Pd-PEPPSI complexes based on 1,2,4-triazol-3-ylidene ligands as efficient catalysts in the Suzuki—Miyaura reaction

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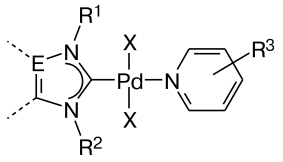
The palladium complexes of the Pd-PEPPSI type with *N*-heterocyclic carbenes of the 1,2,4-triazole series were synthesized in 76—99% yields by the reactions of $PdCl_2$ with 1,4-dialkyl-1,2,4-triazolium salts in pyridine in the presence of KBr or KI as sources of halide ions and tetrabutylammonium salts as phase-transfer catalysts. The obtained complexes can be used as efficient catalysts for the Suzuki—Miyaura cross-coupling and are not inferior to the commercially available Pd-PEPPSI catalysts in activity.

Key words: *N*-heterocyclic carbenes, 1,2,4-triazoles, Suzuki—Miyaura cross-coupling, catalysis, palladium complexes.

Since the first use of the palladium complexes with *N*-heterocyclic carbenes (NHC) as catalysts of the Mizoroki—Heck reaction,[1] diverse metal—NHC complexes have become very popular in catalysis of organic transformations.[2—12] A high stability of the metal—NHC bond combined with a wide variability of steric and electronic parameters is an important advantage of the NHC ligands compared to ligands of other types, for example, phosphine and cyclopentadienyl ligands.[2] The easily accessible and resistant to air moisture and oxygen complexes of palladium halides with NHC ligands and pyridine, so-called Pd-PEPPSI complexes (PEPPSI implies pyridine-enhanced precatalyst preparation, stabilization, and initiation)[13—16] turned out to be convenient in practice.



Pd-PEPPSI

R^1, R^2 = Alk, Ar; R^3 = H, Alk, Cl; X = Cl, Br, I

The Pd-PEPPSI complexes with the NHC ligands of imidazole and benzimidazole series (E = C) are most popular,[6,14,16] whereas other types of NHC, for example, the derivatives of π-deficient 1,2,4-triazoles (E = N), are studied to a significantly lower extent.[17—21] Nevertheless, in some cross-coupling reactions the Pd-PEPPSI complexes with 1,2,4-triazol-3-ylidene ligands can exhibit a higher catalytic activity compared to similar imidazol-2-ylidene complexes.[18,21] Thus, the study of the potential of Pd-PEPPSI complexes with 1,2,4-triazol-3-ylidene ligands for catalysis of cross-coupling reactions is an urgent task. One of the most important methods for C—C bond formation is the Suzuki—Miyaura cross-coupling.[6,22—26] However, the catalytic activity of the Pd-PEPPSI complexes based on the 1,2,4-triazol-3-ylidene ligands in this reaction was not studied.

In this work, we improved a procedure for the synthesis of Pd-PEPPSI complexes based on 1,2,4-triazol-3-ylidene ligands and various halogens as co-ligands and studied the potential of these compounds as catalysts in the Suzuki—Miyaura reaction.

Triazolium salts **2a—e** were used for the synthesis of Pd-PEPPSI complexes **1a—f** as NHC proligands[21,27] (Scheme 1). Attempts to synthesize complexes **1** (Y = Br, I) using the reactions of $PdCl_2$ with NHC formed *in situ* by the deprotonation of bromides **2b**,**c**,**e** and iodide **2a** in pyridine in the presence of K_2CO_3[13,17,28] gave mixtures of the complexes containing various halogen atoms coordinated to the Pd atom (Scheme 1, method *A*). For example, the signals are trebled in the ^1H and ^{13}C NMR spectra of mix complexes **1b´**,**f´** obtained from $PdCl_2$ and triazolium bromides **2b**,**e**, indicating that the solutions contain three compounds, most probably, dibromide,

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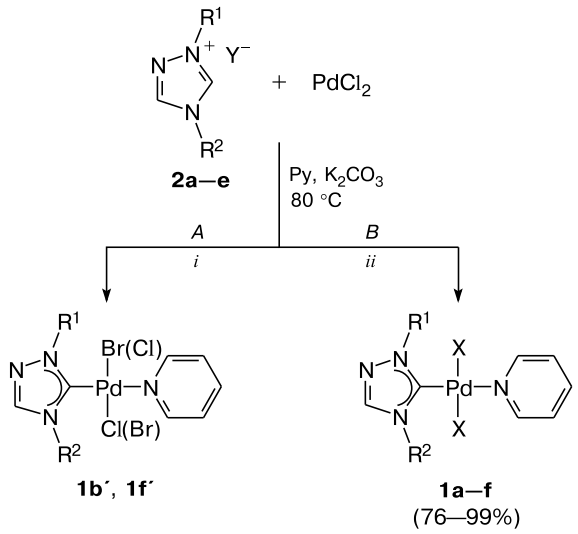
Scheme 1



1b′: R^1 = Me, R^2 = Bu^n (90%)
1f′: R^1 = Bu^t, R^2 = Bn (74%)

2	R^1	R^2	Y
a	Me	Me	I
b	Me	Bu^n	Br
c	Bu^n	Bu^n	Br
d	Bn	Bn	Cl
e	Bu^t	Bn	Br

i. 16 h; *ii*. KX, $[Bu_4N]^+X^-$, 3 h.

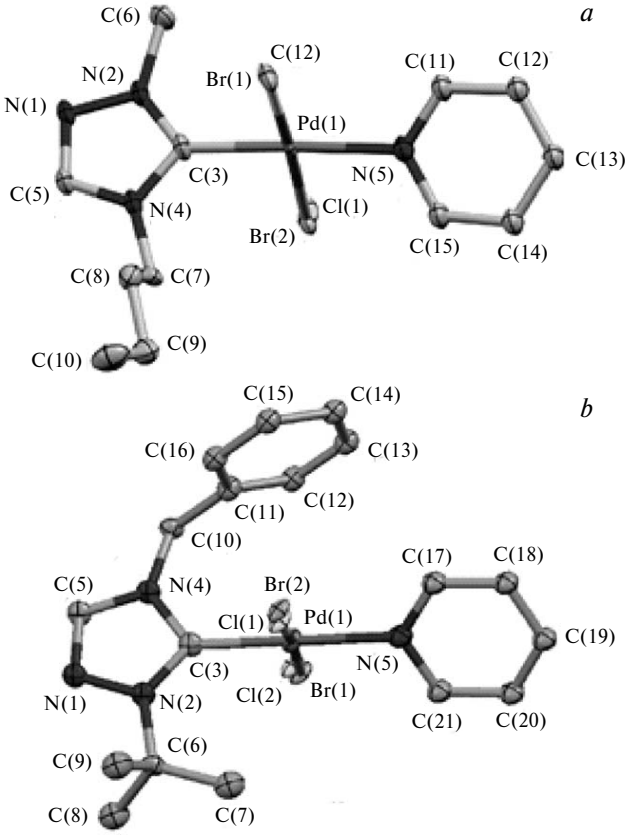


Fig. 1. Structures of compounds **1b′** (*a*) and **1f′** (*b*) (according to the X-ray diffraction data).

dichloride, and bromide—chloride Pd-PEPPSI complexes. These mixtures cannot be separated because of similarity of the chromatographic characteristics of the complexes and their tendency to cocrystallization. For instance, according to the X-ray diffraction data, even after the triple recrystallization of mix compounds **1b′** and **1f′**, the crystals obtained contain the Pd-coordinated chlorine and bromine atoms (Fig. 1).

It is known that the palladium halide complexes tend to the ligand exchange of lighter halide anions by heavier ones, for example, chloride anions are exchanged by bromide or iodide anions upon the reactions with potassium or sodium bromides or iodides.[29—32] The introduction of excess KBr or KI as sources of the corresponding halogen into the reaction mixture results in the shift of the equilibrium and formation of the corresponding bromide or iodide complexes in appropriate yields.[13,17,20,21,29—32] However, this reaction occurs slowly (10—16 h) and is accompanied by the decomposition of the complexes with the precipitation of palladium black under the drastic synthesis conditions. It is most likely that this is explained by a low rate of the target reaction because of an insufficient solubility of KBr and KI in pyridine.

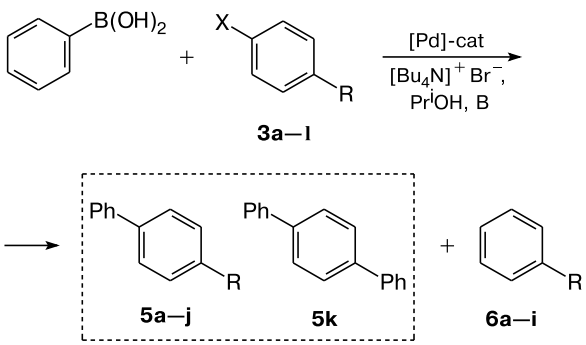
We found that the duration of the synthesis of the bromide and iodide Pd-PEPPSI complexes from $PdCl_2$ and triazolium salts **2** can substantially be shortened and the yield of the target products **1a—f** can be enhanced owing to the application of KBr or KI in combination with the phase-transfer catalysts, tetrabutylammonium bromides or iodides $[Bu_4N]^+X^-$ (X = Br, I). Under the optimized synthesis conditions ($PdCl_2$: **2** : KX : $[Bu_4N]^+X^-$ = = 1 : 1.1 : 6 : 0.18, X = Br, I), the yields of the target products **1a—f** were 76—99% at a reaction time of 3 h (see Scheme 1, method *B*, Table 1).

The cross-couplings of phenylboronic acid $PhB(OH)_2$ with various aryl bromides **3a—j**, iodobenzene **3k**, and 4-chloroacetophenone **3l** in propan-2-ol (Scheme 2, Tables 2 and 3) were studied to evaluate the potential of complexes **1** as catalysts of the Suzuki—Miyaura reac-

Table 1. Synthesis of Pd-PEPPSI complexes **1a—f** by method *B*

1	R^1	R^2	X	Yield (%)
a	Me	Me	I	84
b	Me	Bu^n	Br	93
c	Bu^n	Bu^n	Br	76
d	Bn	Bn	Br	83
e	Bn	Bn	I	87
f	Bu^t	Bn	Br	99

Scheme 2

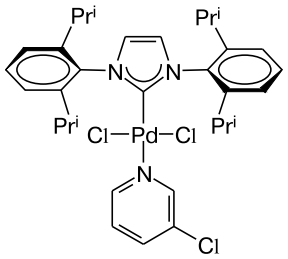


B is base.

Table 2. Yield of compound **5a** in the reaction of phenylboronic acid with 4-bromotoluene (**3a**)

Catalyst (mol.%)	Base	*t*/h	Conversion of **3a** (%)
1a (0.05)	Bu^tOK	2	30
1b (0.05)	Bu^tOK	2	14
1c (0.05)	Bu^tOK	2	14
1d (0.25)	Et_3N	5	1
1d (0.25)	K_2CO_3	5	80
1d (0.25)	Bu^tOK	5	100
1d (0.10)	Bu^tOK	2	97
1d (0.05)	Bu^tOK	2	43
1e (0.05)	Bu^tOK	2	41
1f (0.05)	Bu^tOK	2	34
4 (0.05)	Bu^tOK	2	37
$PdCl_2$ (0.05)	Bu^tOK	2	40

tion. The catalytic properties of compounds **1** were compared with the widely used commercially available catalyst **4**, so-called PEPPSI-IPr,[14—16] as well as with $PdCl_2$.



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The highest conversion of 4-bromotoluene **3a** is achieved in the presence of Bu^tOK (see Table 2). For loads of 0.05 mol.%, complexes **1a—f** exhibit the activity close to exceeding that of $PdCl_2$ and complex **4**. Compound **1d** turned out to be most active among complexes **1a—f** and exhibits the high activity in the reactions with aryl bromides **3b—j** and iodobenzene **3k** (Table 3). In the reaction of $PhB(OH)_2$ with 4-chloroacetophenone **3l**, the catalyst loading should be raised to 1.0 mol.% to provide a high yield of product **5d**, since at loads of 0.1 mol.% the reaction proceeds very slowly (the conversion of **3l** is 6—10%, the yield of **5d** is 4—6%). These results are consistent with the literature data on a lower activity of the Pd-PEPPSI complexes in the reactions with aryl chlorides.[13] The analysis of the reaction mixtures by gas chromatography—mass spectrometry (GC-MS) showed that compounds **6**, products of the dehalogenation of **3**, and biphenyl **5b**, product of homocoupling of phenylboronic acid (the yield of **5b** when using substituted aryl halides

Table 3. Catalytic activity of complexes **1d** and **4** in the cross-coupling of aryl halides **3a—l** with $PhB(OH)_2$[a]

3	X	R	Products	*C* (%)[b]		Yield[c] **5** (%)		Yield[c] **6** (%)	
				1d	**4**	**1d**	**4**	**1d**	**4**
3a	Br	Me	**5a**, **6a**	97	64	96	47	1	17
3b	Br	H	**5b**, **6b**	99	99	85	80	14	19
3c	Br	MeO	**5c**, **6c**	63	56	43	43	20	13
3d	Br	Ac	**5d**, **6d**	100	98	98	91	2	7
3e	Br	Et	**5e**, **6e**	37	53	26	38	11	15
3f	Br	F	**5f**, **6f**	84	80	81	73	3	7
3g	Br	$N(Me)_2$	**5g**, **6g**	77	91	31	45	46	46
3h	Br	PhO	**5h**, **6h**	47	37	42	30	5	7
3i	Br	Cl	**5i**, **6i**	94	78	93	70	1	8
3j[d]	Br	Br	**5j**,**k**, **3b**	84	95	74	87	10	8
3k	I	H	**5b**, **6b**	100	100	80	75	20	25
3l	Cl	Ac	**5d**, **6d**	100	100	72	73	28	27

[a] In the reactions of compounds **3a—k**, $PhB(OH)_2$ (1.4 equiv.) and [Pd]-catalyst (0.25 μmol, 0.1 mol.%) (2.5 μmol (1.0 mol.%) in the case of compound **3l**) were used. The reaction time was 2 h.
[b] *C* is the conversion of ArX in the case of catalysis by complex **1d** or **4**.
[c] Yields of the products in the case of catalysis by complex **1d** or **4**.
[d] $PhB(OH)_2$. (2.8 equiv.) was used.

3a,**c**—**j**,**l** is 4—9% based on $PhB(OH)_2$) are formed as by-products along with target compounds **5a**—**k**. The activity and selectivity of catalysts **1d** and **4** are comparable in the reactions of the majority of aryl halides **3a**—**l**. The close values of yields and selectivities of the cross-coupling for catalysis by complexes **1**, **4**, and $PdCl_2$ (see Tables 2 and 3) suggest that, under the conditions studied, the activity of the Pd-PEPPSI complexes is predominantly determined by the cleavage of the NHC—Pd bond to form the so-called "NHC-free" forms of palladium, which act as active sites.[21,33—36]

To conclude, the procedure for the synthesis of bromide and iodide Pd-PEPPSI complexes by the reactions of $PdCl_2$ with 1,4-dialkyl-1,2,4-triazolium salts and pyridine was improved. The use of excess KBr or KI in combination with the phase-transfer catalyst (tetrabutylammonium halide) makes it possible to substantially increase the yield of the bromide and iodide Pd-PEPPSI complexes (up to 99%) and to shorten the synthesis time to 3 h.

The Pd-PEPPSI complexes with NHC ligands of the 1,2,4-triazole series were studied for the first time as catalysts of the Suzuki—Miyaura reaction. The catalytic activity of 1,2,4-triazole Pd-PEPPSI complexes is comparable with the activity of the widely applied PEPPSI-IPr catalyst in the reactions of phenylboronic acid with various aryl halides. The simplicity of synthesis and high catalytic activity of the 1,2,4-triazole Pd-PEPPSI complexes make it possible to use them in catalysis of the C—C-cross-coupling reactions.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 and 125 MHz, respectively) in $CDCl_3$ using $SiMe_4$ as an internal standard. The melting points were determined by the capillary method on a PTP instrument. Gas chromatography—mass spectrometry was conducted on an Agilent 7890A chromatograph equipped with an Agilent 5975C mass-selective detector (EI, 70 eV) and an HP-5MS capillary column (30 m×0.25 mm×0.25 μm). The yields of the cross-coupling products were determined by GC-MS. The cross-coupling products were identified by a comparison of the mass spectra with standard samples and mass spectra from the NIST database. Elemental analyses (C, H, N) were performed using a Perkin Elmer 2400 analyzer. The contents of halogens and palladium were determined by X-ray fluorescence spectroscopy (XRF) on an ARL QUANT´X spectrometer.

Compounds **2a**—**e** (see Refs 21 and 27) and complex **4** (see Ref. 13) were synthesized using known procedures. Other reagents were commercially available.

Synthesis of compounds 1b´ and 1f´. Method *A*. A mixture of compound **2b** or **2f** (0.55 mmol), $PdCl_2$ (89 mg, 0.5 mmol), K_2CO_3 (345 mg, 2.5 mmol), and pyridine (4 mL) was heated at 80 °C with vigorous stirring for 16 h. The mixture was then cooled to room temperature, CH_2Cl_2 (15 mL) was added, the formed precipitate was filtered, and the solution was washed with water (3×5 mL), dried with Na_2SO_4, and passed through a thin layer of silica gel (height 0.5 cm, diameter 2 cm). The solvent was distilled off *in vacuo* (rotary evaporator) at room temperature, and *n*-hexane (5 mL) was added to the residue. The obtained precipitate was filtered off, washed with *n*-hexane (5 mL), and recrystallized from a CH_2Cl_2—hexane (1 : 3) mixture.

Compound 1b´ (cocrystallizate of the bromide and chloride complexes). The yield was 0.190 g (90%), yellow prismatic crystals, m.p. 95—110 °C. ^1H NMR ($CDCl_3$), δ: 1.04 (t, 3 H, CH_3, J = 7.4 Hz); 1.48 (q, 2 H, CH_2, J = 7.4 Hz); 2.12—2.18 (m, 2 H, CH_2); 4.28, 4.31, 4.34 (all s, 3 H, CH_3); 4.49—4.56 (m, 2 H, CH_2); 7.34—7.39 (m, 2 H, Py); 7.76—7.81 (m, 1 H, Py); 7.93 (s, 1 H, CH of triazole); 8.97—9.02 (m, 2 H, Py). ^{13}C NMR ($CDCl_3$), δ: 13.7; 19.9; 32.0; 32.2; 32.4; 40.30; 40.4; 40.6; 48.8; 49.0; 49.1; 124.8; 138.2; 138.3; 138.4; 142.4; 142.46; 142.49; 151.4; 152.2; 152.8; 155.2; 155.5 (some carbon signals are overlapped). Found (%): Br, 19.61; Cl, 7.42. $C_{12}H_{18}BrClN_4Pd$. Calculated (%): Br, 18.16; Cl, 8.06.

Compound 1f´ (cocrystallizate of the bromide and chloride complexes). The yield was 0.191 g (74%), yellow prismatic crystals, m.p. 119—121 °C. ^1H NMR ($CDCl_3$), δ: 2.08, 2.09, 2.10 (all s, 9 H, CH_3); 5.99—6.07 (m, 2 H, CH_2); 7.33—7.38 (m, 2 H, Ar); 7.40—7.44 (m, 3 H, Ar); 7.53—7.54 (m, 2 H, Ar); 7.63, 7.65, 7.67 (all s, 1 H, CH of triazole); 7.76—7.79 (m, 1 H, Ar); 8.99—9.03 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 31.2; 31.28; 31.30; 54.1; 54.3; 54.5; 62.7; 62.8; 62.8; 124.7; 124.8; 124.8; 129.3; 129.4; 129.6; 129.7; 129.8; 138.1; 138.2; 141.1; 141.2; 151.6; 152.3; 152.9 (some carbon signals are overlapped). Found (%): Br, 15.79; Cl, 6.73. $C_{18}H_{22}BrClN_4Pd$. Calculated (%): Br, 15.48; Cl, 6.87.

Synthesis of complexes 1a—f (general procedure). Method *B*. A mixture of compound **2a**—**e** (0.55 mmol), $PdCl_2$ (89 mg, 0.5 mmol), KBr or KI (3.0 mmol), tetrabutylammonium bromide or iodide (0.1 mmol), K_2CO_3 (345 mg, 2.5 mmol), and pyridine (4 mL) was heated at 80 °C and vigorous stirring for 3 h. Isolation and purification were similar to those in method *A*.

(2,4-Dimethyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)-(diiodo)(pyridine)palladium (1a). The yield was 0.226 g (84%), m.p. 167—169 °C (Ref. 21: 163—165 °C). The ^1H and ^{13}C NMR spectra of the obtained product were identical to those described in the literature.[21]

(4-Butyl-2-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dibromo)(pyridine)palladium (1b). The yield was 0.225 g (93%), m.p. 139—141 °C (Ref. 21: 144—146 °C). The ^1H and ^{13}C NMR spectra of the obtained product were identical to those described in the literature.[21]

(2,4-Dibutyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dibromo)(pyridine)palladium (1c). The yield was 0.200 g (76%), m.p. 110—113 °C (Ref. 21: 106—108 °C). The ^1H and ^{13}C NMR spectra of the obtained product were identical to those described in the literature.[21]

(2,4-Dibenzyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dibromo)(pyridine)palladium (1d). The yield was 0.247 g (83%), m.p. 132—134 °C (Ref. 21: 133—135 °C). The ^1H and ^{13}C NMR spectra of the obtained product were identical to those described in the literature.[21]

(2,4-Dibenzyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dibromo)(pyridine)palladium (1e). The yield was 0.3 g (87%), light orange prosmatic crystals, m.p. 133—135 °C. ^1H NMR ($CDCl_3$),

δ: 5.68 (s, 2 H, CH_2); 5.78 (s, 2 H, CH_2); 7.35—7.44 (m, 8 H, Ar); 7.54—7.55 (m, 2 H, Ar); 7.62—7.64 (m, 2 H, Ar); 7.66 (s, 1 H, CH of triazole); 7.75—7.78 (m, 1 H, Ar); 9.00—9.01 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 54.0; 57.5; 124.8; 128.7; 128.8; 129.4; 129.5; 129.7; 129.8; 133.3; 134.2; 138.0; 142.7; 154.0; 155.0. Found (%): C, 36.49; H, 2.87; N, 8.11; I, 36.93; Pd, 15.38. $C_{21}H_{20}I_2N_4Pd$. Calculated (%): C, 36.63; H, 2.93; N, 8.14; I, 36.86; Pd, 15.45.

(4-Benzyl-2-*tert*-butyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dibromo)(pyridine)palladium (1f). The yield was 0.277 g (99%), m.p. 124—126 °C (Ref. 21: 119—121 °C). The ^{1}H and ^{13}C NMR spectra of the obtained product were identical to those described in the literature.[21]

Study of the catalytic activity of compounds 1a—f and 4 in the Suzuki—Miyaura reaction (general procedure). The corresponding base (0.7 mmol) (see Tables 2 and 3) was mixed with a solution of aryl halide **3a—l** (0.25 mmol), phenylboronic acid (42 mg, 0.35 mmol), and tetrabutylammonium bromide (81 mg, 0.25 mmol) in propan-2-ol (1 mL) in a 7 mL glass vial with a screw cap equipped with a magnetic stirrer. A solution (10 μL) of the corresponding catalyst in DMF was added, and the mixture was purged with argon and stirred at 80 °C for 2—5 h (see Tables 2 and 3). Then the reaction mixture was cooled, and naphthalene (16 mg, 0.125 mmol) as an internal GC-MS standard was added. An aliquot (1 μL) of the reaction mixture was dissolved in acetonitrile (1 mL), and the sample was analyzed by GC-MS.

X-ray diffraction analysis of compounds 1b′ and 1f′. Single crystals of compounds **1b′** and **1f′** were obtained by the slow evaporation of the solutions in CH_2Cl_2 in an atmosphere of saturated *n*-hexane vapors.

Unit cell parameters and reflection intensities were measured on a BELOK Synchrotron Radiation Station of the National Research Center "Kurchatov Institute" using a Rayonix SX165 two-coordinate detector (λ = 0.96990 Å, T = 100 K, φ scan mode). A set of experimental data was processed using the iMOSFLM program, which is s subprogram of the CCP4 complex.[37] An X-ray radiation absorption correction was applied by the semiempirical method using the Scala program.[38] The main crystallographic data and refinement parameters for structures **1b′** and **1f′** are presented in Table 4. The crystal structures were decoded by direct methods and refined by least squares for F^2 in the anisotropic approximation for non-hydrogen atoms. The bromine and chlorine atoms in the crystals of both complexes **1b′** and **1f′** occupy the same coordination sites at the palladium atom with the population 0.60 : 0.40 and 0.50 : 0.50, respectively. The positions of the hydrogen atoms were calculated geometrically and refined in the riding model with fixed isotropic shift parameters (U_{iso}(H) = 1.2U_{eq}(C)). All calculations of structures **1b′** and **1f′** were performed using the SHELXTL program package.[39]

The tables of the atomic coordinates, bond lengths, bond and torsion angles, and anisotropic temperature parameters for compounds **1b′** and **1f′** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos 1573544 (**1b′**) and 1573545 (**1f′**)) and are available at www.ccdc.cam.ac.uk.

Table 4. Crystallographic data and refinement parameters for compounds **1b′** and **1f′**

Parameter	**1b′**	**1f′**
Empirical formula	$C_{12}H_{18}N_4ClPdBr$	$C_{18}H_{22}N_4ClPdBr$
Molecular weight	440.06	516.15
Size of single crystal/mm	0.20×0.20×0.15	0.18×0.15×0.15
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a/Å	8.9500(18)	9.1400(18)
b/Å	13.460(3)	13.990(3)
c/Å	26.230(5)	15.310(3)
α/deg	90	90
β/deg	94.81(3)	90
γ/deg	90	90
V/Å^3	3148.7(11)	1957.7(7)
Z	8	4
d_{calc}/g cm^{-3}	1.857	1.751
F(000)	1728	1024
μ/mm^{-1}	3.898	3.164
$2\theta_{max}$/deg	76.3	76.8
Number of reflections		
measured	50323	22319
independent	6289	3829
with $I > 2\sigma(I)$	5221	2945
Number of refined parameters	234	129
R_1; wR_2 ($I > 2\sigma(I)$)	0.070; 0.163	0.078; 0.164
R_1; wR_2 (all data)	0.084; 0.175	0.107; 0.189
GOOF	0.956	1.073
T_{min}/T_{max}	0.484/0.579	0.555/0.606
ρ_{max}/ρ_{min}, e Å^{-3}	3.135/−2.076	1.897/−2.234

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