Mechanochemical synthesis of platinum(IV) complexes with *N*-heterocyclic carbenes

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A new method for the synthesis of complexes $Pt^{IV}(NHC)X_4L$ (NHC is *N*-heterocyclic carbene of imidazole or benzimidazole series; X = Cl, Br; L is *N*-coordinated pyridine or NHC) based on mechanochemical oxidation of complexes $Pt^{II}(NHC)X_2L$ with dichloroiodobenzene ($PhICl_2$) or pyridinium hydrobromide perbromide ($PyHBr_3$) was proposed. Mechanochemical activation led to reduction in the synthesis time and increase in the selectivity of halogenation and yields of the target Pt^{IV} complexes (74—98%) as compared to the reaction in solutions.

Key words: mechanochemical synthesis, *N*-heterocyclic carbenes (NHC), platinum coordination compounds, oxidation, halogenation.

Platinum complexes with ligands based on *N*-heterocyclic carbenes (Pt—NHC) are widely used in modern metal complex catalysis.[1—5] Available and stable complexes with platinum in the oxidation state +2 (Pt^{II}—NHC)[1—3,6] are the most common and deeply studied. However, in many reactions the catalytic cycle includes complexes with platinum in the oxidation state +4 (Pt^{IV}—NHC).[3,7,8] For example, the complexes $Pt^{IV}(NHC)X_4L$ (X is a halogen) are efficient catalysts of halogenation and C—H functionalization reactions.[9,10] In addition, these complexes are of interest as antitumor drugs.[11]

However, the complexes Pt^{IV}—NHC remain still poorly studied, especially the polyhalide complexes $Pt^{IV}(NHC)X_4L$, the synthesis of which was described in only a few publications.[9—12] The preparation of complexes $Pt^{IV}(NHC)X_4L$ is complicated primarily by their instability in solutions and the possibility of side halogenation reactions of ligands.[9—11] We assumed that the solution of the problem of the synthesis of complexes $Pt^{IV}(NHC)X_4L$ could be the solvent-free halogenation of $Pt^{II}(NHC)X_2L$ with mild halogenating agents under the conditions of mechanochemical activation. Mechanochemical activation can sometimes significantly increase the yield of the target product and reduce the synthesis time, especially if the reagents or products are unstable in solutions.[13—19] The mechanochemical method is increasingly used in the synthesis of coordination compounds,[13,14,20] including for the formation of a metal—NHC bond;[21—26] however, this approach has not been previously used in the oxidation of complexes Pt^{II}—NHC to Pt^{IV}—NHC.

In the present work, we studied different versions of oxidative halogenation of complexes Pt^{II}—NHC with brominating and chlorinating agents, both in solutions and in solvent-free experiments under conditions of mechanochemical activation, which resulted in the development of a new efficient method for mechanochemical synthesis of polyhalide complexes Pt^{IV}—NHC.

Heating of *N*,*N*′-disubstituted (benz)imidazolium salts **1a—f** with $PtCl_2$ and pyridine (or 3-chloropyridine) in the presence of potassium carbonate (Scheme 1) gave complexes Pt^{II}—NHC **2a—f**. Complex **2g** was obtained by the reaction of complex **2c** with triethylamine.[27]

We tried three approaches to the oxidative halogenation of complexes **2** (Scheme 2): (*i*) by the reaction with elemental halogens (Cl_2, Br_2) in solution of CH_2Cl_2 (method *A*); (*ii*) by treatment with mild halogenating agents $PhICl_2$[28] and $PyHBr_3$[29,30] in DMSO (method *B*); (iii) by the solvent-free reaction with $PhICl_2$ and $PyHBr_3$ using mechanochemical activation by trituration in a porcelain mortar (method *C*). Attempts to obtain iodide complexes $Pt^{IV}(NHC)I_4L$ were not undertaken in this work, since the oxidative iodination reaction causes the metal—NHC bond cleavage.[31]

We found that the oxidative halogenation of complexes $Pt^{II}(NHC)X_2L$ **2a**,**b**,**d**,**f** with bromine or chlorine (method *A*) proceeded readily, but the NMR data showed that the reaction is accompanied by side halogenation of the imidazole ring and, apparently, of the aryl substituents in the NHC-ligands. The ^1H NMR spectra of crude compounds **3a**,**b** exhibited impurity signals in the region of δ 7.16—7.18 (synthesis of **3a**) and δ 7.34—7.36 (synthesis **3b**), as well

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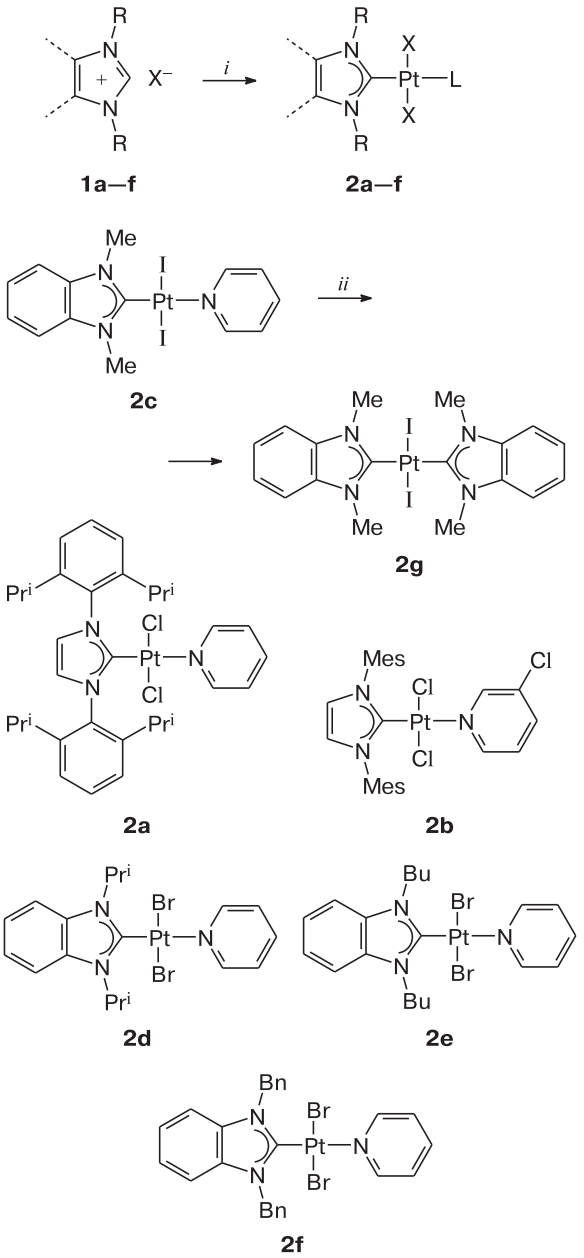
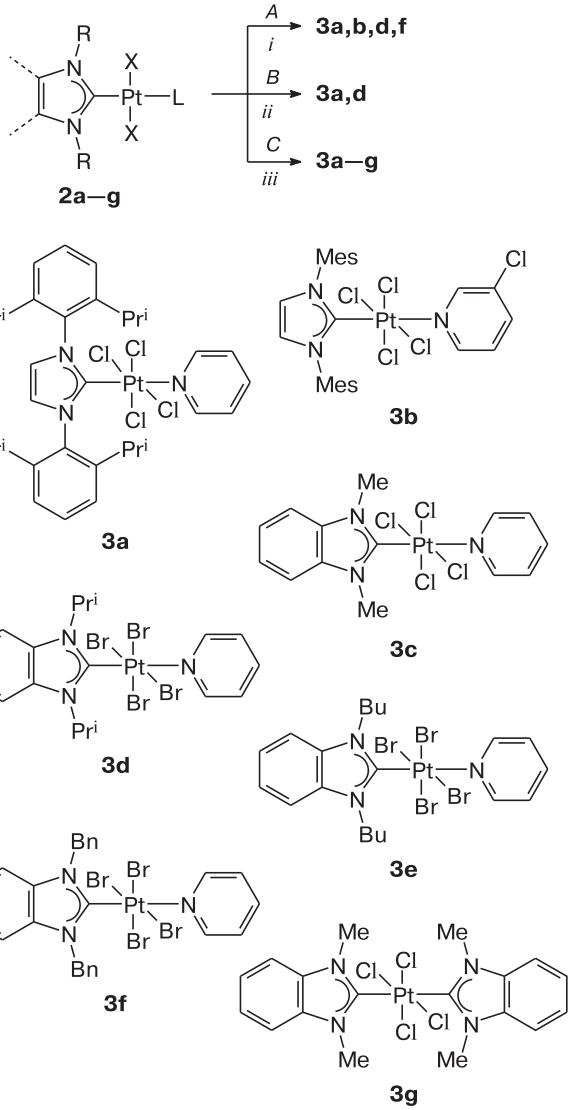
Scheme 1



Compound **2**	Yield (%)	Compound **2**	Yield (%)
a	54	**e**	79
b	70	**f**	84
c	85	**g**	45
d	71		

Reagents and conditions: *i*: $PtCl_2$, K_2CO_3, pyridine (Py) or 3-chloropyridine, 80 °C, 16 h; *ii*: Et_3N, DMF, 140 °C.

Scheme 2



Compound	Method	Yield (%)	Compound	Method	Yield (%)
3a	A	29	**3d**	A	51
	B	51		B	30
	C	78		C	98
3b	A	33	**3e**	C	83
	C	87	**3f**	A	42
3c	C	97		C	78
			3g	C	74

Reagents and conditions: *i*. Cl_2 or Br_2, CH_2Cl_2, 0—5 °C, 1 h; *ii*. $PhICl_2$ or $PyHBr_3$, DMSO, 80 °C, 24 h; *iii*. $PhICl_2$ or $PyHBr_3$, ~20 °C, 20 min.

as a significant decrease in the relative integral intensity of the signals of CH at positions 4 and 5 of the imidazole ring (δ ~ 7.1) as compared to the signals of the alkyl groups and the pyridine fragment. The impurities were separated only by repeated crystallization, which led to a decrease in the yield of the target products to 29—51%. In addition, the impossibility to accurately dose gaseous Cl_2 further complicated the synthesis.

The crystalline halogenating agents $PhICl_2$ and $PyHBr_3$ are more convenient in handling and often provide higher

Table 1. Optimization of conditions for mechanochemical synthesis of complexes **3c,d**

Entry	$PhICl_2$:**2c** (mol/mol)	Inert additive	Yield[a] **3c** (%)	Entry	$PyHBr_3$:**2d** (mol/mol)	Inert additive	Yield[a] **3d** (%)
1	1	—[b]	36	*7*	1	—[b]	40
2	2	—[b]	50	*8*	2	—[b]	52
3	2	Silica gel	59	*9*	2	Silica gel	61
4	3	Silica gel	80	*10*	3	Silica gel	76
5	4	Silica gel	97	*11*	4	Silica gel	98
6	4	Glass	95	*12*	4	Glass	93

[a] Isolated yield.
[b] Without additives.

halogenation selectivity[28—30] than elemental halogens. However, the halogenation of complexes **2a**,**d** with these reagents at room temperature in CH_2Cl_2 or deuterochloroform was too slow, especially the bromination with poorly soluble $PyHBr_3$. The ^1H NMR spectroscopy data showed that even after 24 h, the conversion degree of complexes **2a**,**d** did not exceed 70%. The reaction was more successful in DMSO at 80 °C, complexes **3a**,**d** were obtained in moderate yields (see Scheme 2, method *B*).

To assess the efficiency of mechanochemical synthesis of $Pt^{IV}(NHC)X_4L$, we tested a version of the reaction the most simple and feasible from the point of view of instrumentation design, namely, manual trituration of the mixture of reagents in a porcelain mortar at room temperature in a fume hood without an inert atmosphere. The procedure was optimized on the example of the synthesis of complexes **3c** and **3d** (Table 1). In entries *1*, *2* and *7*, *8* (see Table 1), the synthesis was complicated by the clumping of the reaction mixture. The addition of loose inert additive, silica gel for column chromatography or glass powder, to the reaction mixture greatly facilitated grinding and increased the homogeneity of the reaction mixture (see Table 1, entries *3—6*, *9—12*). Reactions using such solid supports are widely used in organic synthesis.[32—35] The yield of the target products increased significantly with an increase in the molar ratio of halogenating agent : complex **2** to 4 : 1 (entries *5*, *6* and *11*, *12*). An increase in the synthesis time to 20 min and more did not increase the yield. The conditions of entries *5*, *6* and *11*, *12* were regarded as optimal and used to synthesize other Pt^{IV} complexes. The oxidative halogenation of complexes **2a—g** proceeded rapidly and with high selectivity. The chlorination of iodine complexes **2c**,**g** was accompanied by oxidative replacement of iodide ligands with the formation of tetrachloride complexes **3c**,**g**. The yields of compounds **3a—g** after purification were within 74—98% (see Scheme 2, method *C*). We also carried out experiments with the mechanochemical synthesis of compounds **3a** and **3f** in an electromechanical ball mill (the loading of the starting compounds **2a**,**f** was 0.45 mmol), which, however, showed

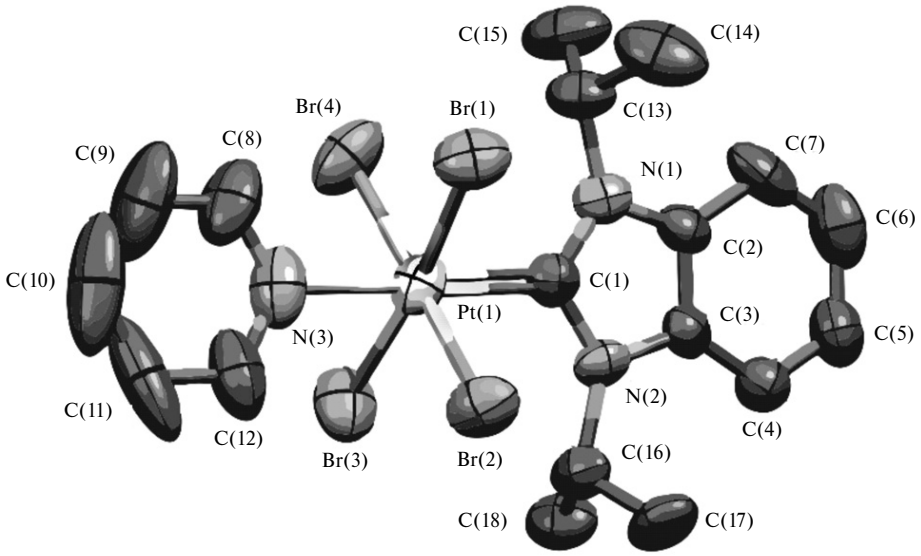


Fig. 1. Structure of complex **3d** according to the X-ray diffraction data.

no noticeable increase in the target product yields. The efficiency of using such simple and affordable equipment as a porcelain mortar makes this method especially convenient in the work with small amounts of reagents (to several grams).

The structure of compounds **3a**—**g** was confirmed by ^{1}H and ^{13}C NMR spectra, elemental analysis, and X-ray diffraction analysis of complex **3d** (Fig. 1).

In the ^{1}H NMR spectra of compounds **3a**—**g** (Pt^{IV}), the signals for the pyridine ligands are noticeably shifted downfield (~0.7—1.7 ppm) as compared to those for the starting compounds **2a**—**g** (Pt^{II}), which agrees with the literature data.[11] In the ^{13}C NMR spectra of compounds **3d**,**e**,**f**, the signals for C(1) atoms of the *N*-alkyl groups are also shifted downfield by ~2.5—5 ppm as compared to those of compounds **2d**,**e**,**f**.

A comparison of the molecular structure of complex **3d** (see Fig. 1) with its precursor **2d**[36] reveals a noticeable elongation of the bonds between the platinum atom and the other ligands in the Pt^{IV} complex. Thus, in complexes **3d** and **2d** the Pt—C bond lengths are 2.08(2) Å and 1.958(4) Å, and the Pt—N bond lengths are 2.15(2) Å and 2.085(4) Å, respectively. The Pt—Br bond lengths in complex **3d** is 2.460(3)—2.480(3) Å, whereas in complex **2d** it is 2.4188(6) Å and 2.4254(5) Å.[36] Such an elongation is apparently caused not only by steric factors, but also by the weakening of the dative interaction upon oxidation of platinum, and may indicate lower stability of $Pt^{IV}(NHC)X_4L$ as compared to $Pt^{II}(NHC)X_2L$.

When stored in air, complexes **3a**—**g** gradually lose a molecule of halogen and within three—four weeks undergo conversion to complexes **2a**—**g**, therefore, they should be stored in a sealed glass container in a refrigerator. The instability of the complexes $Pt^{IV}(NHC)X_4L$ in solutions was also noted earlier.[11] In the presence of aqueous $Na_2S_2O_3$, complexes **3** are rapidly and practically quantitatively converted to complexes **2**. For example, complex **2d** was obtained in 98% yield by stirring of a solution of complex **3d** in CH_2Cl_2 with aqueous $Na_2S_2O_3$ for 5 min.

In conclusion, the oxidative halogenation of complexes $Pt^{II}(NHC)X_2L$ with dichloroiodobenzene or pyridinium hydrobromide perbromide under conditions of mechanochemical activation can be used as an effective method for the synthesis of complexes $Pt^{IV}(NHC)X_4L$. The advantages of the method include the simplicity of equipment for realization of the synthesis, the availability of the starting materials, the high reaction rate, and the convenience of working with small amounts of reagents.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker DRX-500 spectrometer (500 and 125 MHz, respectively) in $CDCl_3$, using $SiMe_4$ as an internal standard. Melting points were determined on a melting point tester (MPT) in sealed capillaries. Elemental analysis was performed on a Perkin Elmer 2400 analyzer.

The starting imidazolium **1a**,**b** and benzimidazolium salts **1c**—**f** were obtained according to the known procedures.[37,38] Complex **2g** was obtained according to the previously described procedure.[27] Other reagents were commercially available and used without additional purification. Silica gel 60 (Alfa Aesar), 0.032—0.063 mm (230—450 mesh) and glass powder SI 1, grade 1 were used as inert additives in mechanochemical synthesis.

*Attention! Due to the toxicity and irritant effect of halogenating agents, all operations (synthesis, purification, drying) with complexes **3a—g** should be carried out in a well-functioning fume hood.*

Synthesis of complexes 2a—f (general procedure). A mixture of the corresponding azolium salt **1a**—**f** (0.55 mmol), pyridine or 3-chloropyridine (4 g), $PtCl_2$ (133 mg, 0.5 mmol), and finely ground anhydrous K_2CO_3 (345 mg, 2.5 mmol) was heated at 80 °C with vigorous stirring for 16 h. In the obtaining of iodide complex **2c** and bromide complexes **2d**—**f**, finely ground KI (498 mg, 3.0 mmol) or KBr (357 mg, 3.0 mmol), respectively, was added to the reaction mixture together with other reactants. Then, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (15 mL), a precipitate formed was filtered off. The solution was washed with water (3×5 mL), dried with Na_2SO_4, and passed through a layer of silica gel (height 1 cm, diameter 2 cm). The solvent was evaporated on a rotary evaporator, *n*-hexane (5 mL) was added to the residue, and the mixture was cooled to ~0 °C. The precipitate formed was collected by filtration, recrystallized from a mixture of CH_2Cl_2—*n*-hexane (1 : 2), and dried *in vacuo* at 40 °C for 24 h.

{1,3-Bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(dichloro)(pyridine)platinum (2a). The yield was 198 mg (54%). ^{1}H and ^{13}C NMR spectra of the obtained product are identical to those described earlier.[21]

[1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](dichloro)(3-chloropyridine-κ*N*)platinum (2b). The yield was 239 mg (70%). ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 12 H, 4 CH_3); 2.36 (s, 6 H, 2 CH_3); 7.02—7.03 (m, 5 H, Ar); 7.11—7.13 (m, 2 H, Py); 7.56—7.59 (m, 1 H, Py); 8.55 (d, 2 H, 2 CH of imidazole, J = 5.3 Hz). Found (%): C, 45.42; H, 4.22; N, 5.84. $C_{26}H_{28}Cl_3N_3Pt$. Calculated (%): C, 45.66; H, 4.13; N, 6.14.

(1,3-Dimethyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)(diiodo)(pyridine)platinum (2c). The yield was 286 mg (85%). ^{1}H and ^{13}C NMR spectra of the obtained product are identical to those described earlier.[39]

Dibromo[1,3-di(propan-2-yl)-1,3-dihydro-2*H*-benzimidazol-2-ylidene](pyridine)platinum (2d). The yield was 226 mg (71%). ^{1}H and ^{13}C NMR spectra of the obtained product are identical to those described earlier.[36]

Dibromo(1,3-dibutyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)(pyridine)platinum (2e). The yield was 262 mg (79%). ^{1}H NMR ($CDCl_3$), δ: 1.07—1.10 (m, 6 H, 2 CH_3); 1.55—1.59 (m, 4 H, 2 CH_2); 2.17—2.19 (m, 4 H, 2 CH_2); 4.82—4.87 (m, 4 H, 2 CH_2); 7.24–7.28 (m, 2 H, Ar); 7.35—7.43 (m, 4 H, Ar); 7.79—7.82 (m, 1 H, Ar); 9.06—9.09 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.0, 20.5, 31.3, 48.1, 110.6, 122.9, 123.4, 125.1, 134.5, 137.9, 152.8. Found (%): C, 35.88; H, 4.02; N, 6.12. $C_{20}H_{27}Br_2N_3Pt$. Calculated (%): C, 36.16; H, 4.10; N, 6.33.

(1,3-Dibenzyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)(dibromo)(pyridine)platinum (2f). The yield was 308 mg (84%).

^{1}H NMR ($CDCl_3$), δ: 6.28 (s, 4 H, 2 CH_2); 7.04—7.07 (m, 4 H, Ar); 7.30—7.33 (m, 2 H, Py), 7.35—7.38 (m, 6 H, Ar); 7.59—7.61 (m, 4 H, Ar); 7.75—7.78 (m, 1 H, Py); 9.03—9.04 (m, 2 H, Py). ^{13}C NMR ($CDCl_3$), δ: 53.1, 111.7, 123.2, 125.1, 128.1, 128.2, 128.8, 129.0, 134.5, 135.5, 138.0, 152.8. Found (%): C, 42.21; H, 3.37; N, 5.86. $C_{26}H_{23}Br_2N_3Pt$. Calculated (%): C, 42.64; H, 3.17; N, 5.74.

Synthesis of complexes 3a,b,d,f by halogenation of compounds 2a,b,d,f with elemental halogens (method *A*). A solution of Br_2 (48 mg, 0.3 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of complex **2d**,**f** (0.15 mmol) in CH_2Cl_2 (5 mL) cooled to 0—5 °C with vigorous stirring, or a vigorous flow of gaseous Cl_2 was passed through a solution of complex **2a**,**b** (0.15 mmol) in CH_2Cl_2 (5 mL) during the synthesis. The mixture was stirred at 0—5 °C for 1 h and cooled to −20 °C. A precipitate formed was collected by filtration, recrystallized from a mixture of CH_2Cl_2—*n*-hexane (1 : 2), and dried at room temperature in air.

Synthesis of complexes 3a,d by halogenation of 2a,d with $PhICl_2$ and $PyHBr_3$ in DMSO (method *B*). A solution of complex **2a**,**d** (0.15 mmol) and the corresponding halogenating agent ($PhICl_2$ in the synthesis of **3a**, $PyHBr_3$ in the synthesis of **3d**) (0.3 mmol) in DMSO (5 mL) was heated at 80 °C for 24 h with stirring, then cooled to 20 °C and diluted with water (10 mL). A precipitate formed was collected by filtration, washed with 50% aqueous dioxane (10 mL) and water (50 mL), dried in air at room temperature. The dry product was recrystallized from a mixture of CH_2Cl_2—*n*-hexane (1 : 2).

Mechanochemical synthesis of complexes 3a—g (method *C*). The starting complex **2a**—**g** (0.15 mmol), silica gel or glass powder (0.2 g), as well as $PhICl_2$ (165 mg, 0.6 mmol) in the synthesis of chloride complexes or $PyHBr_3$ (192 mg, 0.6 mmol) in the synthesis of bromide complexes, were mixed in a porcelain mortar. The resulting mixture was intensively ground with a pestle for 20 min. Then the mixture was treated with CH_2Cl_2 (10 mL), the resulting suspension was filtered through a thin layer of silica gel (height 0.5 cm, diameter 2 cm). The filtrate was washed with water (3×2 mL), dried with anhydrous Na_2SO_4, and concentrated *in vacuo* to ~2 mL. *n*-Hexane (4 mL) was added to the residue, and the resulting mixture was cooled to 0—5 °C. The precipitate was collected by filtration and dried in air at room temperature.

{1,3-Bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(tetrachloro)(pyridine)platinum (3a). The yield was 35 mg (29%, method *A*); 62 mg (51%, method *B*), 94 mg (78%, method *C*), yellow crystals, m.p. 195—196 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 1.12 (d, 12 H, 4 CH_3, J = 6.9 Hz); 1.44 (d, 12 H, 4 CH_3, J = 6.7 Hz); 3.05—3.12 (m, 4 H, Ar); 7.05—7.06 (m, 2 H, Ar); 7.23—7.30 (m, 6 H, Ar); 7.43—7.46 (m, 2 H, Ar); 7.69—7.73 (m, 1 H, Ar); 9.04—9.06 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 23.6, 26.0, 29.0, 123.7, 124.3, 127.6, 128.4, 130.1, 139.0, 141.1, 145.8, 151.0. Found (%): C, 47.85; H, 5.09; N, 5.31. $C_{32}H_{41}Cl_4N_3Pt$. Calculated (%): C, 47.77; H, 5.14; N, 5.22.

[1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](tetrachloro)(3-chloropyridine-κ*N*)platinum (3b). The yield was 38 mg (33%, method *A*), 99 mg (87%, method *C*), yellow prismatic crystals, m.p. 220—221 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 2.30 (s, 12 H, 4 CH_3); 2.56 (s, 6 H, 2 CH_3); 7.09—7.11 (m, 2 H, Ar); 7.29—7.32 (m, 4 H, Ar); 7.75—7.78 (m, 1 H, Ar); 8.92—9.06 (m, 3 H, Py). The ^{13}C NMR spectrum could not be recorded because of the low solubility of compound **3b**. Found (%): C, 41.92; H, 3.62; N, 5.89. $C_{26}H_{28}Cl_5N_3Pt$. Calculated (%): C, 41.37; H, 3.74; N, 5.57.

(1,3-Dimethyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)(tetrachloro)(pyridine)platinum (3c). The yield was 82 mg (97 %, method *C*), beige prismatic crystals, m.p. 258 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 4.54 (s, 3 H, CH_3); 4.57 (s, 3 H, CH_3); 7.41—7.52 (m, 2 H, Ar); 7.56—7.59 (m, 4 H, Ar); 7.97—8.00 (m, 1 H, Py); 9.30—9.35 (m, 2 H, Py). The ^{13}C NMR spectrum could not be recorded because of the low solubility of compound **3c**. Found (%): C 29.66; H, 2.83; N, 7.71. $C_{14}H_{15}Cl_4N_3Pt$. Calculated (%): C, 29.91; H, 2.69; N, 7.47.

[1,3-Di(propan-2-yl)-1,3-dihydro-2*H*-benzimidazol-2-ylidene] (pyridine)(tetrabromo)platinum (3d). The yield was 61 mg (51%, method *A*); 36 mg (30%, method *B*); 117 mg (98%, method *C*), dark red cubic crystals, m.p. 150—152 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 1.88 (d, 12 H, 4 CH_3, J = 6.9 Hz); 6.67—6.72 (m, 2 H, Ar); 7.31—7.33 (m, 2 H, Ar); 7.44—7.47 (m, 2 H, Ar); 7.86—7.88 (m, 2 H, Ar); 7.90—7.93 (m, 1 H, Ar); 9.77—9.82 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 22.7, 56.8, 115.1, 123.6, 124.7, 133.8, 136.0, 139.6, 155.0. Found (%): C, 27.21; H, 2.58; N, 5.11. $C_{18}H_{23}Br_4N_3Pt$. Calculated (%): C, 27.16; H, 2.91; N, 5.28.

(1,3-Dibutyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)(tetrabromo)(pyridine)platinum (3e). The yield was 103 mg (83%, method *C*), red orange rhombic crystals, m.p. 201—202 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 1.04 (t, 6 H, 2 CH_3, J = 7.4 Hz); 1.55—1.63 (m, 4 H, 2 CH_2); 2.04—2.10 (m, 4 H, 2 CH_2); 5.13 (t, 4 H, 2 CH_2, J = 8.3 Hz); 7.37—7.39 (m, 2 H, Ar); 7.44—7.47 (m, 2 H, Ar); 7.54—7.56 (m, 2 H, Ar); 7.89—7.93 (m, 1 H, Ar); 9.76—9.82 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.0, 20.1, 32.4, 53.1, 113.1, 121.7, 124.67, 124.70, 124.8, 124.9, 134.7, 139.6, 154.8. Found (%): C, 29.31; H, 3.43; N, 5.22. $C_{20}H_{27}Br_4N_3Pt$. Calculated (%): C, 29.15; H, 3.30; N, 5.10.

(1,3-Dibenzyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)(tetrabromo)(pyridine)platinum (3f). The yield was 56 mg (42 %, method *A*); 104 mg (78 %, method *C*), red orange prismatic crystals, m.p. 183—184 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 6.63 (s, 4 H, 2 CH_2); 7.05—7.07 (m, 5 H, Ar); 7.21—7.23 (m, 5 H, Ar); 7.32—7.35 (m, 4 H, Ar); 7.43—7.48 (m, 2 H, Ar); 7.89—7.92 (m, 1 H, Ar); 9.72—9.77 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 58.0, 113.9, 124.8, 124.9, 127.0, 127.6, 128.7, 135.0, 136.7, 138.8, 139.7, 154.9. Found (%): C, 35.18; H, 2.38; N, 4.86. $C_{26}H_{23}Br_4N_3Pt$. Calculated (%): C, 35.00; H, 2.60; N, 4.71.

Bis(1,3-dimethyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)-(tetrachloro)platinum (3g). The yield was 70 mg (74%, method *C*), yellow prismatic crystals, m.p. 165 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 4.58 (s, 6 H, 2 CH_3); 4.62 (s, 6 H, 2 CH_3); 7.45—7.50 (m, 4 H, Ar); 7.55—7.61 (m, 4 H, Ar). The ^{13}C NMR spectrum could not be recorded because of the low solubility of compound **3g**. Found (%): C, 34.59; H, 3.32; N, 8.78. $C_{18}H_{20}Cl_4N_4Pt$. Calculated (%): C, 34.36; H, 3.20; N, 8.90.

Reduction of complex 3d to 2d. A solution of $Na_2S_2O_3$ (158 mg, 1 mmol) in water (2 mL) was added to a solution of complex **3d** (80 mg, 0.1 mmol) in CH_2Cl_2 (4 mL) and the resulting mixture was vigorously stirred for 5 min at room temperature. Then, the organic layer was separated, washed with water (3×2 mL), and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* to obtain pure compound **2d** (62 mg, 98%). ^{1}H and ^{13}C NMR spectra of product **2d** are identical to those described in the literature.[36]

X-ray diffraction study. A single crystal of compound **3d** was obtained by slow evaporation of its solution in CH_2Cl_2 under

Table 2. Crystallographic data and refinement parameters for complex **3d**

Compound	**3d**
Molecular formula	$C_{18}H_{23}Br_4N_3Pt$
Molecular weight	796.12
Crystal size/mm	0.26×0.2×0.18
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/Å	17.352 (1)
b/Å	14.2894 (8)
c/Å	8.9872 (5)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	2228.4 (2)
Z	4
d_c/g cm^{-3}	2.373
F(000)	1480
μ/mm^{-1}	13.48
θ_{max}/deg	29.4
θ_{min}/deg	1.9
Number of reflections	
measured	34113
independent	5223
with $I > 2\sigma(I)$	2624
Number of refined parameters	239
R_1 ($I > 2\sigma(I)$)	0.125
wR_2	0.055
Flack parameter (x)	0.08 (3)
S	0.869
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	1.21/−0.93

hexane atmosphere. The unit cell parameters of **3d** were determined using a StadiVari Pilatus 100K (STOE) diffractometer, λ (CuKα) = 0.71073 Å, at 295 K, θ/2θ-scan technique, a GeniX^{3D}, Cu HF radiation generator with a microfocus X-ray tube and a Xenocs FOX3D HF multilayer thin-film ellipsoidal monochromator (France). Data collection, solution and refinement of unit cell parameters, processing of diffraction data were carried out using the STOE X-Area software package (STOE & Cie GmbH, Darmstadt, Germany, 2013). The intensities of diffraction reflections were processed by the LANA program (part of the X-Area program) to minimize the difference in the intensities of equivalent reflections (multi-scan method). The absolute structure was solved by the classical Flack method implemented in the SHELXS-97 software package.[40,41] Positional and thermal parameters of nonhydrogen atoms were refined in the full-matrix anisotropic approximation. Hydrogen atoms were calculated and refined using a riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.2U_{eq}(C)$). The principal crystallographic parameters are listed in Table 2. Tables of atomic coordinates, bond lengths, bond and torsion angles, and anisotropic temperature parameters for compound **3d** were deposited with the Cambridge Crystallographic Data Center (CCDC 1835408) and are available online: www.cdc.cam.ac.uk.

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References

1. *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes*, Eds B. Cornils, W. A. Herrmann, M. Beller, and R. Paciello, John Wiley & Sons, 2017, 1745 p.
2. J. A. Labinger, *Chem. Rev.*, 2017, **117**, 8483.
3. Y. Fort, C. Comoy, in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, The Royal Society of Chemistry, 2016, p. 375.
4. G. A. Abakumov, A. V. Piskunov, V. K. Cherkasov, I. L. Fedushkin, V. P. Ananikov, D. B. Eremin, E. G. Gordeev, I. P. Beletskaya, A. D. Averin, M. N. Bochkarev, A. A. Trifonov, U. M. Dzhemilev, V. A. D'yakonov, M. P. Egorov, A. N. Vereshchagin, M. A. Syroeshkin, V. V. Jouikov, A. M. Muzafarov, A. A. Anisimov, A. V. Arzumanyan, Y. N. Kononevich, M. N. Temnikov, O. G. Sinyashin, Y. H. Budnikova, A. R. Burilov, A. A. Karasik, V. F. Mironov, P. A. Storozhenko, G. I. Shcherbakova, B. A. Trofimov, S. V. Amosova, N. K. Gusarova, V. A. Potapov, V. B. Shur, V. V. Burlakov, V. S. Bogdanov, M. V. Andreev, *Russ. Chem. Rev.*, 2018, **87**, 393.
5. A. A. Shteinman, *Russ. Chem. Bull.*, 2016, **65**, 1930.
6. V. M. Chernyshev, O. V. Khazipov, M. A. Shevchenko, A. Y. Chernenko, A. V. Astakhov, D. B. Eremin, D. V. Pasyukov, A. S. Kashin, V. P. Ananikov, *Chem. Sci.*, 2018, **9**, 5564.
7. A. Vigalok, *Acc. Chem. Res.*, 2015, **48**, 238.
8. D. A. Petrone, J. Ye, M. Lautens, *Chem. Rev.*, 2016, **116**, 8003.
9. D. Meyer, S. Ahrens, T. Strassner, *Organometallics*, 2010, **29**, 3392.
10. V. Khlebnikov, M. Heckenroth, H. Müller-Bunz, M. Albrecht, *Dalton Trans.*, 2013, **42**, 4197.
11. M. Bouche, G. Dahm, M. Wantz, S. Fournel, T. Achard, S. Bellemin-Laponnaz, *Dalton Trans.*, 2016, **45**, 11362.
12. V. N. Demidov, Yu. N. Kukushkin, L. N. Vedeneeva, A. N. Belyaev, *J. Gen. Chem. USSR*, 1988, **58**, 652.
13. N. R. Rightmire, T. P. Hanusa, *Dalton Trans.*, 2016, **45**, 2352.
14. J. L. Howard, Q. Cao, D. L. Browne, *Chem. Sci.*, 2018, **9**, 3080.
15. V. V. Boldyrev, *Russ. Chem. Bull.*, 2018, **67**, 933.
16. J. G. Hernández, T. Friščić, *Tetrahedron Lett.*, 2015, **56**, 4253.
17. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev*, 2012, **41**, 413.

18. M. Leonardi, M. Villacampa, J. C. Menéndez, *Chem. Sci.*, 2018, **9**, 2042.
19. N. Z. Lyakhov, T. F. Grigorieva, A. P. Barinova, I. A. Vorsina, *Russ. Chem. Rev.*, 2010, **79**, 189.
20. J. D. Egbert, A. M. Z. Slawin, S. P. Nolan, *Organometallics*, 2013, **32**, 2271.
21. C. J. Adams, M. Lusi, E. M. Mutambi, A. Guy Orpen, *Chem. Commun.*, 2015, **51**, 9632.
22. A. Beillard, E. Golliard, V. Gillet, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *Chem. Eur. J.*, 2015, **21**, 17614.
23. A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez, F. Lamaty, *Dalton Trans.*, 2016, **45**, 17859.
24. A. Beillard, X. Bantreil, T.-X. Metro, J. Martinez, F. Lamaty, *New J. Chem.*, 2017, **41**, 1057.
25. C. J. Adams, M. Lusi, E. M. Mutambi, A. G. Orpen, *Cryst. Growth Des.*, 2017, **17**, 3151.
26. A. Beillard, T.-X. Métro, X. Bantreil, J. Martinez, F. Lamaty, *Chem. Sci.*, 2017, **8**, 1086.
27. O. V. Khazipov, M. A. Shevchenko, A. Y. Chernenko, A. V. Astakhov, D. V. Pasyukov, D. B. Eremin, Y. V. Zubavichus, V. N. Khrustalev, V. M. Chernyshev, V. P. Ananikov, *Organometallics*, 2018, **37**, 1483.
28. J. A. Davies, C. M. Hockensmith, V. Y. Kukushkin, Y. N. Kukushkin, in *Synthetic Coordination Chemistry: Principles and Practice*, World Scientific, Singapore, 1996, p. 222.
29. C. Djerassi, C. R. Scholz, *J. Am. Chem. Soc.*, 1948, **70**, 417.
30. M. V. Raman, N. S. Ravichandran, *J. Indian Chem. Soc.*, 2005, **82**, 443.
31. E. Lee, J. Lee, D. V. Yandulov, *Eur. J. Inorg. Chem.*, 2017, **2017**, 2058.
32. A. K. Banerjee, M. S. Laya, W. J. Vera, *Russ. Chem. Rev.*, 2001, **70**, 971.
33. Y. A. Titova, O. V. Fedorova, G. L. Rusinov, V. N. Charushin, *Russ. Chem. Rev.*, 2015, **84**, 1294.
34. L. Andre, in *Modern Solvents in Organic Synthesis. Topics in Current Chemistry*, Ed. P. Knochel, Springer, Berlin, Heidelberg, 1999, vol. 206, p. 153.
35. V. A. Basiuk, *Russ. Chem. Rev.*, 1995, **64**, 1003.
36. Y. Han, H. V. Huynh, G. K. Tan, *Organometallics*, 2007, **26**, 4612.
37. A. V. Astakhov, O. V. Khazipov, E. S. Degtyareva, V. N. Khrustalev, V. M. Chernyshev, V. P. Ananikov, *Organometallics*, 2015, **34**, 5759.
38. A. V. Astakhov, O. V. Khazipov, A. Y. Chernenko, D. V. Pasyukov, A. S. Kashin, E. G. Gordeev, V. N. Khrustalev, V. M. Chernyshev, V. P. Ananikov, *Organometallics*, 2017, **36**, 1981.
39. M. Bouché, G. Dahm, A. Maisse-François, T. Achard, S. Bellemin-Laponnaz, *Eur. J. Inorg. Chem.*, 2016, **2016**, 2828.
40. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2008, **64**, 112.
41. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.

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