DOI 10.1007/s10593-019-02445-1

Chemistry of Heterocyclic Compounds **2019**, *55*(3), 217–228

Adamantanyl-substituted PEPPSI-type palladium(II) N-heterocyclic carbene complexes: synthesis and catalytic application for CH activation of substituted thiophenes

Vladimir A. Glushkov[1,2], Michail S. Denisov[1]*, Aleksey A. Gorbunov[1], Yurii A. Myalitzin[2], Maksim V. Dmitriev[2], Pavel A. Slepukhin[3,4]

[1] *Institute of Technical Chemistry, Perm Federal Scientific Centre, Ural Branch of Russian Academy of Sciences, 3 Academician Korolev St., Perm 614013, Russia; e-mail: denisov.m@itcras.ru*

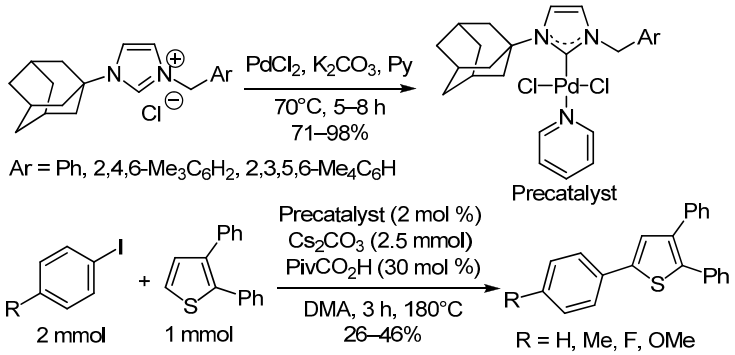
[2] *Perm State National Research University, 15 Bukireva St., Perm 614099, Russia; e-mail: maxperm@yandex.ru*

[3] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 22 S. Kovalevskoi St. / 20 Akademicheskaya St., Yekaterinburg 620990, Russia; e-mail: slepukhin@ios.uran.ru*

[4] *Ural Federal University named after the first President of Russia B. N. Yeltsin, 19 Mira St., Yekaterinburg 620002, Russia*

Published in Khimiya Geterotsiklicheskikh Soedinenii, 2019, *55*(3), 217–228

Submitted January 28, 2019
Accepted February 21, 2019



Starting from 1-adamantanyl-3-imidazole, a number of new 1-adamantanyl-3-benzylimidazolium salts and corresponding unsymmetrically substituted Pd(II) PEPPSI-type complexes were prepared, including dichloride, dibromide, and diiodide. Single crystal X-ray crystallography confirmed solid state structures in six cases. The complexes reported in this work displayed moderate activities as precatalysts for CH activation/arylation reaction of substituted thiophenes.

Keywords: N-heterocyclic carbene, palladium(II) complexes, thiophene, arylation, CH activation.

At the present time, N-heterocyclic carbenes (NHC) represent a prominent class of ligands, widely used in organometallic and inorganic chemistry.[1] A special family of bench-stable precatalysts named PEPPSI-complexes (Pyridine Enhanced Precatalysts: Preparation, Stabilization, and Initiation) were successfully introduced by Organ et al.[2] To date a numerous analogs of PEPPSI family complexes with different N-ligands were synthesized; among them complexes with 2-, 3-, 4-pyridinecarboxylic and pyridine-2,6-dicarboxylic acids,[3] quinoline and isoquinoline ligands,[4] *N*-methylimidazole,[5] *N*-alkyl-, *N*-arylimidazoles,[6] morpholine,[7] diethanolamine,[8] triethylamine,[9] aniline,[10] pyrazine,[11] and other ligands.[12]

PEPPSI-complexes have found numerous applications in organic chemistry, including Mizoroki–Heck reaction,[13] Suzuki,[14] Sonogashira,[15] Negishi[16] cross-coupling, amination,[17] sulfination,[18] arylation,[19] and carbonylation[20] reactions.

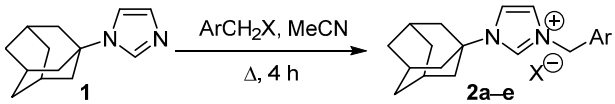
Modification of the NHC moiety of PEPPSI-complexes has attracted great interest as a strategy to obtain better catalytic performance. Complexes with nonsymmetric substitution pattern emerged recently as one of the modern

approaches in catalysis design,[21] especially in the field of PEPPSI complexes.[22] On the other hand, catalysts containing adamantane ligand are highly demanded in catalysis.[23] First adamantanyl-substituted PEPPSI complex was described by Organ,[24] but there are rare examples of such type of catalysts in literature.[25]

In this work, we present the synthesis of novel unsymmetrical imidazolium salts with adamantanyl scaffold and PEPPSI complexes thereof. We also want to elucidate utilization of these complexes in CH activation/arylation reaction of 2,3-disubstituted thiophenes.

Our study started from 1-(adamantan-1-yl)-3-(arylmethyl)-imidazolium salts. In spite of the simple structure, and in contrast to the well-known 1,3-bisadamantanylimidazolium salts,[26] 1-(adamantan-1-yl)-3-(arylmethyl)imidazolium salts[27] and compounds with two imidazolium moieties, linked by 1,3-dimethylbenzene,[28] our starting compounds were not synthesized before our investigation. Imidazolium salts **2a**–**e** were prepared in good yields (70–92%) from 1-adamantanyl-imidazole **1** and the corresponding benzyl halides in MeCN under heating conditions (Scheme 1). Salts **2a**–**e** are soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, alcohols, DMSO, DMF. They are poorly soluble in EtOAc and insoluble in Et_2O and hexane. They are all stable toward both air and moisture.

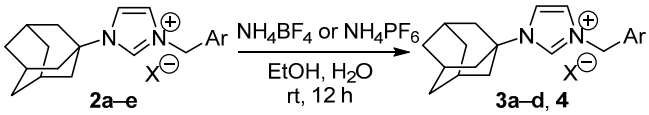
Scheme 1. Synthesis of adamantanylimidazolium salts **2a**–**e**



2 a Ar = Ph, X = Cl (70%); **b** Ar = 2,4,6-$Me_3C_6H_2$, X = Cl (78%); **c** Ar = 2,3,5,6-Me_4C_6H, X = Cl (92%); **d** Ar = Ph, X = Br (86%); **e** Ar = 3,5-$Me_2C_6H_3$, X = Br (87%)

It is well known that imidazolium tetrafluoroborates are usually easier to purify than their chloride or bromide congeners; for this reason, we have prepared the corresponding tetrafluoroborates **3a**–**d** and hexafluorophosphate **4** by salt metathesis (Scheme 2).

Scheme 2. Preparation of tetrafluoroborates **3a**–**d** and hexafluorophosphate **4**



3 a Ar = Ph, X = BF_4 (94%); **b** Ar = 3,5-$Me_2C_6H_3$, X = BF_4 (87%); **c** Ar = 2,4,6-$Me_3C_6H_2$, X = BF_4 (73%); **d** Ar = 2,3,5,6-Me_4C_6H, X = BF_4 (98%); **4** Ar = 2,4,6-$Me_3C_6H_2$, X = PF_6 (70%)

The most characteristic feature of salts **2**–**4** is the signal at 8.73–11.19 ppm in ^{1}H NMR spectra and at 132.9–135.4 ppm in ^{13}C NMR spectra, indicative of C-2 atom.

Single crystals that were suitable for X-ray diffraction study were obtained for salts **2d**,**e** and **3c** by slow evaporation of salt solution from MeCN–EtOAc mixture. Crystal data for compounds **2d**,**e** and **3c** are presented in the Supplementary information file, Table S1.

According to X-ray diffraction data, compound **2e** contains one water molecule to one molecule of the salt (Fig. 2). IR spectra and elemental analysis data directly indicate inclusion of water into crystals of compounds **2a**–**c**,**e**. Recently we have demonstrated inclusion of water to the crystals of imidazolium salts with bulky diterpene[29] and triterpene[30] moieties.

Compounds **2d**,**e** and **3c** (Figs. 1–3) crystallize in the centrosymmetric space groups. The two independent molecules of salt **2e** are crystallized as hydrates, H atoms

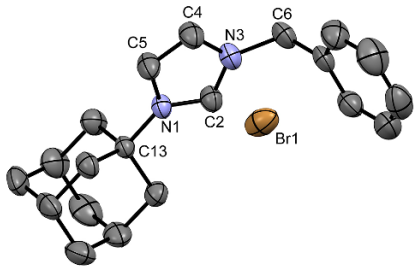


Figure 1. Molecular structure of compound **2d** with atoms represented by thermal vibration ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity.

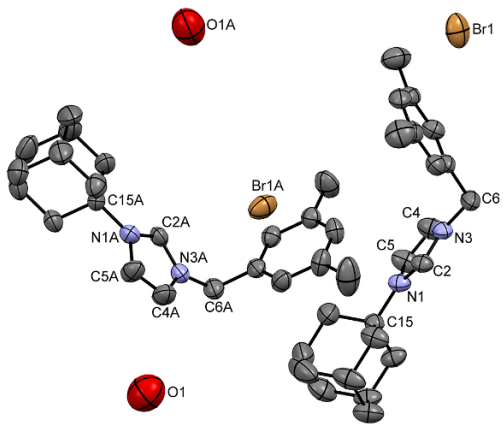


Figure 2. Asymmetric cell containing two molecules of compound **2e** and two molecules of water. Atoms are represented by thermal vibration ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity.

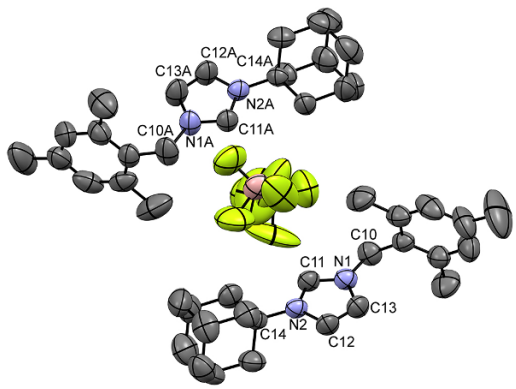
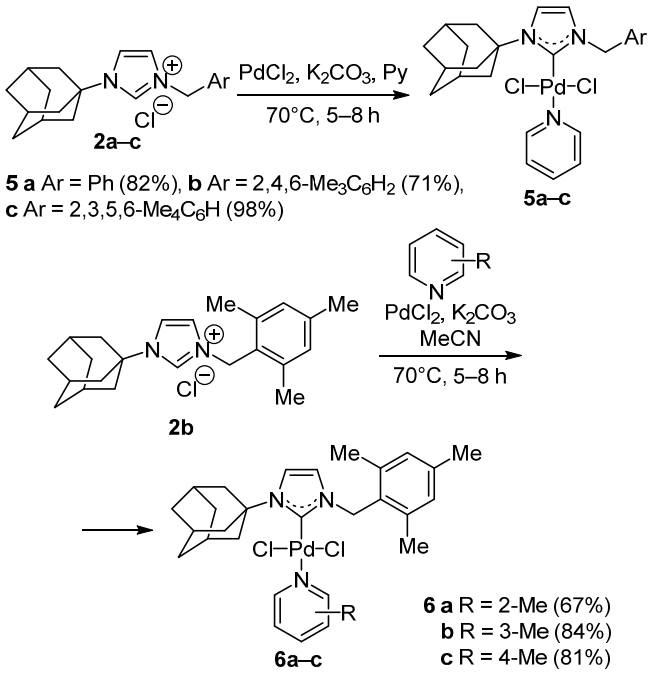


Figure 3. Asymmetric cell of compound **3c** containing two molecules. Atoms are represented by thermal vibration ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity. The F atoms in both tetrafluoroborate anions of compound **3c** are disordered over three positions.

of the H_2O were not localized. All bond lengths and angles in compounds **2d**,**e**, **3c** are in the normal range. The molecules of compounds **2d**,**e** have a L-like conformation. The dihedral angle between plane N_{Het}–C–Ar of the methylene group and plane of the aryl substituent is 88° for compound **2d** and –78° and +76° for independent molecules of compound **2e**. The dihedral angles between planes of the aryl substituent and azole ring are 65–70°. In the crystals of both compounds **2d**,**e**, the shortened cation–anion contacts CH···Br are observed with the distance 0.18–0.20 Å less than the sum of the individual van der Waals radii. These contacts may be regarded as the weak H bonds between Br^- and H atoms at the activated positions of the azole. The asymmetric unit of salt **3c** also contains two independent molecules. The dihedral angles between plane N_{Het}–C–Ar of the methylene group and plane of the aryl substituent are 90° and +74° (for independent molecules of compound **3c**).

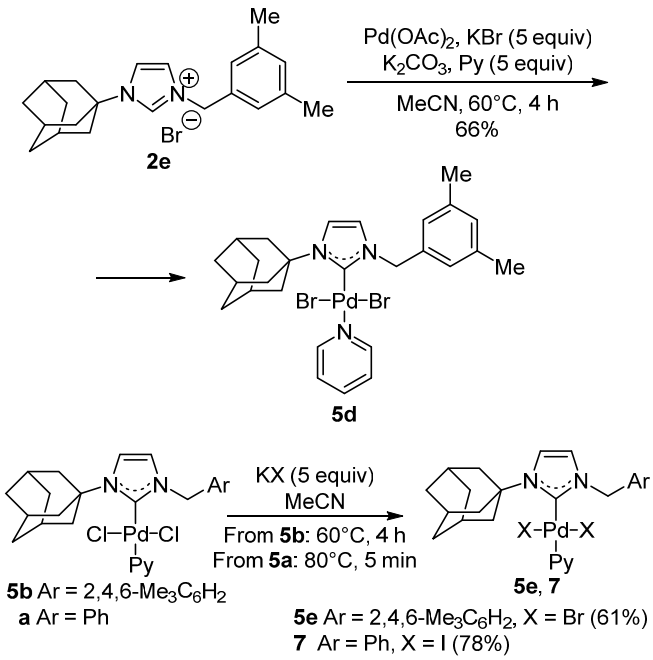
Palladium PEPPSI-like complexes **5a**–**c** were prepared by reacting the ligand precursors **2a**–**c** with $PdCl_2$, K_2CO_3, in neat pyridine. Complexes **6a**–**c** were prepared with the 5-fold excess of substituted pyridine in MeCN solution (Scheme 3).

Scheme 3. Preparation of complexes **5a**–**c**, **6a**–**c**



Chloride salt **2a** smoothly afforded complex **5a** with 82% yield. When we performed the reaction with bromide salts **2d**,**e** and $PdCl_2$, scrambling of halogens Br/Cl occurred, and triple signals at 118–119 (CH Im), 59–60 (C Ad), 56–57 (NCH_2), 44 ppm (CH_2 Ad) (as well as for some aromatic C atoms) appeared in the ^{13}C NMR spectra, which are consistent with three different complexes. Pure bromide complex **5d** with 3,5-dimethylbenzyl substituent was obtained from reaction of bromide salt **2e**, $Pd(OAc)_2$, pyridine, K_2CO_3, and 5-fold excess of KBr under the reaction conditions (Scheme 4). In a similar manner,

Scheme 4. Preparation of complexes **5d**,**e** and **7**



bromide complex **5e** was synthesized by heating chloride complex **5b** in MeCN with 5-fold excess of KBr. Heating of chloride complex **5a** with 5-fold excess of KI in MeCN afforded iodide complex **7** (Scheme 4).

The formation of complexes **5a**–**e** was easily monitored by disappearance of the 2-CH signal in ^1H NMR spectra (8.70–11.2 ppm). Signals of the carbene atom C-2 in the ^{13}C NMR spectra fall in the range of 143.0–144.6 ppm for compounds **5a**–**e** and at 145.1–146.4 ppm for compounds **6a**–**c**, which is comparable to that observed in other *trans*-Pd(L)-(Py)Cl_2-PEPPSI complexes, according to literature reports (135–157 ppm).[31]

To escape the pyridine impurities in the target complexes, some authors suggested washing the reaction mixture with aqueous $CuSO_4$.[31a] However, in our hands this workup was not effective. Pyridine and substituted pyridines were separated by three steps: washing of complexes solutions in CH_2Cl_2 with H_2O, chromatography on silica gel column, and subsequent crystallization from petroleum ether – CH_2Cl_2 mixture.

The molecular structure of complexes **5d**, **6a**, and **7** was unambiguously confirmed by an X-ray diffraction analysis (Figs. 4–6). Single crystals that were suitable for X-ray diffraction study were obtained for bromide Pd(II) complex **5d**, chloride Pd(II) complex **6a**, and iodide Pd(II) complex **7**. Complexes **5d** and **6a** were obtained by slow evaporation of their solutions in hexane–CH_2Cl_2 mixture at ambient temperature. Complex **7** was crystallized from Me_2CO. Crystal data for compounds **5d**, **6a**, and **7** are presented in the Supplementary information file, Table S1.

Compounds **5d**, **6a**, and **7** crystallize in the centrosymmetric space groups. The asymmetric unit of complex **6a** contains two independent molecules. Pd–$C_{carbene}$ bond length for compounds **5d**, **6a**, and **7** fall in the range of 1.96–1.97 Å**,** which is consistent with the bond distances in the

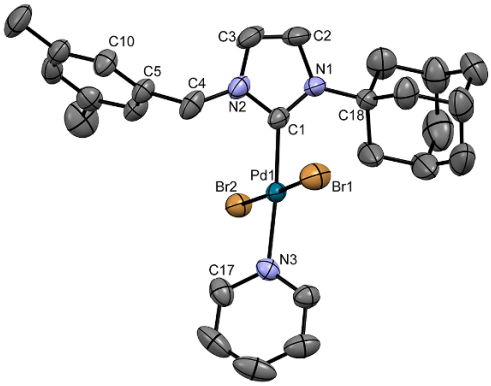


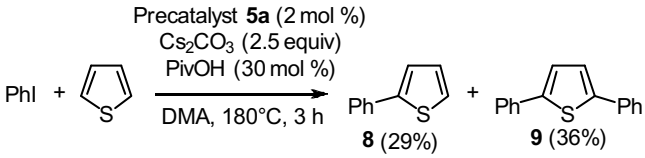
Figure 4. Molecular structure of compound **5d** with atoms represented by thermal vibration ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C(1) 1.960(4), Pd–Br(1) 2.4252(8), Pd–Br(2) 2.4426(8), C(1)–N(1) 1.356(5), C(1)–N(2) 1.354(5), N(1)–C(1)–N(2) 106.0(4), Pd–C(1)–N(1) 133.3(3), Pd–C(1)–N(2) 120.6(3), Br(1)–Pd–Br(2) 177.86(2), Br(1)–Pd–C(1) 88.6(1), Br(1)–Pd–N(3) 89.13(9), C(1)–Pd–N(3) 174.0(2).

related PEPPSI complexes.[17i,31b,32] Pd atoms in the complexes **5d**, **6a**, **7** have slightly distorted square planar geometry; C–Pd–C angles are ranging from 174 to 178°. The X-ray diffraction study along with ^{1}H and ^{13}C NMR data confirm the presence of the metal-bound pyridine moiety in complexes **5d**, **6a**, **7**. The complexes display the coordination of the pyridine ligand *trans* to the N-heterocyclic carbene ligand. The Pd–$N_{pyridine}$ distances in complexes **5d** (2.00 Å), **6a** (2.00 Å), and **7** (2.105(3) Å) are comparable to those in PEPPSI analogs reported by Ghosh et al. (2.092–2.107 Å).[33]

The deprotonation of the azole lead to significant transformation of bond distances in the azole ring of compound **7**. In particular, bond lengths are slightly longer than those in the corresponding imidazolium salts. The dihedral angle between plane N_{Het}–C–Ar of the methylene group and plane of the aryl substituent (27°) in complex **7** are much smaller to that of imidazolium salt **2b**. Any significantly shortened intermolecular contacts in the crystal are not observed.

Having Pd complexes in hand, we studied CH activation/arylation reaction of thiophene (1 equiv), taking PhI (2 equiv) as arylation agent, complexes **5a**–**c**,**e** and **6a** (2 mol %) as precatalysts, Cs_2CO_3 and pivalic acid as additives (Scheme 5). There are some examples in literature: arylation at the C-2[34] and C-3[35] positions of thiophene ring was reported, polyarylation is also known;[36] in one case, Pd-PEPPSI-complexes were used in this reaction.[37] In our hands the arylation was carried out at the C-2 and C-5 atoms by the concerted metalation-deprotonation pathway.[38] To our regret, reaction of simple thiophene afforded a

Scheme 5. Arylation of thiophene



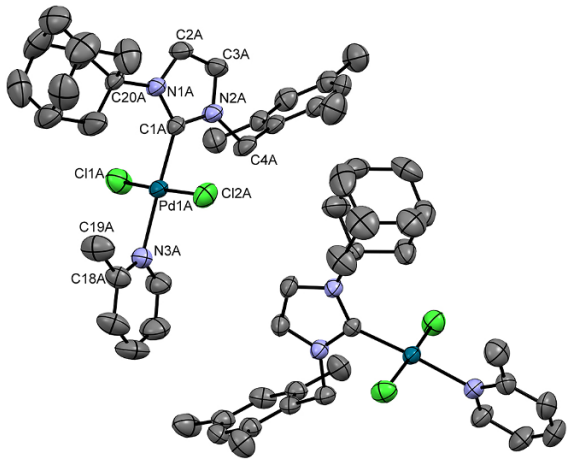


Figure 5. Molecular structure of compound **6a** with atoms represented by thermal vibration ellipsoids of 50% probability (two independent molecules are shown). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for molecule A: Pd–C(1) 1.97(3), Pd–Cl(1) 2.3159(9), Pd–Cl(2) 2.308(1), Pd–N(3) 2.107(3), C(1)–N(1) 1.346(5), N(1)–C(2) 1.388(4), N(1)–C(20) 1.503(4), C(1)–N(2) 1.344(3), N(2)–C(3) 1.371(5), N(2)–C(4) 1.482(5), C(2)–C(3) 1.338(5), Cl(1)–Pd–Cl(2) 174.00(4), Cl(1)–Pd–N(3) 93.64(8), Cl(1)–Pd–C(1) 87.92(9), Cl(2)–Pd–N(3) 88.76(8), Cl(2)–Pd–C(1) 89.23(9), N(3)–Pd–C(1) 174.8(1).

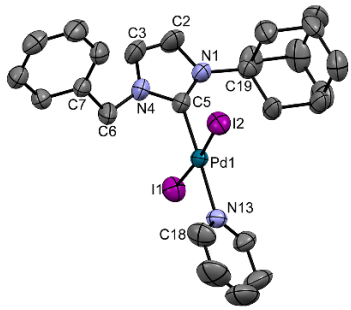


Figure 6. Molecular structure of compound **7** with atoms represented by thermal vibration ellipsoids of 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C(5) 1.972(4), Pd–I(1) 2.6269(5), Pd–I(2) 2.6135(5), Pd–N(13) 2.105(3), C(5)–N(4) 1.361(5), C(5)–Pd–I(2) 89.00(12), N(13)–Pd–I(2) 92.23(9), N(13)–Pd–I(1) 91.67(9), Pd–C(5) 1.972(4), C(5)–Pd–I(1) 87.02(12).

mixture of mono- and diarylated products with comparable low yields (Scheme 5). It is reasonable to assume that introduction of one phenyl group into thiophene moiety facilitates second arylation stage.

Since thiophene arylation under the explored conditions was not selective, we decided to take 2,3-diphenylthiophene as a more robust substrate (Scheme 6). The results of catalyst's scope are presented in Table 1. In comparison to precatalysts **5**, **6**, a conventional Pd-PEPPSI-IPr catalyst (**10**) and complex $PdBr_2Py_2$ (**11**) were also taken.

According to literature data,[2a,c,9] catalysis is initiated after rapid reduction of the Pd(II) species to Pd(0) complex with subsequent pyridine dissociation from the generated Pd(0) complex. So, it is suggested that pyridine ligand in complexes **5a**–**c**,**e**, **6a** plays a role of "throw-away ligand" during the catalytic cycle; thence the nature of pyridine

Scheme 6. General reaction scheme for catalyst screening in arylation reaction

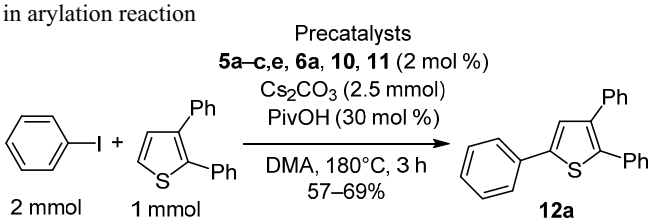


Table 1. Catalyst's scope for the arylation of 2,3-diphenylthiophene by PhI*

Entry	Catalyst	Conversion**, %	Yield of compound **12a**, %
1	**5a**	98	59
2	**5b**	98	58
3	**5c**	97	60
4	**5e**	99	57
5	**6a**	100	57
6	PEPPSI-IPr (**10**)	100	69
7	$PdBr_2Py_2$ (**11**)	99	62

* Yields were determined by gas chromatography/mass spectrometry with phenanthrene (17.5 mol %) as internal standard. Averaged over two runs.
** Conversion was estimated by depletion of starting 2,3-diphenylthiophene.

Scheme 7. General reaction scheme for substrate scope (using various aryliodides)

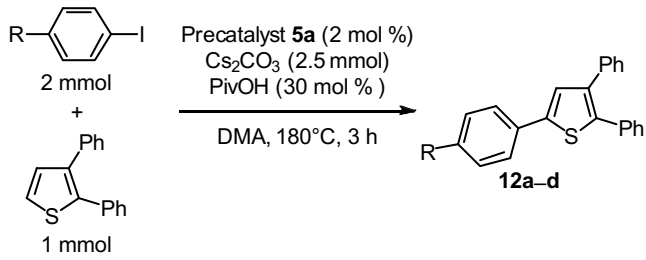


Table 2. Substrate scope of the arylation reaction

Entry	Compound	R	Conversion, %	Yield*(**), %
1	**12a**	H	99	59 (46)
2	**12b**	Me	98	47 (29)
3	**12c**	F	100	37 (28)
4	**12d**	OMe	98	33 (26)

* Yields were determined by gas chromatography/mass spectrometry (GC/MS) with phenanthrene (17.5 mol %) as internal standard. Averaged over two runs.
** Preparative yields of pure compounds were estimated after column chromatography.

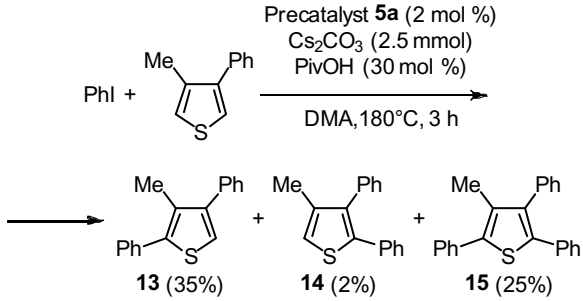
ligand may be crucial for catalytic performance. It is reasonable to propose that precatalysts **5a**–**c**,**e**, **6a** in arylation reaction are activated in a similar manner. From the Table 1, it is clear that the use of precatalysts **5a**–**c**,**e** and **6a** (entries 1–5) led to the lower yields (57–60%) of compound **12a** relative to PEPPSI-IPr (**10**) (69%, entry 6) or even to precatalyst **11** (62%, entry 7). In the absence of catalyst no arylation takes place. On comparison of conversion and yields data for precatalysts **5a**–**c**,**e** and **6a**, we can recognize that both yields and conversion are unaffected by chemical structure of precatalysts. So, it is safe to assume that full decomposition of complexes occurred, generating metal clusters or Pd nanoparticles (PNP), which perform the catalysis at high temperatures (>120°C).[39] In this scenario, NHC ligands are transformed in mostly into azolium salts, which are responsible for the stabilization of Pd clusters and PNP.[40] It is worth to mention that along with target product, a reasonable quantities of stilbene (29–36%, configuration was not determined) were formed in all experiments, probably as a result of 2,3-diphenylthiophene decomposition.

Next, we took precatalyst **5a** and a set of *para*-substituted aryl iodides to determine the scope of iodoaryls for the synthesis of compounds **12a**–**d** under the same conditions (Scheme 7, Table 2).

It is interesting to note that we have found correlation of chromatographic yields (y, %) with Hammett resonance constants[41] σ_r: $y = 61.244\sigma_r + 57.167$ ($R^2 = 0.97$). Similar correlation of distortion-activation parameters with Hammett σ_p constants have been elucidated recently for the thiophene arylation reactions.[38c]

3-Methyl-4-phenylthiophene arylation proved to be site-selective, giving predominately 3-methyl-2,4-diphenylthiophene (**13**) (35%, GC/MS); the alternative product – 4-methyl-2,3-diphenylthiophene (**14**) – was obtained only with 2% yield. Unfortunately, a side diarylation product – 3-methyl-2,4,5-triphenylthiophene (**15**) was also formed with 25% yield (Scheme 8).

Scheme 8. Phenylation of 4-methyl- 2,3-diphenylthiophene



Phenylation of 4-methyl-2,3-diphenylthiophene (**14**) under the same conditions predictably gave 3-methyl-2,4,5-triphenylthiophene (**15**) with 81% yield (GC/MS), 62% isolable yield. Finally, we tried to introduce phenyl group at the C-3 atom of thiophene ring, but arylation of 2-methyl-5-phenylthiophene was unsatisfactory (conversion ~5%).

We have synthesized PEPPSI-type complexes of Pd(II) with 1-adamantanyl-3-benzyl ligands. Complexes with pyridine, 2-, 3-, and 4-picoline were synthesized, including dichloride, dibromide, and diiodide examples. The catalytic performance of the new precatalysts in thiophene arylation is rather low in comparison to the sterically more crowded well-known catalyst IPr-PEPPSI-Pd® introduced by Organ. This result indirectly reaffirms the theory of "flexible bulk",[42] according to which higher catalytic activity one can expect from the branched di-*ortho*-aryl-substituted PEPPSI-type precatalysts.[43]

So, we can conclude that use of 1-adamantanyl-3-benzylimidazole-based Pd-PEPPSI complexes with additional methylene group next to imidazole ring (comparing to traditional PEPPSI precatalysts) exert a detrimental effect on catalytic activity in our case (CH activation/arylation reaction of thiophenes). Use of new precatalysts in other Pd-catalyzed reactions is under development in our laboratory.

Experimental

IR spectra were recorded on a Bruker FT-IR Vertex 80v apparatus in a thin layer, obtained by immediate evaporation of a solution of compound in $CHCl_3$ on a NaCl glass or nujol (compound **7**). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury+ spectrometer (300 and 75 MHz, respectively) or on a Bruker Avance III HD 400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$. Hexamethyldisiloxane was used as internal standard for ^1H spectra, the residual peak of deuterated solvent was used as reference for ^{13}C spectra. GC analyses were conducted using an Agilent Technologies 6890N/5975B System (capillary column 15 m × 0.25 mm, 0.25 μm); EI, 70 eV; temperature of evaporator 290°C. Elemental analyses (C, H, N) were performed with a Leco CHNS-9321P elemental analyzer. Melting points were determined in open glass capillaries with an OptiMelt MPA100 apparatus (Stanford Research Systems, USA) and are uncorrected. Analytical TLC was performed using precoated silica gel plates (Sorbfil, Russia), eluent $CHCl_3$–MeOH, 10:1, and the spots were visualized with UV light.

All reactions were carried out in air. Commercially available reagents and dry solvents (MeCN, *i*-PrOH, EtOAc) were used as recieved. PEPPSI-IPr® was purchased from Aldrich.

^1H NMR spectra and melting points of the synthesized thiophenes are in good correlation with the literature reported: 2-phenylthiophene (**8**),[44] 2,3-diphenylthiophene,[45] 2,5-diphenylthiophene (**9**),[45] 2,3,5-triphenylthiophene (**12a**),[45] 5-(4-methylphenyl)-2,3-diphenylthiophene (**12b**),[46a] 5-(4-fluorophenyl)-2,3-diphenylthiophene (**12c**),[46a] 5-(*p*-methoxyphenyl)-2,3-diphenylthiophene (**12d**),[46] 3-methyl-2,4-diphenylthiophene (**13**),[47] 2,3-diphenyl-4-methylthiophene (**14**),[48] 2-methyl-5-phenylthiophene[49] and 3-methyl-2,4,5-triphenylthiophene (**15**).[50] 1-Adamantanylimidazole (**1**) was synthesized by a known method.[51]

Synthesis of adamantanylimidazolium salts 2a–e (General method). 1-Adamantanylimidazole (**1**) (450 mg, 2.25 mmol) was dissolved in MeCN (10 ml), substituted benzyl chloride or benzyl bromide (2.25 mmol) was added, and the mixture was refluxed for 4 h. Solvent was removed under reduced pressure, residue was treated with hot EtOAc (15 ml), the resulting powder was washed with EtOAc and dried in air.

1-(Adamantan-1-yl)-3-benzyl-1*H*-imidazol-3-ium chloride hydrate (2a). Yield 546 mg (70%), colorless crystals, mp 214–216°C (EtOAc). IR spectrum, ν, cm^{-1}: 3407 (br, OH), 2916, 2855, 1547, 1455, 1309, 1255, 1154, 1104, 751, 713. ^1H NMR spectrum (400 MHz), δ, ppm: 11.00 (1H, s, NCH=N); 7.53–7.51 (2H, m, H Ph); 7.50–7.49 (1H, m, H Im); 7.41–7.40 (1H, m, H Im); 7.30–7.28(3H, m, H Ph); 5.68 (2H, s, NCH_2); 2.23 (3H, s, H Ad); 2.16 (6H, s, H Ad); 1.72–1.70 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz), δ, ppm: 135.2 (C-2 Im); 133.1 (C-1 Ph); 128.7 (C-2,3,5,6 Ph); 128.6 (C-4 Ph); 121.2 (C Im); 118.1 (C Im); 59.8 (C Ad); 52.5 (NCH_2); 42.4 (CH_2 Ad); 34.8 (CH_2 Ad); 28.8 (CH Ad). Found, %: C 68.94; H 7.91; N 7.48. $C_{20}H_{25}ClN_2 \cdot H_2O$. Calculated, %: C 69.25; H 7.85; N 7.56.

1-(Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-1*H*-imidazol-3-ium chloride semihydrate (2b). Yield 650 mg (78%), colorless powder, mp 210–215°C (EtOAc). ^1H NMR spectrum (300 MHz), δ, ppm: 11.09 (1H, s, NCH=N); 7.50 (1H, s, H Im); 6.87 (2H, s, 3,5-H Ar); 6.71 (1H, s, H Im); 5.72 (2H, s, NCH_2); 2.30–2.21 (18H, m, 9H Ad, $3CH_3$); 1.75 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 139.5 (C-1 Ar); 138.2 (C-2,6 Ar); 136.2 (C-2 Im); 129.8 (C-3,5 Ar); 125.9 (C-4 Ar); 120.1 (C Im); 118.3 (C Im); 60.5 (C Ad); 47.8 (NCH_2); 42.8 (CH_2 Ad); 35.3 (CH_2 Ad); 29.4 (CH Ad); 20.9 (CH_3); 19.7 (CH_3). Found, %: C 73.02; H 8.24; N 7.13. $C_{23}H_{31}ClN_2 \cdot 0.5H_2O$. Calculated, %: C 72.70; H 8.49; N 7.37.

1-(Adamantan-1-yl)-3-(2,3,5,6-tetramethylbenzyl)-1*H*-imidazol-3-ium chloride semihydrate (2c). Yield 797 mg (92%), colorless powder, mp 232–235°C (EtOAc). ^1H NMR spectrum (300 MHz), δ, ppm: 11.19 (1H, s, NCH=N); 7.47 (1H, s, H Im); 7.01 (1H, s, H-4 Ar); 6.69 (1H, s, H Im); 5.80 (2H, s, NCH_2); 2.28–2.17 (21H, m, 9H Ad, $4CH_3$); 1.75 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 136.1 (C-2 Im); 134.8 (C-1 Ar); 134.0 (C-3,5 Ar); 133.1 (C-4 Ar); 128.7 (C-2,6 Ar); 120.2 (C Im); 118.1 (C Im); 60.5 (C Ad); 48.5 (NCH_2); 42.9 (CH_2 Ad); 35.3 (CH_2 Ad); 29.6 (CH Ad); 20.3 (3,5-CH_3); 15.7 (2,6-CH_3). Found, %: C 73.49; H 8.37; N 7.00. $C_{24}H_{33}ClN_2 \cdot 0.5H_2O$. Calculated, %: C 73.16; H 8.70; N 7.11.

1-(Adamantan-1-yl)-3-benzyl-1*H*-imidazol-3-ium bromide (2d). Yield 720 mg (86%), colorless powder, mp 197–199°C (EtOAc). ^1H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 9.99 (1H, s, NCH=N); 7.59–7.54 (2H, m, H-3,5 Ph); 7.52 (1H, d, ^3J = 1.5, H Im); 7.47 (1H, d, ^3J = 1.5, H Im); 7.37–7.34 (3H, m, H-2,4,6 Ph); 5.58 (2H, s, NCH_2); 2.25 (6H, s, H Ad); 2.17 (3H, s, H Ad); 1.74 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 134.4 (C-1 Ph); 133.4 (C-2 Im); 129.3 (C-3,5 Ph); 129.2 (C-2,6 Ph); 121.9 (C Im); 118.8 (C Im); 60.6 (C Ad); 53.2 (NCH_2); 42.6 (CH_2 Ad); 35.2 (CH_2 Ad); 29.4 (CH Ad). Found, %: C 63.97; H 6.60; N 7.44. $C_{20}H_{25}BrN_2$. Calculated, %: C 64.34; H 6.75; N 7.50.

1-Adamantan-1-yl-3-(3,5-dimethylbenzyl)-1*H*-imidazol-3-ium bromide hydrate (2e). Yield 820 mg (87%), colorless powder, mp 249–250°C (EtOAc). ^1H NMR spectrum (300 MHz), δ, ppm: 10.81 (1H, s, NCH=N); 7.46–7.45 (1H, m, H Im); 7.24 (1H, s, H Im); 7.10 (2H, s, H-2,6 Ar); 6.99 (1H, s, H-4 Ar); 5.64 (2H, s, NCH_2); 2.32–2.23 (15H, m, 9H Ad, $2CH_3$); 1.78 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 138.9 (C-3,5 Ar); 135.5 (C-2 Im); 133.2 (C-1 Ar); 131.0 (C-4 Ar); 126.9 (C-2,6 Ar); 121.5 (C Im); 118.3 (C Im); 60.7 (C Ad); 53.3 (NCH_2); 42.9 (CH_2 Ad); 35.3 (CH_2 Ad); 29.4 (CH Ad); 21.2 (CH_3). Found, %: C 62.88; H 7.31; N 6.71. $C_{22}H_{29}BrN_2 \cdot H_2O$. Calculated, %: C 63.00; H 7.45; N 6.68.

Synthesis of tetrafluoroborate and hexafluorophosphate imidazolium salts 3a–d, 4 (General method). A solution of NH_4BF_4 or NH_4PF_6 (3 mmol) in H_2O (5 ml) was added to a solution of corresponding imidazolium salt **2b**–**e** (2.25 mmol) in EtOH (10 ml, slightly warmed until full dissolution, if necessary). After 12 h, the crystals formed were filtered off and dried in air.

1-(Adamantan-1-yl)-3-benzyl-1*H*-imidazol-3-ium tetrafluoroborate (3a). Yield 805 mg (94%), colorless crystals, mp 143–144°C (EtOH–H_2O). ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 9.12 (1H, s, NCH=N); 7.52–7.45 (2H, m, H-3,5 Ar); 7.42–7.35 (5H, m, H-2,4,6 Ar, 2H Im); 5.43 (2H, s, NCH_2); 2.27–2.16 (9H, m, H Ad); 1.76 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 133.1 (C-1 Ar); 132.7 (NHC=N); 128.9 (C-2,3,5,6 Ph); 128.6 (C-4 Ph); 121.5 (C Im); 118.4 (C Im); 60.0 (C Ad); 52.9 (NCH_2); 42.0 (CH_2 Ad); 34.7 (CH_2 Ad); 28.9 (CH Ad). Found, %: C 63.02; H: 6.45; N: 7.38. $C_{20}H_{25}BF_4N_2$. Calculated, %: C 63.18; H 6.63; N 7.37.

1-(Adamantan-1-yl)-3-(3,5-dimethylbenzyl)-1*H*-imidazol-3-ium tetrafluoroborate (3b). Yield 800 mg (87%), colorless crystals, mp 167–170°C (EtOH–H_2O). ^{1}H NMR spectrum (300 MHz), δ, ppm: 8.98 (1H, s, NCH=N); 7.51 (1H, s, H Im); 7.30 (1H, s, H-2 Ar); 7.03 (1H, s, H-6 Ar); 6.92 (1H, s, H-4 Ar); 5.27 (2H, s, NCH_2); 2.60–2.13 (15H, m, 9H Ad, $2CH_3$); 1.72 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 139.0 (C-3,5 Ar); 133.4 (NHC=N); 132.9 (C-1 Ar); 130.9 (C-4 Ar); 126.8 (C-2,6 Ar); 121.9 (C Im); 119.0 (C Im); 60.5 (C Ad); 53.3 (NCH_2), 42.4 (CH_2 Ad); 35.1 (CH_2 Ad); 29.3 (CH Ad); 21.1 (3,5-CH_3). Found, %: C 64.57; H 7.19; N 6.71. $C_{22}H_{29}BF_4N_2$. Calculated, %: C 64.72; H 7.16; N 6.86.

1-(Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-1*H*-imidazol-3-ium tetrafluoroborate (3c). Yield 691 mg (73%), colorless crystals, mp 220–221°C (EtOH–H_2O). ^{1}H NMR spectrum (300 MHz), δ, ppm: 9.10 (1H, s, NCH=N); 7.44 (1H, s, H Im); 6.93 (2H, s, H-3,5 Ar); 6.82 (1H, s, H Im); 5.52 (2H, s, NCH_2); 2.30 (6H, s, H Ad); 2.26 (6H, s, $2CH_3$); 2.20–2.18 (6H, m, 3H Ad, CH_3); 1.79–1.78 (6H, m, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 139.3 (C-1 Ar); 137.7 (C-4 Ar); 133.3 (NHC=N); 129.3 (C-3,5 Ar); 124.8 (C-2,6 Ar); 120.1 (C Im); 118.1 (C Im); 60.3 (C Ad); 47.2 (NCH_2); 42.0 (CH_2 Ad); 34.9 (CH_2 Ad); 28.9 (CH Ad); 20.4 (CH_3); 19.0 (CH_3). Found, %: C 65.37, H 7.49; N 6.52. $C_{23}H_{31}BF_4N_2$. Calculated, %: C 65.41; H 7.40; N 6.63.

1-(Adamantan-1-yl)-3-(2,3,5,6-tetramethylbenzyl)-1*H*-imidazol-3-ium tetrafluoroborate (3d). Yield 960 mg (98%), colorless crystals, mp 232–235°C (EtOH–H_2O). ^{1}H NMR spectrum (300 MHz), δ, ppm: 9.06 (1H, s, NCH=N); 7.52 (1H, s, H Im); 7.05 (1H, s, 4-H Ar); 6.80 (1H, s, H Im); 5.57 (2H, s, NCH_2); 2.28–2.17 (21H, m, 9H Ad, $4CH_3$); 1.78–1.77 (6H, m, 6H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 134.8 (C-1 Ar); 134.1 (C-3,5 Ar); 133.4 (NHC=N); 133.3 (C-4 Ar); 128.1 (C-2,6 Ar); 120.8 (C Im); 118.9 (C Im); 60.6 (C Ad); 48.3 (NCH_2); 42.4 (CH_2 Ad); 35.2 (CH_2 Ad); 29.4 (CH Ad); 20.3 (3,5-CH_3); 15.4 (2,6-CH_3). Found, %: C 65.97; H 7.49; N 6.35. $C_{24}H_{33}BF_4N_2$. Calculated, %: C 66.06; H 7.62; N 6.42.

1-(Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-1*H*-imidazol-3-ium hexafluorophosphate (4). Yield 757 mg (70%), colorless crystals, mp 221–225°C (EtOH–H_2O). ^{1}H NMR spectrum (300 MHz), δ, ppm: 8.76 (1H, s, NCH=N); 7.37 (1H, s, H Im); 6.96 (2H, s, H-3,5 Ar); 6.84 (1H, s, H Im); 5.48 (2H, s, NCH_2); 2.32 (6H, s, H Ad); 2.27 (6H, s, 3H Ad, CH_3); 2.19 (6H, s, $2CH_3$); 1.80 (6H, s, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 140.2 (C-2,6 Ar); 138.0 (C-1 Ar); 133.4 (NCH=N); 129.7 (C-3,5 Ar); 125.1 (C-4 Ar); 120.8 (C Im); 118.6 (C Im); 61.0 (C Ad); 47.8 (NCH_2); 42.6 (CH_2 Ad); 35.2 (CH_2 Ad); 29.3 (CH Ad); 21.0 (CH_3); 19.5 (CH_3). Found, %: C 57.38; H 6.49; N 5.75. $C_{23}H_{31}F_6N_2P$. Calculated, %: C 57.50; H 6.50; N 5.83.

Synthesis of PEPPSI complexes 5a–c (General method). To a solution (suspension) of $PdCl_2$ (142 mg, 0.8 mmol) in pyridine (5 ml), imidazolium salt (0.72 mmol) and K_2CO_3 (297 mg, 2.15 mmol) were added, and the mixture was stirred for 5–8 h at 70°C. Pyridine was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (50 ml), washed with H_2O (3×30 ml), brine (30 ml), and dried over $MgSO_4$. CH_2Cl_2 was removed under reduced pressure. Compounds were purified by column chromatography on silica gel, eluent CH_2Cl_2. Pure Pd–NHC complexes **5a**–**c** were isolated as yellow crystals or powders after crystallization from hexane–CH_2Cl_2 mixture.

***trans*-[(1-Adamantan-1-yl)-3-benzyl-2,3-dihydro-1*H*-imidazol-2-yl](pyridin-2-yl)palladium(IV) chloride (5a)**. Yield 324 mg (82%), yellow powder, mp 205–209°C. IR spectrum, ν, cm^{-1}: 2982, 2909, 2852, 1603, 1496, 1484, 1447, 1419, 1406, 1350. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 9.04 (2H, dd, ^3J = 6.6, ^4J = 1.5, H-2,6 Py); 7.79–7.77 (1H, m, 4-H Py); 7.54 (2H, dd, ^3J = 6.6, ^4J = 1.5, H-3,5 Py); 7.42–7.34 (5H, m, H Ph); 7.12 (1H, s, H Im); 6.69 (1H, s, H Im); 6.18 (2H, s, NCH_2); 2.87 (6H, s, H Ad); 2.37 (3H, s, H Ad); 1.85–1.80 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz), δ, ppm: 151.0 (C-2,6 Py); 145.3 (C ImPd); 137.2 (C-4 Py); 134.9 (C-1'); 129.0 (C-3',5'); 128.7 (C-2',6'); 128.1 (C-4'); 124.1 (C-3,5 Py); 119.9 (C Im); 119.2 (C Im); 59.5 (C Ad); 55.6 (NCH_2), 43.8 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad). Found, %: C 54.78; H 5.66; N 7.53. $C_{25}H_{29}Cl_2N_3Pd$. Calculated, %: C 54.71; H 5.73; N 7.66.

***trans*-[(1-Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](pyridin-2-yl)palladium(IV) chloride (5b)**. Yield 302 mg (71%), yellow powder, mp 265–270°C (decomp.). IR spectrum, ν, cm^{-1}: 3162, 3126, 3094, 2910, 2853, 1613, 1603, 1545, 1484, 1447, 1402, 1359, 1307, 1254, 1216, 1193, 1170, 1154, 1104, 1070, 1046, 853, 830, 753, 697, 689, 660. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 9.08 (2H, dd, ^3J = 6.3, ^4J = 1.5, H-2,6 Py); 7.78 (1H, ddd, ^3J = 7.8, ^3J = 6.3, ^4J = 1.5, H-4 Py); 7.37 (2H, dd, ^3J = 7.8, ^3J = 6.3, H-3,5 Py); 7.02 (1H, d, ^3J = 2.4, H Im); 6.96 (2H, s, H-3,5 Ar); 6.31 (1H, d, ^3J = 2.4, H Im); 6.07 (2H, s, NCH_2); 2.87–2.86 (6H, m, H Ad); 2.36–2.34 (12H, m, 3H Ad, $3CH_3$); 1.85 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 151.1 (C-2,6 Py); 144.6 (C ImPd); 138.4 (C-1 Ar); 138.0 (C-2,6 Ar); 137.2 (C-4 Py); 128.6 (C-3,5 Ar); 127.0 (C-4 Ar); 124.0 (C-3,5

Py); 118.3 (C Im); 117.6 (C Im); 59.3 (C Ad); 49.7 (CH_2N); 43.9 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad); 20.5 (4-CH_3); 19.4 (2,6-CH_3). Found, %: C 56.88; H 5.96; N 6.93. $C_{28}H_{35}Cl_2N_3Pd$. Calculated, %: C 56.91; H 5.97; N 7.11.

***trans*-[(1-Adamantan-1-yl)-3-(2,3,5,6-tetramethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](pyridin-2-yl)palladium(IV) chloride (5c)**. Yield 427 mg (98%), yellow powder, mp 260–263°C. IR spectrum, ν, cm^{-1}: 3168, 3130, 3100, 2934, 2904, 2848, 1602, 1567, 1481, 1446, 1407, 1359, 1352, 1339, 1305, 1257, 1217, 1192, 1171, 1133, 1102, 1065, 1046, 1031, 1015, 888, 829, 759, 744, 709, 695, 665, 648, 641. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 9.08 (2H, d, ^3J = 5.1, H-2,6 Py); 7.78 (1H, dd, ^3J = 7.5, ^4J = 1.5, H-4 Py); 7.37 (2H, dd, ^3J = 7.5, ^4J = 5.1, H-3,5 Py); 7.06 (1H, s, H-4 Ar); 7.01 (1H, d, ^3J = 2.1, H Im); 6.32 (1H, d, ^3J = 2.1, H Im); 6.15 (2H, s, NCH_2); 2.87 (6H, d, *J* = 2.7, H Ad); 2.37 (3H, s, H Ad); 2.29 (6H, s, $2CH_3$); 2.26 (6H, s, $2CH_3$); 1.90–1.80 (6H, m, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 150.8 (C-2,6 Py); 144.6 (C Im–Pd); 137.2 (C-4 Py); 134.5 (C-1 Ar); 133.8 (C-3,5 Ar); 132.0 (C-4 Ar); 129.6 (C-2,6 Ar); 124.1 (C-3,5 Py); 118.7 (C Im); 117.4 (C Im); 59.1 (C Ad); 50.8 (NCH_2); 43.8 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad); 19.7 (3,5-CH_3); 15.2 (2,6-CH_3). Found, %: C 57.28; H 5.97; N 6.92. $C_{29}H_{37}Cl_2N_3Pd$. Calculated, %: C 57.58; H 6.16; N 6.95.

***trans*-[(1-Adamantan-1-yl)-3-(3,5-dimethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](pyridin-2-yl)palladium(IV) bromide (5d)**. To a solution of $Pd(OAc)_2$ (245 mg, 1.09 mmol) in MeCN (30 ml), imidazolium salt **2e** (401 mg, 1.00 mmol), K_2CO_3 (553 mg, 4.00 mmol), KBr (595 mg, 5.00 mmol), and pyridine (0.403 ml, 396 mg, 5.00 mmol) were added. The resulting mixture was stirred for 4 h at 60°C. Solvents were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (50 ml) and washed with H_2O (3×30 ml) and brine (30 ml), dried over $MgSO_4$; CH_2Cl_2 was removed under reduced pressure. Compound **5d** was purified by column chromatography on silica gel, eluent CH_2Cl_2. Yield 439 mg (66%), yellow prisms, mp 267–271°C (CH_2Cl_2). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 9.08–9.06 (2H, m, H-2,6 Py); 7.76–7.74 (1H, m, H-4 Py); 7.36–7.34 (2H, m, H-3,5 Py); 7.18 (2H, s, H-2,6 Ar); 7.13 (1H, d, ^3J = 2.0, H Im); 7.00 (1H, s, 4-H Ar); 6.86 (1H, d, ^3J = 2.0, H Im); 5.99 (2H, s, NCH_2); 2.87 (6H, d, *J* = 2.8, H Ad); 2.37 (3H, s, H Ad); 2.34 (6H, s, 3,5-CH_3); 1.88 (3H, d, *J* = 12.0, H Ad); 1.84 (3H, d, *J* = 12.0, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 152.3 (C-2,6 Py); 143.1 (C ImPd); 138.0 (C-4 Py); 137.2 (C-1 Ar); 134.3 (C-3,5 Ar); 129.7 (C-4 Ar); 127.0 (C-2,6 Ar); 124.0 (C-3,5 Py); 119.9 (C Im); 119.0 (C Im); 59.1 (C Ad); 56.3 (NCH_2); 44.0 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad); 20.8 (CH_3). Found, %: C 48.38; H 5.16; N 6.27. $C_{27}H_{33}Br_2N_3Pd$. Calculated, %: C 48.71; H 5.00; N 6.31.

***trans*-[(1-Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](pyridin-2-yl)palladium(IV) bromide (5e)**. Synthesized from salt **2b** according to the general method for complexes **5a**–**c**, but KBr (428 mg, 5 equiv) was added to the reaction mixture. Yield 308 mg (61%), yellow powder, mp 267–271°C (decomp.). IR spectrum, ν, cm^{-1}: 1714, 1602, 1401, 1303, 1254, 1216, 1193, 1170, 1104, 1070, 1046, 855, 831, 762, 750, 697, 687. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 9.11 (2H, dd, ^3J = 6.6, ^4J = 1.8, H-2,6 Py); 7.78–7.77 (1H, m, H-4 Py); 7.37–7.34 (2H, m, H-3,5 Py); 7.03 (1H, s, H Im); 6.96 (2H, s, H-3,5 Ar); 6.30 (1H, s, H Im); 5.97 (2H, s, NCH_2); 2.86 (6H, d, *J* = 2.4, H Ad); 2.37 (3H, s, H Ad); 2.34 (6H, s, 2,6-CH_3); 2.33 (3H, s, 4-CH_3); 1.87–1.80 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz), δ, ppm: 152.4 (2,6-C Py); 143.0 (C Im-Pd); 138.6 (1-C Ar); 138.1 (4-C Ar); 137.1 (4-C Py); 128.8 (3,5-C Ar); 127.1 (2,6-C Ar); 124.0 (3,5-C Py); 118.6 (C Im); 117.8 (C Im); 59.0 (C Ad); 50.5 (NCH_2), 44.1 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad); 20.5 (4-CH_3); 19.6 (2,6-CH_3). Found, %: C 49.34; H 5.00; N 6.39. $C_{28}H_{35}Br_2N_3Pd$. Calculated, %: C 49.47; H 5.19; N 6.18.

Synthesis of PEPPSI complexes 6a–c (General method). To a solution of $PdCl_2$ (142 mg, 0.8 mmol) in MeCN (20 ml), imidazolium salt **2b** (267 mg, 0.72 mmol), K_2CO_3 (552 mg, 3.2 mmol), and substituted pyridine (4.0 mmol) were added. The mixture was stirred for 5–8 h at 70°C. MeCN was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (50 ml), washed with H_2O (2×30 ml), brine (30 ml), and dried over $MgSO_4$. Compounds were purified by column chromatography on silica gel, eluent CH_2Cl_2. Pure Pd–NHC complexes **6a**–**c** were isolated as powders or yellow crystals after crystallization from hexane–CH_2Cl_2 mixture.

***trans*-[(1-Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](2-methylpyridin-2-yl)-palladium(IV) chloride (6a)**. Yield 292 mg (67%), yellow powder, mp 132–135°C. IR spectrum, ν, cm^{-1}: 2978, 2910, 2853, 1608, 1583, 1571, 1486, 1457, 1419, 1400, 1379, 1360, 1299, 1255, 1216, 1194, 1171, 1104, 1030, 855, 831, 755, 724, 688, 664. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.94 (1H, d, ^3J = 5.7, H-6 Py); 7.62 (1H, ddd, ^3J = 7.8, ^3J = 7.8, ^4J = 1.5, H-4 Py); 7.23–7.18 (2H, m, H-3,5 Py); 7.00 (1H, d, ^3J = 2.1, H Im); 6.98 (2H, s, H-3,5 Ar); 6.33 (1H, d, ^3J = 2.1, H Im); 6.19 (2H, s, NCH_2); 3.28 (3H, s, 2-CH_3 Py); 2.91 (6H, s, H Ad); 2.40–2.38 (3H, m, H Ad); 2.37 (6H, s, 2,6-CH_3 Ar); 2.35 (3H, s, 4-CH_3 Ar); 1.95–1.89 (6H, m, H Ad). ^{13}C NMR spectrum (75 MHz), δ, ppm: 159.4 (C-2 Py); 151.2 (C-6 Py); 146.9 (C–Pd); 139.1 (C-1 Ar); 138.7 (C-4 Ar); 137.6 (C-4 Py); 129.3 (C-3,5 Ar); 127.6 (C-2,6 Ar); 125.7 (C-3 Py); 121.9 (C-5 Py); 118.7 (C Im); 117.9 (C Im); 59.6 (C Ad); 50.3 (NCH_2), 44.4 (CH_2 Ad); 36.0 (CH_2 Ad); 30.1 (CH Ad); 26.0 (CH_3 Py); 21.0 (4-CH_3); 19.9 (2,6-CH_3). Found, %: C 57.25; H 6.26; N 6.84. $C_{29}H_{37}Cl_2N_3Pd$. Calculated, %: C 57.58; H 6.16; N 6.95. In some cases, the formation of negligible quantities of orange complex $PdCl_2$·(2-methylpyridine)$_2$[52] was detected.

***trans*-[(1-Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](3-methylpyridin-2-yl)-palladium(IV) chloride (6b)**. Yield 365 mg (84%), yellow crystals, mp 218–220°C. IR spectrum, ν, cm^{-1}: 3137, 3104, 2981, 2911, 2853, 1612, 1583, 1483, 1450, 1419, 1403, 1307, 1218, 1197, 1171, 1105, 855, 794, 756, 699, 683, 665. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 8.87 (2H, s, 2,6-H Py); 7.59–7.57 (1H, m, H-4 Py); 7.26–7.24

(1H, m, H-5 Py); 7.01 (1H, d, ^3J = 1.8, H Im); 6.96 (2H, s, H-3,5 Ar); 6.31 (1H, d, ^3J = 1.8, H Im); 6.08 (2H, s, NCH_2); 2.86 (6H, d, J = 2.4, H Ad); 2.39 (3H, s, CH_3 Py); 2.35–2.33 (12H, m, 3H Ad, $3CH_3$); 1.90–1.80 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz), δ, ppm: 151.1 (C-2 Py); 148.2 (C-6 Py); 145.1 (C Im–Pd); 138.5 (C-1 Ar); 138.1 (C-4 Ar); 137.9 (C-4 Py); 134.0 (C-2,6 Ar); 128.8 (C-3,5 Ar); 127.1 (C-3 Py); 123.4 (C-5 Py); 118.3 (C Im); 117.6 (C Im); 59.1 (C Ad); 49.8 (NCH_2); 43.9 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad); 20.5 (4-CH_3); 19.4 (2,6-CH_3); 18.0 (CH_3 Py). Found, %: C 57.55; H 6.01; N 6.92. $C_{29}H_{37}Cl_2N_3Pd$. Calculated, %: C 57.58; H 6.16; N 6.95.

***trans*-[(1-Adamantan-1-yl)-3-(2,4,6-trimethylbenzyl)-2,3-dihydro-1*H*-imidazol-2-yl](4-methylpyridin-2-yl)-palladium(IV) chloride (6c)**. Yield 353 mg (81%), yellow powder, mp 215–218°C (hexane–CH_2Cl_2). IR spectrum, ν, cm^{-1}: 3137, 3071, 2980, 2853, 1617, 1503, 1448, 1420, 1403, 1307, 1229, 1212, 1195, 1170, 1105, 1071, 1033, 855, 810, 755, 688, 665, 495. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 8.90 (2H, dd, ^3J = 5.2, ^4J = 1.6, H-2,6 Py); 7.16 (2H, dd, ^3J = 5.2, ^4J = 1.6, H-3,5 Py); 7.00 (1H, d, ^3J = 2.4, H Im); 6.95 (2H, s, H-3,5 Ar); 6.31 (1H, d, ^3J = 2.4, H Im); 6.07 (2H, s, NCH_2); 2.88 (6H, d, J = 2.4, H Ad); 2.39 (3H, s, CH_3 Py); 2.36–2.34 (12H, m, 3H Ad, $3CH_3$); 1.89–1.79 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz), δ, ppm: 150.4 (C-2,6 Py); 149.4 (C-4 Py); 145.2 (C Im–Pd); 138.5 (C-1 Ar); 138.1 (C-4 Ar); 128.8 (C-3,5 Ar); 127.1 (C-2,6 Ar); 124.6 (C-3,5 Py); 118.3 (C Im); 117.6 (C Im); 59.1 (C Ad); 49.8 (NCH_2); 43.9 (CH_2 Ad); 35.5 (CH_2 Ad); 29.6 (CH Ad); 20.5 (4-CH_3); 20.4 (4-CH_3 Py); 19.3 (2,6-CH_3). Found, %: C 57.37; H 6.05; N 7.03. $C_{29}H_{37}Cl_2N_3Pd$. Calculated, %: C 57.58; H 6.16; N 6.95.

***trans*-[(1-Adamantan-1-yl)-3-benzyl-2,3-dihydro-1*H*-imidazol-2-yl](pyridin-2-yl)palladium(IV) iodide (7)**. Compound **5a** (219 mg, 0.4 mmol) and KI (199 mg, 1.2 mmol, 3 equiv) were refluxed in dry MeCN (20 ml) for 5 min and filtered hot. Solvent was removed under reduced pressure, the residue was recrystallyzed from Me_2CO. Yield 228 mg (78%), orange crystals, mp 221–224°C (Me_2CO). IR spectrum, ν, cm^{-1}: 1603, 1495, 1417, 1405, 1354, 1304, 1255, 1225, 1215, 1162, 1067, 759, 729, 695, 680, 644. ^{1}H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 9.06–9.01 (2H, m, H-2,6 Py); 7.75–7.72 (1H, m, H-4 Py); 7.58–7.54 (2H, m, H-3,5 Py); 7.43–7.29 (5H, m, H Ph); 7.15 (1H, d, ^3J = 2.1, H Im); 6.61 (1H, d, ^3J = 2.1, H Im); 5.86 (2H, s, NCH_2); 2.87 (6H, s, H Ad); 2.39 (3H, s, H Ad); 1.89–1.80 (6H, m, H Ad). ^{13}C NMR spectrum (100 MHz), δ, ppm: 153.6 (C-2,6 Py); 140.6 (C Im–Pd); 137.0 (C-4 Py); 134.4 (C-1 Ar); 129.4 (C-3,5 Ar); 128.4 (C-2,6 Ar); 128.0 (C-4 Ar); 124.1 (C-3,5 Py); 120.2 (C Im); 119.4 (C Im); 59.1 (C Ad); 57.3 (NCH_2); 44.1 (CH_2 Ad); 35.5 (CH_2 Ad); 29.5 (CH Ad). Found, %: C 40.80; H 4.07; N 5.66. $C_{25}H_{29}I_2N_3Pd$. Calculated, %: C 41.03; H 3.99; N 5.74.

Thiophene arylation reaction (General method). An oven-dried flask was charged with *N*,*N*-dimethylacetamide (6 ml), thiophene (substituted thiophene) (1 mmol), aryl iodide (2 mmol), Cs_2CO_3 (815 mg, 2.5 mmol), pivalic acid (31 mg, 30 mol %), and precatalyst (2 mol %). The mixture was refluxed for 3 h in air. After cooling to room temperature, phenanthrene was added (10% per weight to starting thiophene) and stirred carefully. Aliquote containing approximately 10 mg of the reaction product was taken out, diluted with CH_2Cl_2 up to 2 ml, filtered using an Iso-Disk filter (0.45 μm), and analyzed by GC/MS. The reaction mixture was extracted with EtOAc (2×25 ml), filtered, washed with brine, and dried over $MgSO_4$. The reaction product was purified on a silica gel column and eluted with light petroleum ether, monitoring by TLC (petroleum ether – EtOAc, 10:1). Thiophene fraction was recrystallyzed from EtOH, and ^{1}H NMR spectrum was recorded. Pure substituted thiophene was used for estimation of calibration factor. With this aim in mind, two mixtures (thiophene, 10 mg + phenanthrene, 10 mg and thiophene, 100 mg + phenanthrene, 10 mg) were prepared. These preparations were dissolved in CH_2Cl_2 (2 ml and 20 ml, correspondingly), and analyzed by GC/MS for estimation of calibration factor; after this, real yield was calculated. Every experiment was duplicated.

2-Phenylthiophene (8)[44] was not isolated pure. Mass spectrum, *m*/*z* (I_{rel}, %): 161 $[M+H]^+$ (13), 160 $[M]^+$ (100), 128 $[M–S]^+$ (11), 116 $[M–CS]^+$ (10), 115 $[M–CHS]^+$ (34).

2,5-Diphenylthiophene (9)[45] was obtained in case of 10 times multiplied reaction load. Yield 182 mg (8%), yellow powder, mp 149–151°C (EtOH) (mp 152–153°C[45]). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.62 (4H, dd, ^3J = 8.2, ^5J = 1.0 H Ar); 7.37 (4H, t, ^3J = 8.2, H Ar); 7.27 (2H, s, H Ar); 7.27 (2H, tt, ^3J = 7.0, ^5J = 1.2, H Ar). Mass spectrum, *m*/*z* (I_{rel}, %): 237 $[M+H]^+$ (20), 236 $[M]^+$ (100), 234 $[M–2H]^+$ (10), 202 $[M–H_2S]^+$ (10), 121 $[C_7H_5S]^+$ (13).

2,3,5-Triphenylthiophene (12a).[45] Yield 114 mg (46%), yellow powder, mp 106–107°C (EtOH) (mp 142–143°C[45]). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.58 (2H, d, ^3J = 7.6, H Ar); 7.34–7.18 (14H, m, H Ar). Mass spectrum, *m*/*z* (I_{rel}, %): 313 $[M+H]^+$ (26), 212 $[M]^+$ (100), 311 $[M–H]^+$ (13), 278 $[M–H_2S]^+$ (12), 121 $[C_7H_5S]^+$ (10).

5-(4-Methylphenyl)-2,3-diphenylthiophene (12b).[46a] Yield 95 mg (29%), colorless powder, mp 109–110°C (EtOH). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.58 (2H, dt, ^3J = 8.4, ^5J = 1.8, H Ar); 7.38–7.34 (5H, m, H Ar); 7.32 (2H, dt, ^3J = 7.6, ^5J = 2.9, H Ar); 7.31–7.26 (4H, m, H Ar); 7.24 (2H, d, ^3J = 8.0 Ar); 2.41 (3H, s, CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 327 $[M+H]^+$ (28), 326 $[M]^+$ (100), 325 $[M–H]^+$ (10).

5-(4-Fluorophenyl)-2,3-diphenylthiophene (12c)[46a] was obtained in case of 2 times multiplied reaction load. Yield 93 mg (28%), colorless powder, mp 104–106°C (EtOH). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.57 (2H, ddt, ^3J = 8.8, ^3J= 5.2, ^5J = 2.0, H Ar); 7.31–7.22 (11H, m, H Ar); 7.06 (2H, tt, ^3J = 8.6, ^5J = 1.8, H Ar). Mass spectrum, *m*/*z* (I_{rel}, %): 331$[M+H]^+$ (26), 330 $[M]^+$ (100), 329 $[M–H]^+$ (15), 315 $[M–CH_3]^+$ (10), 296 $[M–H_2S]^+$ (10).

5-(*p*-Methoxyphenyl)-2,3-diphenylthiophene (12d).[46b] Yield 89 mg (26%), colorless powder, mp 105–106°C (EtOH) (mp 133.5–134°C[46b]). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 6.61 (2H, dt, ^3J = 8.8, ^5J = 2.4, H Ar); 7.38–7.26 (11H, m, H Ar); 6.97 (2H, dt, ^3J = 8.8, ^5J = 1.6, H Ar);

3.88 (3H, s, OCH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 343 $[M+H]^+$ (27), 342 $[M]^+$ (100), 328 $[M–CH_2]^+$ (12), 327 $[M–CH_3]^+$ (46).

3-Methyl-2,4-diphenylthiophene (**13**)[47] was recrystallized from EtOAc. Yield 31 mg (12%), colorless powder, mp 154–156°C (EtOAc). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.49 (2H, d, ^3J = 8.2, H Ar); 7.48–7.39 (6H, m, H Ar); 7.36–7.30 (2H, m, H Ar); 7.17 (1H, s, H Ar); 2.24 (1H, s, CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 251 $[M+H]^+$ (21), 250 $[M]^+$ (100).

4-Methyl-2,3-diphenylthiophene (14)[48] was not isolated pure. Mass spectrum, *m*/*z* (I_{rel}, %): 251 $[M+H]^+$ (21), 250 $[M]^+$ (100), 249 $[M–H]^+$ (27), 235 $[M–CH_3]^+$ (26), 234 $[M–CH_4]^+$ (31), 215 $[M–SH_3]^+$ (15), 202 $[M–CH_4S]^+$ (17).

3-Methyl-2,4,5-triphenylthiophene (15).[50] Yield 25 mg (8%), colorless powder, mp 144–146°C (EtOH) (mp 149–150°C[50]). ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 7.58 (2H, d, ^3J = 8.4, H Ar); 7.47 (2H, tt, ^3J = 7.6, ^5J = 1.6, H Ar); 7.41–7.33 (4H, m, H Ar); 7.28–7.19 (7H, m, H Ar); 2.16 (3H, s, CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 327 $[M+H]^+$ (27), 326 $[M]^+$ (100).

The X-ray diffraction analyses were accomplished on a Xcalibur 3 (compounds **2d**,**e**, **7**) diffractometer or on a Xcalibur Ruby diffractometer (compounds **3c**, **5d**, **6a**) by standard procedure (MoKα irradiation, graphite monochromator, ω-scans with 1° step at 295(2) K). Empirical absorption correction was applied. Using Olex2[53] (for compounds **2d**,**e**, **7**) or WinGX[54] (for compounds **3c**, **5d**, **6a**), the structures were solved with the ShelXS[55] structure solution program using Direct Methods and refined with the ShelXL[56] refinement package using least-squares minimization in anisotropic approximation for non-hydrogen atoms. H atoms were placed in the calculated positions and refined in isotropic approximation using riding model. The disordered solvate molecules in crystals of compound **6a** were removed by applying the SQUEEZE routine in PLATON.[57] The crystallographic data have been deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1822210 for compound **2d**, CCDC 1822211 for compound **2e**, CCDC 1822212 for compound **3c**, CCDC 1822213 for compound **5d**, CCDC 1822214 for compound **6a**, CCDC 1822215 for compound **7**).

Supplementary information file containing ^{1}H and ^{13}C NMR spectra of all synthesized compounds and X-ray diffraction data of compounds **2d**,**e**, **3c**, **5d**, **6a**, **7** is available at the journal website at http://link.springer.com/journal/10593.

This work was supported by Russian Foundation for Basic Research (grant 17-03-00456-a).

References

1. (a) Herrmann, W. A.; Köcher, C. *Angew. Chem.*, *Int. Ed. Engl.* **1997**, *36*, 2162. (b) Herrmann, W. A. *Angew. Chem*., *Int. Ed*. **2002**, *41*, 1290. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem*., *Int. Ed*. **2008**, *47*, 3122. (d) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev*. **2009**, *109*, 3612. (e) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485. (f) *N-Heterocyclic Carbenes. Effective Tools for Organometallic Synthesis*; Nolan, S. P., Ed.; Wiley-VCH, 2014, p. 544. (g) Nelson, D. J. *Eur. J. Inorg. Chem*. **2015**, 2012.
2. (a) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem.–Eur. J.* **2006**, *12*, 4743. (b) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem*., *Int. Ed*. **2007**, *46*, 2768. (c) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem.*, *Int. Ed*. **2012**, *51*, 3314. (d) Valente, C.; Pompeo, M.; Sayah, M.; Organ, M. G. *Org. Process Res. Dev.* **2014**, *18*, 180. (e) Diner, C.; Organ, M. G. *Organometallics* **2019**, *38*, 66.
3. (a) Türkmen, H.; Can, R.; Çetinkaya, B. *Dalton Trans*. **2009**, 7039. (b) Li, Y.-J.; Zhang, J.-L.; Li, X.-J.; Geng, Y.; Xu, X.-H.; Jin, Z. *J. Organomet. Chem*. **2013**, *737*, 12.
4. Liu, F.; Zhu, Y.-R.; Song, L.-G.; Lu, J.-M. *Org. Biomol. Chem.* **2016**, *14*, 2563.
5. (a) Batey, R. A.; Shen, M.; Lough, A. J. *Org. Lett*. **2002**, *4*, 1411. (b) Linninger, C. S.; Herdtweck, E.; Hoffmann, S. D.; Herrmann, W. A.; Kühn, F. E. *J. Mol. Struct*. **2008**, *890*, 192. (c) Tang, Y.-Q.; Lu, J.-M.; Shao, L.-X. *J. Organomet. Chem*. **2011**, *696*, 3741. (d) Zhu, L.; Gao, T.-T.; Shao, L.-X. *Tetrahedron* **2011**, *67*, 5150. (e) Wang, Z.-Y.; Chen, G.-Q.; Shao, L.-X. *J. Org. Chem.* **2012**, *77*, 6608. (f) Xiao, Z.-K.; Shao, L.-X. *Synthesis* **2012**, 711. (g) Gu, Z.-S.; Shao, L.-X.; Lu, J.-M. *J. Organomet. Chem*. **2012**, *700*, 132. (h) Zhu, L.; Ye, Y.-M.; Shao, L.-X. *Tetrahedron* **2012**, *68*, 2414. (i) Lin, X.-F.; Li, Y.; Li, S.-Y.; Xiao, Z.-K.; Lu, J.-M. *Tetrahedron* **2012**, *68*, 5806. (j) Yin, H.-Y.; Liu, M-.Y.; Shao, L.-X. *Org. Lett*. **2013**, *15*, 6042. (k) Yin, S.-C.; Zhou, Q.; He, Q.-W.; Li, S.-W.; Qian, P.-C.; Shao, L.-X. *Tetrahedron* **2017**, *73*, 427.
6. (a) Lv, H.; Zhu, L.; Tang, Y.-Q.; Lu, J.-M. *Appl. Organomet. Chem*. **2014**, *28*, 27. (b) Zheng, S.; Wang, Y.; Zhang, C.; Liu, J.; Xia, C. *Appl. Organomet. Chem*. **2014**, *28*, 48. (c) Sikorski, W.; Zawartka, W.; Trzeciak, A. M. *J. Organomet. Chem*. **2018**, *867*, 323.
7. (a) Wang, Z.-Y.; Ma, Q.-N.; Li, R.-H.; Shao, L.-X. *Org. Biomol. Chem*. **2013**, *11*, 7899. (b) Farmer, J. L.; Pompeo, M; Lough, A. J.; Organ, M. G. *Chem.–Eur. J*. **2014**, *20*, 15790.
8. Türkmen, H.; Gök, L.; Kani. I.; Çetinkaya, B. *Turkish J. Chem*. **2013**, *37*, 633.
9. (a) Chen, M. T.; Vicic, D. A.; Turner, M. L.; Navarro, O. *Organometallics* **2011**, *30*, 5052. (b) Guest, D.; Chen, M.-T.; Tizzard, G. J.; Coles, S. J.; Turner, M. L.; Navarro, O. *Eur. J. Inorg. Chem*. **2014**, 2200. (c) Gallop, C. W. D.; Chen, M.-T.; Navarro, O. *Org. Lett*. **2014**, *16*, 3724. (d) Gallop, C. W. D.; Zinser, C.; Guest, D.; Navarro, O. *Synlett* **2014**, 2225.
10. (a) Randell, K.; Stanford, M. J.; Clarkson, G. J.; Rourke, J. P. *J. Organomet. Chem*. **2006**, *691*, 3411. (b) Zheng, S.-Z.; Peng, X.-G.; Liu, J.-M.; Sun, W.; Xia, C.-G. *Chin. J. Chem*. **2007**, *25*, 1065. (c) Wang, F.; Zhu, L.; Zhou, Y.; Bao, X.; Shaefer, H. F. III. *Chem.–Eur. J.* **2015**, *21*, 4153.
11. Türkmen, H.; Kani, I. *Appl. Organomet. Chem*. **2013**, *27*, 489.
12. (a) Huang, P.; Wang, Y.-X.; Yu, H.-F.; Lu, J.-M. *Organometallics* **2014**, *33*, 1587. (b) Borré, E.; Dahm, G.; Aliprandi, A.; Mauro, M.; Dagorne, S.; Bellemin-Laponnaz, S. *Organometallics* **2014**, *33*, 4374. (c) Baier, H.; Metzner, P.; Körzdörfer, T.; Kelling, A.; Holdt, H.-J. *Eur. J. Inorg. Chem*. **2014**, 2952. (d) Wang, Y.; Yang, X.; Zhang, C.; Yu, J.; Liu, J.; Xia, C. *Adv. Synth. Catal*. **2014**, *356*, 2539. (e) Dahm, G.; Borré, E.; Guichard, G.; Bellemin-Laponnaz, S. *Eur. J. Inorg. Chem*. **2015**, 1665. (f) Yang, J. *Appl. Organomet. Chem.* **2017**, *31*, e3734. (g) Sun, K.-X.; He, Q.-W.; Xu, B.-B.; Wu, X.-T.; Lu, J.-M. *Asian J. Org. Chem*. **2018**, *7*, 781.
13. (a) Gao, T.-T.; Jin, A.-P.; Shao, L.-X. *Beilstein J. Org. Chem*. **2012**, *8*, 1916. (b) Lin, Y.-C.; Hsueh, H.-H.; Kanne, S.;

Chang, L.-K.; Liu, F.-C.; Lin, I. J. B. *Organometallics* **2013**, *32*, 3859. (c) Martínez-Olid, F.; Andrés, R.; Flores, J. C.; Gómez-Sal, P. *Eur. J. Inorg. Chem*. **2015**, 4076.

14. (a) Organ, M. G.; Çalimsiz, S.; Sayah, M,; Hoi, K. H.; Lough, A. J. *Angew. Chem.*, *Int. Ed*. **2009**, *48*, 2383. (b) Teci, M.; Brenner, E.; Matt, D.; Toupet, L. *Eur. J. Inorg. Chem*. **2013**, 2841. (c) Azua, A.; Mata, J. A.; Heymes, P.; Peris, E.; Lamaty, F.; Martinez, J.; Colacino, E. *Adv. Synth. Catal.* **2013**, *355*, 1107. (d) Rajabi, F.; Trampert, J.; Sun, Y.; Busch, M.; Bräse, S.; Thiel, W. R. *J. Organomet. Chem*. **2013**, *744*, 101. (e) Benhamou, L.; Besnard, C.; Kündig, E. P. *Organometallics* **2014**, *33*, 260. (f) Teci, M.; Brenner, E.; Matt, D.; Gourlaouen, C.; Toupet, L. *Dalton Trans*. **2015**, *44*, 9260. (g) Yaşar, S.; Şahin, Ç.; Arslan, M.; Özdemir, İ. *J. Organomet. Chem*. **2015**, *776*, 107. (h) Groomridge, B. J.; Goldup, S. M.; Larossa, I. *Chem. Commun*. **2015**, *51*, 3832. (i) Baier, H.; Kelling, A.; Holdt, H.-J. *Eur. J. Inorg. Chem*. **2015**, 1950. (j) Akkoç, S.; Gök, Y.; İlhan, İ. Ö.; Kayser, V. *Beilstein J. Org. Chem*. **2016**, *12*, 81. (k) Lei, P.; Meng, G.; Ling, Y.; An, J.; Szostak, M. *J. Org. Chem.* **2017**, *82*, 6638. (l) Lu, D.-D.; He, X.-X.; Liu, F.-S. *J. Org. Chem.* **2017**, *82*, 10898. (m) Chernenko, A. Yu.; Astakhov, A. V.; Pasyukov, D. V.; Dorovatovskii, P. V.; Zubavichus, Ya. V.; Khrustalev, V. N.; Chernyshev, V. M. *Russ. Chem. Bull*. **2018**, *67*, 79. [*Izv. Akad. Nauk*, *Ser. Khim.* **2018**, 79.]
15. (a) Yang, L.; Li, Y.; Chen, Q.; Du, Y.; Cao, C.; Shi, Y.; Pang, G. *Tetrahedron* **2013**, *69*, 5178. (b) Dahm, G.; Bailly, C.; Karmazin, L.; Bellemin-Laponnaz, S. *J. Organomet. Chem*. **2015**, *794*, 115.
16. (a) Çalimsiz, S.; Sayah, M.; Mallik, D.; Organ, M. G. *Angew. Chem.*, *Int. Ed*. **2010**, *49*, 2014. (b) Pompeo, M.; Froese, R. D. J.; Hadei, N.; Organ, M. G. *Angew. Chem.*, *Int. Ed*. **2012**, *51*, 11354. (c) Liu, Z.; Dong, N.; Xu, M.; Sun, Z.; Tu, T. *J. Org. Chem*. **2013**, *78*, 7436. (d) Atwater, B.; Chandrasoma, N.; Mitchell, D.; Rodriguez, M. J.; Pompeo, M.; Froese, R. D. J.; Organ, M. G. *Angew. Chem.*, *Int. Ed*. **2015**, *54*, 9502. (e) Atwater, B.; Chandrasoma, N.; Mitchell, D.; Rodriguez, M. J.; Organ, M. G. *Chem.–Eur. J.* **2016**, *22*, 14531.
17. (a) Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Sayah, M. *Chem.–Eur. J.* **2008**, *14*, 2443. (b) Chartoire, A.; Frogneux, X.; Boreux, A.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2012**, *31*, 6947. (c) Chen, W.-X.; Shao, L.-X. *J. Org. Chem*. **2012**, *77*, 9236. (d) Hoi, K. H.; Coggan, J. A.; Organ, M. G. *Chem.–Eur. J*. **2013**, *19*, 843. (e) Fang, W.; Jiang, J.; Xu, Y.; Zhou, J.; Tu, T. *Tetrahedron* **2013**, *69*, 673. (f) Krinsky, J. L.; Martínez, A.; Godard, C.; Castillón, S.; Claver, C. *Adv. Synth. Catal*. **2014**, *356*, 460. (g) Zhang, Y.; César, V.; Storch, G.; Lugan, N.; Lavigne, G. *Angew. Chem.*, *Int. Ed*. **2014**, *53*, 6482. (h) Zhang, Y.; César, V.; Lavigne, G. *Eur. J. Org. Chem*. **2015**, 2042. (i) Lombardi, C.; Day, J.; Chandrasoma, N.; Mitchell, D.; Rodriguez, M. J.; Farmer, J. L.; Organ, M. G. *Organometallics* **2017**, *36*, 251. (j) Khadra, A.; Mayer, S.; Organ, M. G. *Chem.–Eur. J*. **2017**, *23*, 3206. (k) Shi, S.; Szostak, M. *Chem. Commun*. **2017**, *53*, 10584. (l) Huang, F.-D.; Xu, C.; Lu, D.-D.; Shen, D.-S.; Li, T.; Liu, F.-S. *J. Org. Chem*. **2018**, *83*, 9144.
18. Sayah, M.; Lough, A. J.; Organ, M. G. *Chem.–Eur. J.* **2013**, *19*, 2749.
19. (a) He, P.; Du, Y.; Wang, S.; Cao, C.; Wang, X.; Pang, G.; Shi, Y. *Z. Anorg. Allg. Chem*. **2013**, *639*, 1004. (b) Xiap, Z.-K.; Yin, H.-Y.; Shao, L.-X. *Org. Lett.* **2013**, *15*, 1254. (c) Shen, X.-B.; Zhang, Y.; Chen, W.-X.; Xiao, Z.-K.; Hu, T.-T.; Shao, L.-X. *Org. Lett.* **2014**, *16*, 1984. (d) Gu, Z.-S.; Chen, W.-X.; Shao, L.-X. *J. Org. Chem*. **2014**, *79*, 5806. (e) Akkoç, S.; Gök, Y. *Inorg. Chim. Acta.* **2015**, *429*, 34. (f) Akkoç, S.; Gök, Y.; İlhan, İ. Ö.; Kayser, V. *Beilstein J. Org. Chem*. **2016**, *12*, 81. (g) Marelli, E.; Corpet, M.; Minenkov, Yu.; Neyyappadath, R. M.; Bismuto, A.; Buccolini, G.; Curcio, M.; Cavallo, L.; Nolan, S. P. *ACS Catal*. **2016**, *6*, 2930. (h) He, X.-X.; Li, Y.; Ma, B.-B.; Ke, Z.; Liu, F.-S. *Organometallics* **2016**, *35*, 2655. (i) Hu, L.-Q.; Deng, R.-L.; Li, Y.-F.; Zeng, C.-J.; Shen, D.-S.; Liu, F.-S. *Organometallics* **2018**, *37*, 214. (j) Liu, F.; Hu, Y.-Y.; Li, D.; Zhou, Q.; Lu, J.-M. *Tetrahedron* **2018**, *74*, 5683. (k) Panyam, P. K. R.; Ugale, B.; Gandhi, T. *J. Org. Chem*. **2018**, *83*, 7622. (l) Kaloğlu, N.; Kaloğlu, M.; Tahir, M. N.; Arici, C.; Bruneau, C.; Doucet, H.; Dixneuf, P. H.; Çetinkaya, B.; Özdemir, İ. *J. Organomet. Chem.* **2018**, *867*, 404. (m) Chen, W.; Yang, J. *J. Organomet. Chem*. **2018**, *872*, 24.
20. Zheng, S.; Peng, X.; Liu, J.; Sun, W.; Xia, C. *Helv. Chim. Acta* **2007**, *90*, 1471.
21. (a) Tornatzky, J.; Kannenberg, A.; Blechert, S. *Dalton Trans*. **2012**, *41*, 8215. (b) Queval, P.; Jahier, C.; Rouen, M.; Artur, I.; Legeay, J.-C.; Falivene, L.; Toupet, L.; Crévisy, C.; Cavallo, L.; Baslé, O.; Mauduit, M. *Angew. Chem.*, *Int. Ed*. **2013**, *52*, 14103. (c) Mangold, S. L.; O'Leary, D. J.; Grubbs, R. H. *J. Am. Chem. Soc*. **2014**, *136*, 12469. (d) Paradiso, V.; Bertolasi, V.; Costabile, C.; Grisi, F. *Dalton Trans.* **2016**, *45*, 561. (e) Tarrieu, R.; Dumas, A.; Thongpaen, J.; Vives, T.; Roisnel, T.; Dorcet, V.; Crévisy, C.; Baslé, O.; Mauduit, M. *J. Org. Chem*. **2017**, *82*, 1880. (f) Box, H. K.; Howell, T. O.; Kennon, W. E.; Burk, G. A.; Valle, H. U.; Hollis, T. K. *Tetrahedron.* **2017**, *73*, 2191. (g) Paradiso, V.; Bertolasi, V.; Costabile, C.; Caruso, T.; Dąbrowski, M.; Grela, K.; Grisi, F. *Organometallics* **2017**, *36*, 3692. (h) Pape, F.; Teichert, J. F. *Eur. J. Org. Chem*. **2017**, 4206.
22. (a) Ray, L.; Shaikh, M. M.; Ghosh, P. *Dalton Trans*. **2007**, 4546. (b) Ray, L.; Barman, S.; Shaikh, M. M.; Ghosh, P. *Chem.–Eur. J*. **2008**, *14*, 6646. (c) Fang, W.; Jiang, J.; Xu, Y.; Zhou, J.; Tu, T. *Tetrahedron* **2013**, *69*, 673. (d) Yang, L.; Li, Y.; Chen, Q.; Du, Y.; Cao, C.; Shi, Y.; Pang, G. *Tetrahedron* **2013**, *69*, 5178. (e) Lin, Y.-C.; Hsueh, H.-H.; Kanne, S.; Chang, L.-K.; Liu, F.-C.; Lin, I. J. B. *Organometallics* **2013**, *32*, 3859. (f) Zheng, S.; Wang, Y.; Zhang, C.; Liu, J.; Xia, C. *Appl. Organomet. Chem*. **2014**, *28*, 48. (g) Benhamou, L.; Besnard, C.; Kündig, E. P. *Organometallics* **2014**, *33*, 260. (h) Rouen, M.; Borré, E.; Falivene, L.; Toupet, L.; Berthod, M.; Cavallo, L.; Olivier-Borbigou, H.; Maudit, M. *Dalton Trans*. **2014**, *43*, 7044. (i) Osińska, M.; Gniewek, A.; Trzeciak, A. M. *J. Mol. Catal. A: Chem*. **2016**, *418–419*, 9. (j) Topchiy, M. A.; Zotova, M. A.; Masoud, S. M.; Mailyan, A. K.; Ananyev, I. V.; Nefedov, S. E.; Asachenko, A. F.; Osipov, S. N. *Chem.–Eur. J*. **2017**, *23*, 6663. (k) Halter, O.; Plenio, H. *Eur. J. Inorg. Chem.* **2018**, 2935.
23. Agnew-Francis, K. A.; Williams, C. M. *Adv. Synth. Catal*. **2016**, *358*, 675.
24. Nasielski, J.; Hadei, N.; Achonduh, G.; Kantchev, E. A. B.; O'Brien C. J.; Lough, A.; Organ, M. G. *Chem.–Eur. J.* **2010**, *16*, 10844.
25. (a) Zeiler, A.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Chem.–Eur. J*. **2015**, *21*, 11065. (b) Bolbat, E.; Wendt, O. F. *Eur. J. Org. Chem*. **2016**, 3395. (c) Shao, L.; Lu, J.; Liu, F. CN Patent 106892945A.
26. (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc*. **1991**, *113*, 361. (b) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem.*, *Int. Ed*. **2002**, *41*, 1363.
27. (a) Queval, P.; Jahier, C.; Rouen, M.; Artur, I.; Legeay, J.-C.; Falivene, L.; Toupet, L.; Crévisy, C.; Cavallo, L.; Baslé, O.; Mauduit, M. *Angew. Chem.*, *Int. Ed.* **2013**, *52*, 14103. (b) Tarrieu, R.; Dumas, A.; Thongpaen, J.; Vives, T.; Roisnel, T.; Dorcet, V.; Crévisy, C.; Baslé, O.; Mauduit, M. *J. Org. Chem*.

2017, *82*, 1880. (c) Dumas, A.; Tarrieu, R.; Vives, T.; Roisnel, T.; Dorcet, V.; Baslé, O.; Mauduit, M. *ACS Catal.* **2018**, *8*, 3257.
28. Alcalde, E.; Mesquida, N.; Alemany, M.; Alvares-Rúa, C.; García-Granda, S.; Pacheco, P.; Pérez-Garcia, L. *Eur. J. Org. Chem*. **2002**, 1221.
29. Glushkov, V. A.; Arapov, K. A.; Kotelev, M. S.; Rudowsky, K. S.; Suponitsky, K. Yu.; Gorbunov, A. A.; Maiorova, O. A.; Slepukhin, P. A. *Heteroat. Chem*. **2012**, *23*, 5.
30. Glushkov, V. A.; Zhiguleva, M. A.; Maiorova, O. A.; Gorbunov, A. A. *Russ. J. Org. Chem.* **2012**, *48*, 699. [*Zh. Org. Khim.* **2012**, *48*, 701.]
31. (a) Ray, L.; Shaikh, M. M.; Ghosh, P. *Dalton Trans*. **2007**, 4546. (b) Liao, C.-Y.; Chan, K.-T.; Zeng, J.-Y.; Hu, C.-H.; Tu, C.-Y.; Lee, H. M. *Organometallics* **2007**, *26*, 1692. (c) Yang, L.; Zhao, J.; Li, Y.; Ge, K.; Zhuang, Y.; Cao, C.; Shi, Y. *Inorg. Chem. Commun*. **2012**, *22*, 33.
32. (a) Dunsford, J. J.; Cavell, K. J. *Organometallics* **2014**, *33*, 2902. (b) Dahm, G.; Bailly, C.; Karmazin, L.; Bellemin-Laponnaz, S. *J. Organomet. Chem*. **2015**, *794*, 115. (c) Lan, X.-B.; Li, Y.; Li, Y.-F.; Shen, D.-S.; Ke, Z.; Liu, F.-S. *J. Org. Chem*. **2017**, *82*, 2914.
33. Dash, C.; Shaikh, M. M.; Ghosh, P. *Eur. J. Inorg. Chem*. **2009**, 1608.
34. (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev*. **2007**, *107*, 174. (b) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Org. Chem*. **2012**, *77*, 658. (c) Steinmetz, M.; Ueda, K.; Grimme, S.; Yamaguchi, J.; Kirchberg, S.; Itami, K.; Studer, A. *Chem.–Asian J*. **2012**, *7*, 1256. (d) Fu, H.; Chen, H.; Doucet, H. *Appl. Organomet. Chem*. **2013**, *27*, 595. (e) Jiang, H.; Bellomo, A.; Zhang, M.; Carroll, P. J.; Manor, B. C.; Jia, T.; Walsh, P. J. *Org. Lett*. **2018**, *20*, 2522.
35. (a) Steinmetz, M.; Ueda, K.; Grimme, S.; Yamaguchi, J.; Kirchberg, S.; Itami, K.; Studer, A. *Chem.–Asian J*. **2012**, *7*, 1256. (b) Shibahara, F.; Asai, Y.; Murai, T. *Asian J. Org. Chem.* **2018**, *7*, 1323.
36. (a) Okazawa, T.; Satoh, T.; Miura, M.; Nomura. M. *J. Am. Chem. Soc*. **2002**, *124*, 5286. (b) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett*. **2008**, *10*, 1851.
37. Kaloğlu, M.; Özdemir, I.; Dorcet, V.; Bruneau, C.; Doucet, H. *Eur. J. Inorg. Chem.* **2017**, 1382.
38. (a) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc*. **2008**, *130*, 10848. (b) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826. (c) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Org. Chem.* **2012**, *77*, 658.
39. (a) de Vries, J. G. *Dalton Trans*. **2006**, 421. (b) Zhang, W.; Qi, H.; Li, L.; Wang, X.; Chen, J.; Peng, K.; Wang, Z. *Green Chem*. **2009**, *11*, 1194. (c) Tsvelikhovsky, D.; Popov, I.; Gutkin, V.; Rozin, A.; Shvartsman, A.; Blum, J. *Eur. J. Org. Chem.* **2009**, 98. (d) Ohtaka, A.; Tamaki, Y.; Igawa, Y.; Egami, K.; Shimomura, O.; Nomura, R. *Tetrahedron* **2010**, *66*, 5642. (e) Balanta, A.; Godard, C.; Claver, C. *Chem. Soc. Rev*. **2011**, *40*, 4973. (f) Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.; Basset, J.-M.; Polshettiwar, V. *Chem. Soc. Rev*. **2011**, *40*, 5181. (g) Wang, W.; Yang, Q.; Zhou, R.; Fu, H.-Y.; Li, R.-X.; Chen, H.; Li, X.-J. *J. Organomet. Chem*. **2012**, *697*, 1. (h) Gildner, P. G.; Colacot, T. J. *Organometallics* **2015**, *34*, 5497.
40. Astakhov, A. A.; Khazipov, O. V.; Chernenko, A. Yu.; Pasyukov, D. V.; Kashin, A. S.; Gordeev, E. G.; Khrustalev, V. N.; Chernyshev, V. M.; Ananikov, V. P. *Organometallics* **2017**, *36*, 1981.
41. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev*. **1991**, *91*, 165.
42. Würtz, S.; Glorius, F. *Acc. Chem. Res*. **2008**, *41*, 1523.
43. (a) Froese, R. D. J.; Lombardi, C.; Pompeo, M.; Rucker, R. P.; Organ, M. G. *Acc. Chem. Res*. **2017**, *50*, 2244. (b) Zhang, Y.; Lavigne, G.; Lugan, N.; César, V. *Chem.–Eur. J*. **2017**, *23*, 13792.
44. (a) Horton, A. W. *J. Org. Chem*. **1949**, *14*, 761. (b) Voronkov, M. G.; Brown, A. S.; Karpenko, A. S.; Gol'shtein, B. L. *Zh. Obshch. Khim.* **1949**, *19*, 1356. (c) Oae, S; Ishihara, H.; Yoshihara, M. *Chem. Heterocycl. Compd.* **1995**, *31*, 917. [*Khim. Geterotsikl. Soedin.* **1995**, 1053.]
45. Voronkov, M. G.; Udre, V.; Taube, A. *Chem. Heterocycl. Compd.* **1971**, *7*, 703. [*Khim. Geterotsikl. Soedin.* **1971**, 755.]
46. (a) Relyea, D. I.; Hubbard, W. L.; Grahame, R. E., Jr. DE Patent 2724494A1, 1977. (b) Gotthardt, H.; Weisshuhn, C. M. *Chem. Ber*. **1978**, *111*, 2028.
47. (a) Kang, K-T.; Lee, S. J.; Jyung, K. K. *J. Korean Chem. Soc*. **1998**, *42*, 584. (b) Ueda, K.; Yanagisawa, S.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed*. **2010**, *49*, 8946.
48. Shklyaeva, E. V.; Shklyaev, Yu. V. SU Patent 1395636, 1988,.
49. Voronkov, M. G.; Gol'shtein, B. L. *Zh. Obshch. Khim.* **1950**, *20*, 1218.
50. Nagano, T.; Kimoto, H.; Nakatsuji, H.; Motoyoshiya, J.; Aoyama, H.; Tanabe, Y.; Nishii, Y. *Chem. Lett*. **2007**, *36*, 62.
51. Raenko, G. F.; Korotkikh, N. I.; Pekhtereva, T. M.; Shvaika, O. P. *Russ. J. Org. Chem.* **2001**, *37*, 1153. [*Zh. Org. Khim*. **2001**, *37*, 1212.]
52. (a) Pfeffer, M.; Braunstein, P.; Dehand, J. *Spectrochim. Acta, Part A* **1974**, *30A*, 331. (b) Mostafa Hossain, A. G. M.; Nagaoka, T.; Ogura, K. *Electrochim. Acta* **1996**, *41*, 2773. (c) Biagini, M. C.; Ferrari, M.; Lanfranchi, M.; Marchiò, L.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1575. (d) Pazderski, L.; Tousek, J.; Sitkowski, J.; Malinakova, K.; Kozerski, L.; Szlyk, E. *Magn. Reson. Chem* **2009**, *47*, 228.
53. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr*. **2009**, *42*, 339.
54. Farrugia, L. J. *J. Appl. Crystallogr*. **2012**, *45*, 849.
55. Sheldrick, G. M. *Acta Crystallogr.*, *Sect A*: *Found. Crystallogr.* **2008**, *A64*, 112.
56. Sheldrick, G. M. *Acta Crystallogr.*, *Sect C*: *Struct. Chem.* **2015**, *C71*, 3.
57. Spek, A. L. *Acta Crystallogr.*, *Sect C*: *Struct. Chem.* **2015**, *C71*, 9.