_2$ of adamantane); 6.34 (s, 1 H, CH of imidazole); 6.53 (s, 2 H, $CH_2$); 6.95 (s, 1 H, CH of imidazole); 7.21 (t, 1 H, 5-CH of pyridine, $J$ = 6.4 Hz); 7.45—7.55 (m, 4 H, 3 3,6,7-CH of naphthalene + 4-CH of pyridine); 7.62 (d, 1 H, 2-CH of naphthalene, $J$ = 7.2 Hz); 7.88 (t, 2 H, 4,5-CH of naphthalene, $J$ = 8.2 Hz); 8.28 (d, 1 H, 8-CH of naphthalene, $J$ = 8.4 Hz); 8.83 (br.s, 2 H, 2 2,6-CH of pyridine). $^{13}$C NMR, δ: 18.4; 30.0; 35.9; 44.4; 54.2; 59.7; 118.7; 119.9; 123.9; 124.5; 125.3; 126.2; 127.3; 128.5; 129.4; 129.7; 130.1; 131.9; 133.9; 134.4; 138.4; 145.8; 148.7; 151.5.

***trans*-Dichloro[1-adamantyl-3-(diphenylmethyl)imidazol-2-yliden](3-methylpyridin)palladium(II) semihydrate (4c).** Palladium(II) chloride (181 mg, 1.02 mmol), 3-methylpyridine (0.199 mL, 2.04 mmol), salt **2c** (466 mg, 1.02 mmol), and potassium carbonate (423 mg, 3.06 mmol) were suspended in acetonitrile (10 mL). The reaction mixture was stirred for 5 h at 65 °C; the solvent was evaporated *in vacuo*. The bottom residue was dissolved in dichloromethane (25 mL), washed with saturated NaCl solution (50 mL), and dried over $MgSO_4$. Complex was purified by column chromatography on silica gel, eluting with dichloromethane. The product was precipitated with petroleum ether. Yield 171 mg (27%), yellow powder, m.p. 164—165 °C. Found (%): C, 59.35; H, 5.36; N, 5.72. $C_{32}H_{35}Cl_2N_3Pd \cdot 0.5H_2O$. Calculated (%): C, 59.31; H, 5.60; N, 6.48. IR ($CHCl_3$), ν/cm$^{-1}$: 3063; 3031; 2948; 2910; 2853; 1496; 1483; 1453; 1419; 1405; 1360; 1343; 1307; 1255; 1200; 1180; 1165; 1130; 1105; 1032; 841; 827; 794; 752; 727; 696; 665; 649. $^1$H NMR, δ: 1.81 (qd, 6H, 3 4-$CH_2$ of adamantane, $J_1$ = 10.7 Hz, $J_2$ = 1.2 Hz); 2.31—2.35 (m, 6 H, $CH_3$ of picoline + 3 3-CH of adamantane); 2.40 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 2.4 Hz); 6.81 (d, 1 H, CH of imidazole, $J$ = 2.0 Hz); 7.13 (d, 1 H, CH of imidazole, $J$ = 2.0 Hz); 7.16 (dd, 1 H, 5-CH of picoline, $J_1$ = 7.6 Hz, $J_2$ = 5.6 Hz); 7.29—7.38 (m, 10 H, Ph); 7.49 (d of heptetes, 1 H, 4-CH of picoline, $J_1$ = 7.6 Hz, $J_2$ = 0.4 Hz); 8.63 (s, 1 H, C<u>H</u>$Ph_2$); 8.68—8.71 (m, 2 H, 2 2,6-CH of picoline). $^{13}$C NMR, δ: 18.4; 30.1; 36.0; 44.4; 60.1; 69.1; 119.1; 120.1; 123.8; 127.9; 128.4; 129.1; 134.3; 138.3; 139.21; 148.0; 148.7; 151.6.

***trans*-Dichloro[1-adamantyl-3-methylimidazol-2-yliden]-(4-methylpyridin)palladium(II) (5a)** was obtained similarly to complex **4c** from palladium(II) chloride (177 mg, 1 mmol), 4-methylpyridine (0.187 mL, 2 mmol), compound **2a** (304 mg, 1 mmol), and potassium carbonate (415 mg, 3 mmol). Yield 0.202 g (41%), yellow powder, m.p. 244—258 °C (decomp.). Found (%): C, 48.11; H, 5.33; N, 7.85. $C_{20}H_{27}Cl_2N_3Pd \cdot 0.5H_2O$. Calculated (%): C, 48.45; H, 5.69; N, 8.48. IR ($CHCl_3$), ν/cm$^{-1}$: 3136; 3106; 2983; 2910; 2853; 1619; 1503; 1454; 1404; 1360; 1347; 1326; 1307; 1259; 1230; 1208; 1180; 1105; 1070; 1035; 830; 811; 754; 711; 687; 665; 501; 492. $^1$H NMR, δ: 1.80 (q, 6 H, 3 4-$CH_2$ of adamantane, $J$ = 10.0 Hz); 2.31 (t, 3 H, 3 3-CH of adamantane, $J$ = 8.8 Hz); 2.35 (s, 3 H, $CH_3$); 2.80 (s, 6 H, 3 2-$CH_2$ of adamantane); 4.31 (s, 3 H, $CH_3$ of picoline); 6.90 (d, 1 H, CH of imidazole, $J$ = 1.6 Hz); 7.09—7.13 (m, 3 H, CH of imidazole 2 3,5-CH of pyridine); 8.81 (d, 2 H, 2 2,6-CH of pyridine, $J$ = 6.0 Hz). $^{13}$C NMR, δ: 20.9; 30.1; 36.0; 39.2; 44.5; 59.7; 118.9; 122.1; 125.2; 149.7; 150.8; 152.6.

***trans*-Dichloro[1-adamantyl-3-(1-naphthylmethyl)imidazol-2-yliden](4-methylpyridin)palladium(II) (5b).** To a solution of palladium(II) chloride (0.72 mmol) in boiling acetonitrile (5 mL) cooled to 80 °C, and 4-methylpyridine (3 mmol), compound **1b** (273 mg, 0.72 mmol) were added, followed by potassium carbonate (279 mg, 2.15 mmol). The reaction mixture was stirred for 5 h at 80 °C. Then, the solvent was distilled *in vacuo*. The bottom residue was dissolved in THF (200 mL) and passed through silica gel. The solvent was distilled off. The product was purified by recrystallization from acetone. Yield 0.182 g (39%), yellow powder, m.p. 118—120 °C (acetone). Found (%): C, 57.57; H, 5.47; N, 6.86. $C_{30}H_{33}Cl_2N_3Pd$. Calculated (%): C, 58.79; H, 5.43; N, 6.86. IR ($CHCl_3$), ν/cm$^{-1}$: 3069; 3046; 2982; 2909; 2852; 1618; 1597; 1582; 1511; 1502; 1448; 1423; 1397; 1306; 1255; 1211; 1195; 1172; 1070; 1033; 994; 792; 783; 753; 722; 687; 665; 634. $^1$H NMR, δ: 1.76—1.88 (m, 6 H, 3 4-$CH_2$ of adamantane); 2.33 (dt, 3 H, 3 3-CH of adamantane, $J_1$ = 4.8 Hz, $J_2$ = 2.4 Hz); 2.35 (s, 3 H, $CH_3$); 2.84 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 2.4 Hz); 6.34 (d, 1 H, CH of imidazole, $J$ = 2.0 Hz); 6.52 (s, 2 H, $CH_2$); 6.95 (d, 1 H, CH of imidazole, $J$ = 2.0 Hz); 7.13 (dd, 2 H, 2 3,5-CH of pyridine, $J_1$ = 6.0 Hz, $J_2$ = 1.5 Hz); 7.45—7.55 (m, 3 H, 3 3,6,7-CH of naphthalene); 7.61 (dd, 1 H, 2-CH of naphthalene, $J_1$ = 6.4 Hz, $J_2$ = 0.9 Hz); 7.87 (dd, 1 H, 4-CH of naphthalene, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz); 7.89 (d, 1 H, 5-CH of naphthalene, $J$ = 8.0 Hz); 8.28 (dd, 1 H, 8-CH of naphthalene, $J_1$ = 8.4 Hz, $J_2$ = 1.2 Hz); 8.86 (dd, 2 H, 2 2,6-CH of pyridine, $J_1$ = 5.2 Hz, $J_2$ = 1.6 Hz). $^{13}$C NMR, δ: 21.0; 30.0; 35.9; 44.4; 54.2; 59.7; 118.7; 119.9; 124.5; 125.3; 125.3; 126.2; 127.2; 128.5; 129.4; 129.7; 130.1; 131.9; 133.9; 145.9; 149.8; 150.8.

***trans*-Dichloro[1-adamantyl-3-(diphenylmethyl)imidazol-2-yliden](4-methylpyridin)palladium(II) (5c).** To a solution of palladium(II) chloride (0.72 mmol) in boiling acetonitrile (5 mL) cooled to 80 °C, 4-methylpyridine (3 mmol) and compound **2c** (273 mg, 0.72 mmol) were added, followed by potassium carbonate (279 mg, 2.15 mmol). The reaction mixture was stirred for 5 h at 80 °C. Then, the solvent was distilled *in vacuo*. The bottom residue was washed with water. The product was purified by recrystallization from acetonitrile. Yield 0.210 mg (46%), yellow crystals, m.p. 140—141 °C (MeCN). Found (%): C, 60.22; H, 5.08; N, 7.14. $C_{32}H_{35}Cl_2N_3Pd$. Calculated (%): C, 60.15; H, 5.52; N, 6.58. IR ($CHCl_3$), ν/cm$^{-1}$: 3063; 3031; 2983; 2910; 2853; 1619; 1497; 1451; 1419; 1406; 1360; 1341; 1307; 1255; 1231; 1212; 1200; 1179; 1165; 1104; 1073; 1033; 842; 812; 752; 728; 694; 666; 649. $^1$H NMR, δ: 1.77 (td, 6 H, 3 4-$CH_2$ of adamantane, $J_1$ = 9.3 Hz, $J_2$ = 2.4 Hz); 2.28 (s, 3 H, $CH_3$); 2.37 (s, 3 H, 3 3-CH of adamantane); 2.80 (d, 6 H, 3 2-$CH_2$ of adamantane, $J$ = 1.6 Hz); 7.29 (d, 1 H, CH of imidazole, $J$ = 2.4 Hz); 7.30—7.40 (m, 12 H, 10 $CH_{Ar}$ + 2 3,5-CH of pyridine); 7.66 (d, 1 H, CH of imidazole, $J$ = 2.4 Hz); 8.55 (s, 1 H, CH); 8.65 (d, 2 H, 2 2,6-CH of pyridine, $J$ = 6.0 Hz). $^{13}$C NMR, δ: 20.5; 29.5; 35.4; 43.5; 59.2; 68.6; 120.2; 121.0; 125.5; 127.8; 128.3; 128.8; 139.1; 147.2; 150.2 150.4.

**2,3,5-Triphenylthiophene (6)[44].** To DMA (6 mL), 2,3-diphenylthiophene (236.3 mg, 1 mmol), iodobenzene (0.11 mL, 2 mmol), $Cs_2CO_3$ (815 mg, 2.5 mmol), pivalic acid (31 mg, 30 mol.%), and precatalyst (2 mol.%) were added. The suspension was heated under reflux for 3 h. Then, to the suspension cooled to ~20 °C, phenanthrene (31.2 mg) was added as an internal standard. An aliquot (0.2 mL) was adjusted with $CH_2Cl_2$ to a volume of 2 mL, and filtered. GC-MS analysis was performed. The reaction mixture was extracted with ethyl acetate (2S25 mL), washed with saturated NaCl solution, and dried over $MgSO_4$. The products were purified by column chromatography on silica gel (eluent was petroleum ether, 40—70 °C), and then recrystallized from ethanol. To calibrate GC-MS for quantitative analysis, solvents were used prepared from quantities of 2,3-diphenylthiophene, 2,3,5-triphenylthiophene (**6**), and phenanthrene. 2,3,5-Triphenylthiophene (**6**) is a yellow powder, m.p. 106—107 °C (EtOH). $^1$H NMR, δ: 7.34—7.18 (m, 14 H, Ar); 7.58 (d, 2 H, Ar, $J$ = 7.6 Hz). MS, $m/z$ ($I_{rel}$ (%)): 313 $[M + 1]^+$ (26), 312 $[M]^+$ (100), 311 $[M - H]^+$ (13), 278 $[M - H_2S]^+$ (12), 121 $[C_7H_5S]^+$ (10).

**4-(1-Methyl-1*H*-imidazo-5-yl)benzonitrile (7)[45,35].** To DMA (4 mL), *p*-bromobenzonitrile (182.0 mg, 1 mmol), 1-methylimidazole (0.16 mL, 2 mmol), $K_2CO_3$ (276 mg, 2 mmol), pivalic acid (31 mg, 30 mol.%), and precatalyst **3a—d** (0.5 mol.%)

**Table 3.** Selected crystallographic parameters and results of refinement of structures **3a**, **5c**, and **7**

| Parameter | **3a** | **5c** | **7** |
|---|---|---|---|
| Molecular formula | $C_{19}H_{25}Cl_2N_3Pd$ | $2(C_{32}H_{35}Cl_2N_3Pd)\cdot C_2H_3N$ | $C_{11}H_9N_3$ |
| $M$ | 472.72 | 1318.91 | 183.21 |
| $T$/K | 295(2) | 295(2) | 295(2) |
| System | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 14.347(2) | 12.2467(8) | 13.666(4) |
| $b$/Å | 14.2736(16) | 16.1196(9) | 7.272(2) |
| $c$/Å | 10.4159(15) | 16.7547(11) | 9.965(3) |
| α/deg | 90.00 | 97.363(5) | 90.00 |
| β/deg | 110.905(16) | 107.521(6) | 107.91(4) |
| γ/deg | 90.00 | 97.375(5) | 90.00 |
| $V$/Å$^3$ | 1992.6(5) | 3079.0(3) | 942.3(5) |
| $Z$ | 4 | 2 | 4 |
| $d_{calc}$/g cm$^{-3}$ | 1.576 | 1.423 | 1.291 |
| μ/mm$^{-1}$ | 1.206 | 0.804 | 0.081 |
| $F$(000) | 960 | 1356 | 384 |
| Crystal size/mm | 0.55×0.30×0.14 | 0.58×0.31×0.26 | 0.60×0.35×0.24 |
| Scattering angles, 2θ/deg | 6.46° < 2θ < 58.57° | 4.38° < 2θ < 58.69° | 6.42° < 2θ < 58.92° |
| Indices of refraction | $-19 \leqslant h \leqslant 13$, $-18 \leqslant k \leqslant 13$, $-11 \leqslant l \leqslant 13$ | $-13 \leqslant h \leqslant 16$, $-21 \leqslant k \leqslant 20$, $-22 \leqslant l \leqslant 22$ | $-18 \leqslant h \leqslant 17$, $-6 \leqslant k \leqslant 9$, $-13 \leqslant l \leqslant 13$ |
| Number of reflection collected | 11578 | 27041 | 4402 |
| Number of independent reflections | 4677 ($R_{int}$ = 0.0304) | 14217 ($R_{int}$ = 0.0288) | 2213 ($R_{int}$ = 0.0293) |
| Number of data/restrictions/parameters | 4677/238/318 | 14217/0/715 | 2213/0/129 |
| Goodness-of-fit on $F^2$ | 1.063 | 1.061 | 1.035 |
| $R$-factors [$I \geq 2\sigma(I)$] | $R_1$ = 0.0503, $wR_2$ = 0.1413 | $R_1$ = 0.0370, $wR_2$ = 0.0894 | $R_1$ = 0.0522, $wR_2$ = 0.1252 |
| $R$-factors (all reflections) | $R_1$ = 0.0614, $wR_2$ = 0.1509 | $R_1$ = 0.0506, $wR_2$ = 0.0988 | $R_1$ = 0.0732, $wR_2$ = 0.1436 |
| Residual electron density/e Å$^{-3}$, $\rho_{max}/\rho_{min}$ | 1.55/−0.83 | 0.742/−0.864 | 0.204/−0.164 |

were added. The suspension was stirred for 10 h at 110 or 130 °C. Then, to the suspension cooled to ~20 °C, phenanthrene (18.3 mg) was added as an internal standard. An aliquot (0.2 mL) was adjusted with $CH_2Cl_2$ to a volume of 2 mL, filtered and analyzed by GC-MS technique. The reaction mixture was extracted with $CH_2Cl_2$ (2S25 mL), washed with saturated NaCl solution, and dried over $MgSO_4$. The products were purified by column chromatography on silica gel, eluting first with dichloromethane, and then with a $CH_2Cl_2$—MeOH (15 : 1, v/v) mixture. Compound **7** is yellow-brown crystals, m.p. 131—132 °C ($CH_2Cl_2$). To calibrate GC-MS for quantitative analysis, solvents were used prepared from quantities of *p*-bromobenzonitrile, 4-(1-methyl-1*H*-imidazo-5-yl)benzonitrile, and phenanthrene. $^1$H NMR, δ: 3.77 (s, 3 H, $CH_3$); 7.21 (s, 1 H, 4-H of imidazole); 7.51 (dt, 2 H, Ar, $J_1$ = 8.4, $J_2$ = 1.4 Hz); 7.58 (s, 1 H, 2-H of imidazole); 7.71 (dt, 2 H, Ar, $J_1$ = 8.4 Hz, $J_2$ = 1.4 Hz). MS, $m/z$ ($I_{rel}$ (%)): 184 $[M + 1]^+$ (14), 183 $[M]^+$ (100), 155 $[M - CH_2N]^+$ (13), 128 $[M - C_2H_3N_2]^+$ (12), 114 $[M - C_3H_5N_2]^+$ (10).

**Structural studies.** Crystals of salt **2a** were obtained by recrystallization from ethanol—water mixture; crystals of complexes **3a** and **5c** were grown by a slow evaporation of their solutions in MeCN. X-ray diffraction analysis of salt **2a** as well as complexes **3a** and **5c** was performed on a Xcalibur Ruby diffractometer according to a standard procedure (Mo-Kα-radiation, graphite monochromator, ω-scanning with an incremental step of 1°). Empirical absorption corrections were introduced. Structures were solved using SHELXS (see Ref. 46) and refined by full-matrix least-squares calculations against $F^2$ in anisotropic approximation for all non-hydrogen atoms using SHELXL (see Ref. 47) software with graphical interface OLEX2.[48] Hydrogen atoms were placed to calculated positions and refined using a riding model. Main crystallopraphic parameters and results of structure refinement of structures **3a** and **5c** are summarized in Table 3. Structure of salt **2a** was also confirmed by the X-ray diffraction analysis, however due to the strong disordering of an anion it was not possible to achieve acceptable divergence factors.

The X-ray crystallographic data were deposited with the Cambridge Crystallographic Data Centre as a cif file with numbers CCDC 1910036 (complex **3a)** and 1910037 (complex **5c**). The structure of compound **7** has been deposited earlier and had the deposition number CCDC 1837277. These data are free available and can be requested at www.ccdc.cam.ac.uk.

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