A study of the reactivity and transformations of Pd/NHC complexes in the reaction of oxidative C—H acetoxylation

V. V. Chesnokov, M. A. Shevchenko, and A. V. Astakhov★

M. I. Platov South-Russian State Polytechnic University,
132 ul. Prosveshcheniya, 346428 Novocherkassk, Russian Federation.
E-mail: astakhow@mail.ru

A comparative study of the reactivity and transformation and degradation pathways under conditions of the oxidative acetoxylation was carried out for various palladium complexes. The implementation was confirmed for the NHC-connected mechanism of catalysis. Effects of the process of pyridine coligand elimination on catalysis were investigated. It was found that free pyridine inhibits the catalysis of oxidative acetoxylation of 2-phenylpyridine. Mono- and diacetoxyphenylpyridines were obtained regioselectively in 84—94% yields using Pd/NHC complexes of various structures.

Key words: acetoxylation, palladium, catalysis, pyridine, NHC, CH-activation, Pd/NHC, C—O cross-coupling reaction.

Direct functionalization of C—H bonds involving auxiliary directing groups is widely employed in modern organic synthesis as a strategy for C—C and C—Heteroatom bond formation.[1,2] In particular, oxidative C—H acyloxylation is a relatively simple and economically affordable method for the transformation of C—H into C—O bond, does not require any pre-activation of reagents, and produces less byproducts than the traditional methods.

Acyloxylation of arenes containing a targeting azo group at the β-position in the side chain, including that in a cycle, has been most explored. In this reaction, a hydrogen atom at the *ortho*- position undergoes the substitution. Various catalysts based on compounds of transition metals (Pd,[3—9] Cu,[10—17] Ru,[18—22] Rh,[23—26] *etc*.) have been developed for the reaction of oxidative C—H acyloxylation, whereas palladium(II) acetate is the most widely used among them. The mechanism of this reaction has been already investigated in details.[27—29] Palladium complexes with *N*-heterocyclic carbene (NHC) ligands are of significant interest as the CH-activation catalysts due to their high thermal stability, low sensitivity to air and moisture, and wide range of possibilities for fine-tuning the stereoelectronic properties of catalyst.[2] However, there are only few reports on the catalysis of acyloxylation by Pd/NHC complexes.[30—37] It was assumed in the most of works that the catalysis proceeds *via* an NHC-connected mechanism, although the conclusions about the nature of active species were based on catalytic poisoning experiments (mercury test), which often lead to erroneous results.[38—40] The processes of transformation and degradation of Pd/NHC complexes were also not considered under the conditions of the oxidative C—H acetoxylation reaction. It should be noted that investigations of the transformations of M/NHC complexes under the conditions of catalytic reactions are of great importance for preventing the deactivation of catalytic systems.[38,41—48]

In the present work, we competitively evaluated the transformation and degradation pathways of various Pd/NHC complexes under conditions of the oxidative acetoxylation in order to either confirm or decline the NHC-connected mechanism.

Results and Discussion

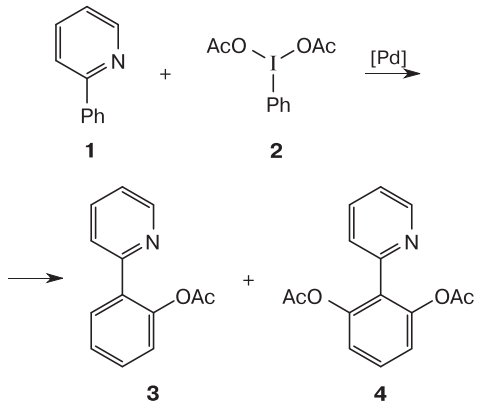
A Pd-catalyzed reaction of 2-phenylpyridine (**1**) with diacetoxyiodobenzene (**2**) was chosen as the model reaction (Scheme 1).

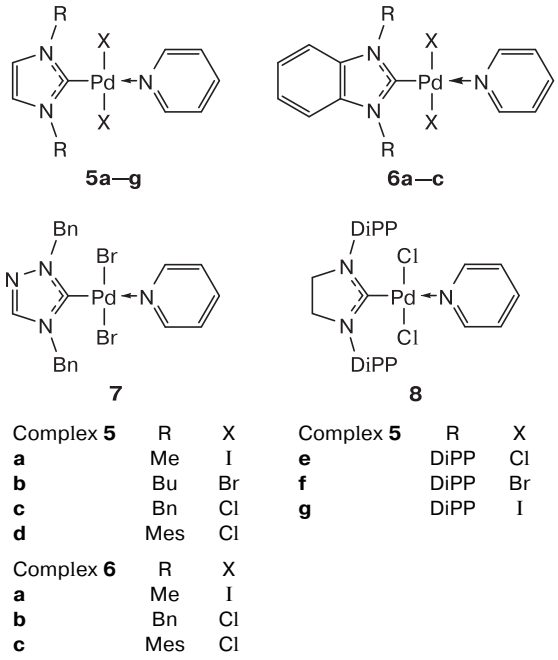
One of the most popular class of Pd/NHC complexes used in modern metal-complex catalysis[39,41,43,46,49—59] is Pd-PEPPSI (Pyridine Enhanced Precatalysts: Preparation, Stabilization and Initiation) containing a pyridine coligand. Herein, we selected Pd-PEPPSI complexes (**5—8**) of different steric bulkiness to estimate their catalytic activity.

It was found that the highest yield of monoacetoxylated product **3** was achieved in acetonitrile in the presence of acetic anhydride at 90 °C (Table 1, entry *12*).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1247—1256, June, 2022.

Scheme 1





Complex **5**	R	X
a	Me	I
b	Bu	Br
c	Bn	Cl
d	Mes	Cl
e	DiPP	Cl
f	DiPP	Br
g	DiPP	I

Complex **6**	R	X
a	Me	I
b	Bn	Cl
c	Mes	Cl

Mes is mesityl (2,4,6-trimethylphenyl), and DiPP is 2,6-di(isopropyl) phenyl.

The catalytic properties of compounds **5—8** were compared with those of commercially available $Pd(OAc)_2$ and $PdPy_2Cl_2$ catalysts (Table 2).

According to the data listed in Table 2, the structure of NHC ligand caused no any significant effect on the conversion and selectivity in the acetoxylation reaction at 90 °C, which is consistent with literature data.[34] Complex **5d** containing mesityl (Mes) as substituent R demonstrated the best result (see Table 2, entry *8*).[61]

Decreasing the temperature down to 70 °C resulted in a significant increase in the selectivity towards monosubstituted product **3** (in combination with a high degree of conversion) of low bulkiness complexes **5a,b** and **6a** compared to that of $Pd(OAc)_2$ or $PdPy_2Cl_2$ and sterically hindered systems (see Table 2). Complex **6a** exhibited the highest activity and selectivity at 70 °C (see Table 2, entry *15*).

Figure 1 shows the kinetic curves for the formation of compounds **3** and **4** upon the catalysis by the

Table 1. Optimization of parameters of the model reaction of oxidative acetoxylation[a]

Entry	Solvent	Additive (equiv.)	*T*/°C	*C*[b] (%)	*S*[c] **3** : **4**	Yield (%)	
						3	**4**
1	AcOH	—	90	53	11.8 : 1	47	4
2	MeCN	—	90	7	7 : 0	7	0
3	AcOH	Ac_2O (10)	90	77	2.9 : 1	56	19
4	MeCN	Ac_2O (10)	90	78	6.3 : 1	69	11
5	MeCN	$Na_2CO_3 \cdot H_2O_2$ (10)	90	0	—	0	0
6	MeCN	$AgNO_3$ (10)	90	0	—	0	0
7	MeCN	I_2O_5 (10)	90	0	—	0	0
8	MeCN	$K_2S_2O_8$ (10)	90	0	—	0	0
9	MeCN	Ac_2O (5)	90	83	6.3 : 1	69	11
10	MeCN	Ac_2O (1)	90	83	6.3 : 1	69	11
11	MeCN	Ac_2O (0.5)	90	81	8.5 : 1	68	8
12	MeCN	Ac_2O (0.1)	90	78	9.6 : 1	67	7
13[d]	MeCN	Ac_2O (0.1)	90	78	9.6 : 1	67	7
14	MeCN	Ac_2O (0.1)	70	78	23 : 0	23	0
15	MeCN	Ac_2O (0.1)	110	92	1.6 : 1	55	34

[a] Reaction conditions: 2-phenylpyridine (15.5 mg, 0.1 mmol), $PhI(OAc)_2$ (38.5 mg, 0.12 mmol), complex **5d** (2 mol.%), solvent (200 μL), Ac_2O, 70—110 °C, 20 h.
[b] Conversion of compound **1** according to GC-MS.
[c] Reaction selectivity as the relative content of compounds **3** and **4**.
[d] The reaction was carried out under inert atmosphere.

Table 2. Catalytic activity of palladium compounds in the model reaction of acetoxylation[a]

Entry	Catalyst	*T*/°C	C[b] (%)	*S*[c] **3** : **4**	Yield (%)	
					3	**4**
1	Without catalyst	90	0	0	0	0
2	**5a**	90	82	5 : 1	65	13
3	**5a**	70	78	76 : 1	76	1
4	**5b**	90	71	3.6 : 1	54	15
5	**5b**	70	70	69 : 1	69	1
6	**5c**	90	81	3.1 : 1	59	19
7	**5c**	70	37	37 : 0	37	0
8	**5d**	90	78	9.6 : 1	67	7
9	**5d**	70	23	23 : 0	23	0
10	**5e**	90	84	6.3 : 1	69	11
11	**5e**	70	25	25 : 0	25	0
12	**5f**	90	91	3.9 : 1	70	18
13	**5g**	90	79	6.5 : 1	65	10
14	**6a**	90	80	7.4 : 1	67	9
15	**6a**	70	85	84 : 1	84	1
16	**6b**	90	90	3.5 : 1	67	19
17	**6c**	90	84	3.1 : 1	61	20
18	**7**	90	38	18 : 1	36	2
19	**8**	90	88	3.9 : 1	67	17
20	$Pd(OAc)_2$	90	85	3 : 1	63	21
21	$Pd(OAc)_2$	70	78	12 : 1	71	6
22	$PdPy_2Cl_2$	90	82	6.3 : 1	69	11
23	$PdPy_2Cl_2$	70	93	3.7 : 1	73	20

[a] Reaction conditions: 2-phenylpyridine (15.5 mg, 0.1 mmol), $PhI(OAc)_2$ (38.5 mg, 0.12 mmol), catalyst (2 mol.%), acetonitrile (200 μL), Ac_2O (10 μL), 70 or 90 °C, 20 h.
[b] Conversion of compound **1** according to GC-MS.
[c] Reaction selectivity as the relative content of compounds **3** and **4**.

Pd/NHC complexes and palladium salts. Attention is drawn to the different shapes of kinetic curves, *viz.* the presence of an induction period prolonged upon an increase in the steric bulkiness of ligand. In the case of minimally sterically hindered complex **5a**, there was no any induction period observed.

Table 3. Comparison of the catalytic activity of some pretreated complexes and complexes **9**,**10** in the model reaction of acetoxylation[a]

Entry	Catalyst	X[b]	*T*/°C	C[c] (%)	S[d] **3** : **4**	Yield (%)	
						3	**4**
1	**5c**[e]	1.2	90	83	2.2 : 1	57	26
2	**5d**[e]	1.2	90	79	7.8 : 1	70	9
3	**6a**[e]	1.2	70	90	4.9 : 1	72	15
4	**9**	1.2	70	85	7.5 : 1	75	10
5	**10**	1.2	70	98	2.5 : 1	70	28
6	**10**	2.4	70	99	1 : 5.3	14	74
7	**10**	2.4	90	99	1 : 18.8	5	94

[a] Reaction conditions: 2-phenylpyridine (15.5 mg, 0.1 mmol), $PhI(OAc)_2$ (38.5 mg, 0.12 mmol), catalyst (2 mol.%), acetonitrile (200 μL), Ac_2O (10 μL), 70 or 90 °C, 20 h. The yields were estimated using GC-MS.
[b] Excess of $PhI(OAc)_2$ towards 2-phenylpyridine.
[c] Conversion of compound **1** according to GC-MS.
[d] Reaction selectivity as the relative content of compounds **3** and **4**.
[e] The catalyst was preliminary heated in $AcOH/Ac_2O$ mixture (10 : 1) for 20 h at 100 °C.

Taking into account the observed correlation between the duration of induction period and the steric bulkiness of compounds **5**, we assumed that the catalytic system is activated due to the gradual release of NHC-disconnected forms of palladium. The release process is hindered by the presence of bulky substituents in the NHC-complex molecule. To verify this assumption, we compared the catalytic activity of complexes **5c,d** and **6a** preliminarily heated in the presence of oxidant **2** in an $AcOH/Ac_2O$ mixture (Table 3, entries *1*—*3*),

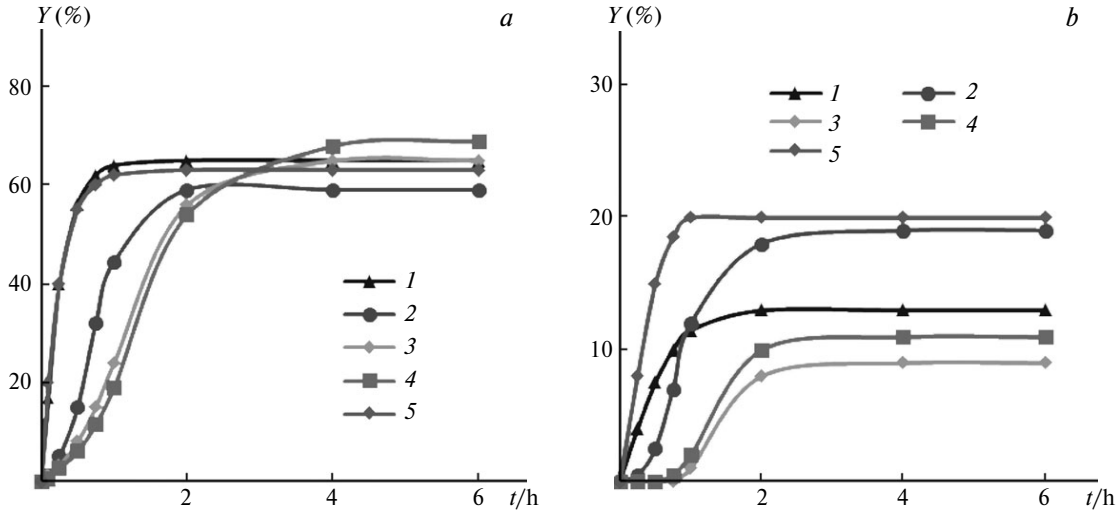
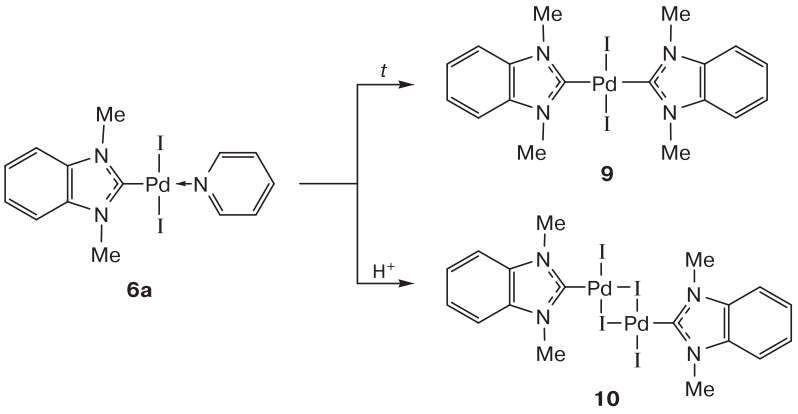


Fig. 1. Kinetic curves for the formation of products **3** (*a*) and **4** (*b*) upon catalysis by various palladium compounds: **5a** (*1*), **5c** (*2*), **5d** (*3*), **5e** (*4*), and $Pd(OAc)_2$ (*5*).

Scheme 2



as well as dicarbene **9** and bridging **10** complexes (Scheme 2). Complexes **9** and **10** were prepared from complex **6a**. The presence of complexes **9** and **10** in the catalytic "cocktail" formed during the decomposition of Pd-PEPPSI is known.[32,51,60]

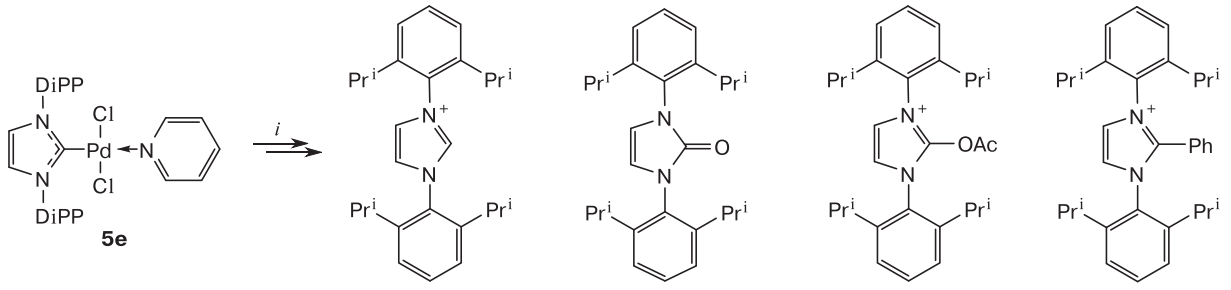
According to the acquired data, the values of conversion and selectivity for the pretreated catalyst **6a** (see Table 3) are intermediate between the corresponding values for the untreated complex **6a** (see Table 2), its transformation products **9** and **10**, and NHC-disconnected $Pd(OAc)_2$ and $PdPy_2Cl_2$ (see Table 2), that may indicate only partial dissociation of the Pd—NHC bond during the reaction. Similar experiments with pretreated complexes **5c** and **5d** (see Table 3) resulted in an even smaller degree of deviation from the standard experiments (see Table 2).

In addition, bridging complex **10** demonstrated a significantly higher overall activity in the reaction as compared to both $Pd(OAc)_2$ or $PdPy_2Cl_2$ and Pd-PEPPSI complexes **5—8**. This allowed obtaining product **4** in the presence of a double excess of reagent **2** in 94% yield (see Table 3) and moreover, with a lower catalyst load (1 mol.%) and under milder conditions. It should be highlighted that the achieved yield of compound **4** exceeds that reported previously[27] (83%) upon using 6 mol.% of $Pd(OAc)_2$ at 100 °C.

The transformation of catalyst under the reaction conditions was monitored by NMR spectroscopy and high resolution mass spectrometry (HRMS) of the reaction mixtures obtained in additional experiments on the oxidation of complexes **5—8** with an excess of compound **2**. These experiments revealed the following trends.

Thus, it was shown that the major products of oxidation (in model experiments) and decomposition of complexes **5—8** during the acetoxylation reaction coincide. They are azolium salts (NHC proligands), azolones, and 2-acetoxyimidazolium salts, including also C—NHC coupling products (Scheme 3). In the cases of *N*-methyl derivatives **5a** and **6a**, the addition of oxidant **2** resulted in an immediate downfield shift of signals of the methyl groups of NHC ligand, observed

Scheme 3



$[M]^+$ $C_{27}H_{37}N_2^+$ m/z = 389.29

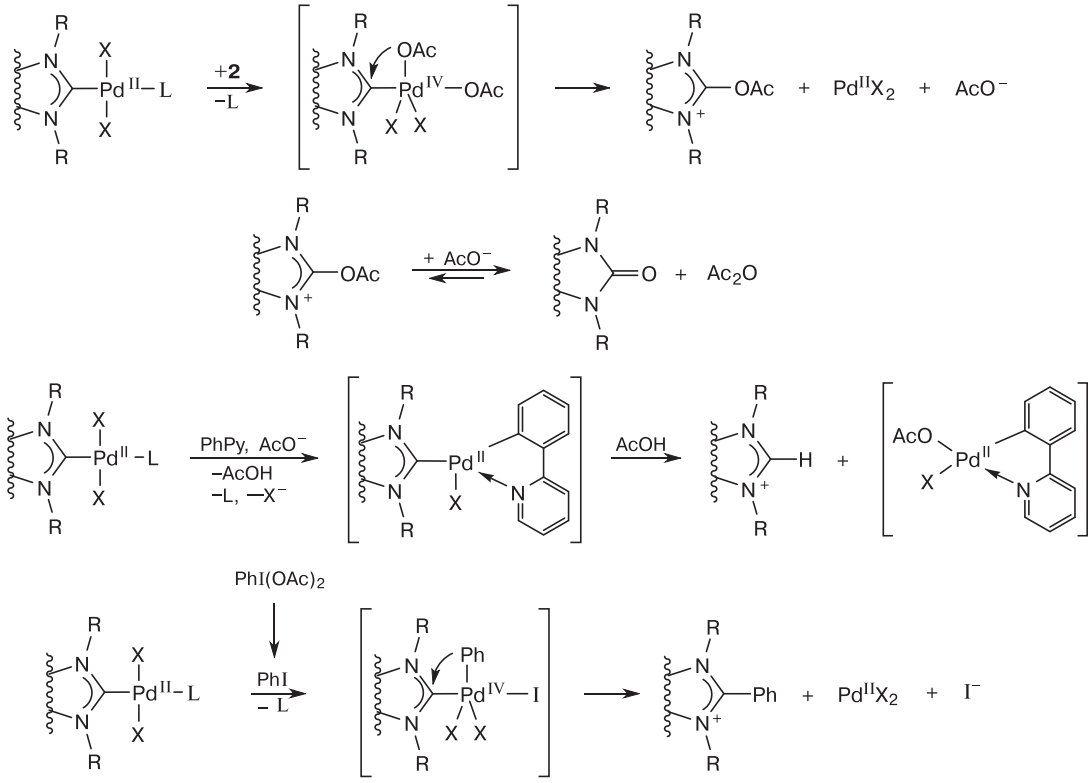
$[M+H]^+$ $C_{27}H_{37}N_2O^+$ m/z = 405.29

$[M]^+$ $C_{29}H_{39}N_2O_2^+$ m/z = 447.30

$[M]^+$ $C_{33}H_{41}N_2^+$ m/z = 465.32

Reagents and conditions: *i.* either $PhI(OAc)_2$, 2-phenylpyridine, Ac_2O, MeCN, 90 °C or $PhI(OAc)_2$, Ac_2O, MeCN, 90 °C.

Scheme 4



already at 20 °C. In contrast, complexes **5b—g**, **6b,c**, **7**, and **8** were fairly stable, so the integrated intensity of NMR signals of NHC ligands decreased only slightly (3—10%) during the entire reaction (2—4 h according to the kinetic curves; see Fig. 1).

Even though signals of azolium salts were being detected in the NMR and HRMS spectra for several hours during the oxidation of complexes **5—8**, these salts completely degraded by themselves upon their oxidation under similar conditions within the same period of time. This proves that the NHC-connected forms of palladium are persisting and slowly generating proligands until the complete consumption of oxidant **2**. Upon further heating, complexes **5—8** degraded *via* the reductive pathway, while gradual formation of palladium black was observed.[61]

These results acquired by NMR spectroscopy and mass spectrometry indicate that the NHC-connected catalytic mechanism is predominant in the acetoxylation reaction under the considered conditions, whereas the decomposition of complexes proceeds mainly *via* the reductive elimination of NHC ligands from Pd^{IV} complexes (Scheme 4).

However, the data discussed above do not explain the nature of induction period observed on the kinetic curves for the formation of reaction products **3** and **4** (see Fig. 1). Over the entire reaction duration, the most of complexes degraded insignificantly (3—10%), while the conversion value was comparable to that of $Pd(OAc)_2$. Therefore, the most probable process being responsible for the presence of induction period and determining its duration is the dissociation of not the C_{carb}—Pd bond, but the C—N one, *i.e.*, the cleavage of pyridine coligand. The facts considered hereinafter can confirm this hypothesis.

Thus, there is an equilibrium between the dissociated and non-dissociated forms of complexes **5—8**, since ^{1}H NMR spectra of the Pd-PEPPSI complexes, both in $CDCl_3$ and DMSO-d_6, do not contain signals of free pyridine,[41] while such signals were observed in deuterated acetonitrile (a doublet at δ 8.59).[62]

Moreover, the lability of pyridine ligand was confirmed by the presence of a cross peak between the α-protons of free and bound pyridine, detected using the nuclear Overhauser effect spectroscopy in a rotating coordinate system (ROESY).[63] Nowadays, this method is fruitfully used to investigate exchange processes (Fig. 2, Scheme 5).

In the interaction of palladium complexes **5—8** with an excess of **2**, the ^{1}H NMR spectra show a decrease

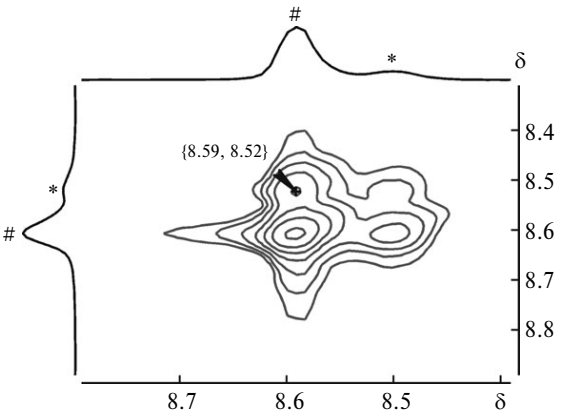
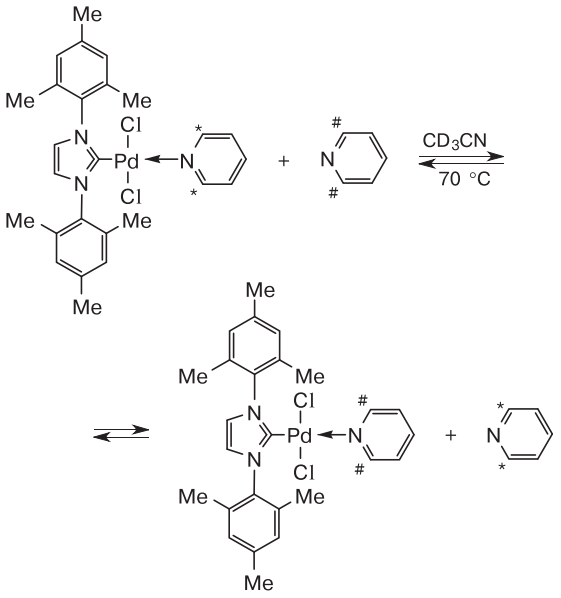


Fig. 2. ROESY NMR spectrum demonstrating the exchange between free (δ 8.59)[62] and bound (δ 8.52) pyridine for compound **5d** in CD_3CN at 70 °C.

Scheme 5



of integral intensities of the signals of bound pyridine relative to those of the signals of NHC ligands, which further decreases upon the addition of Ac_2O (Fig. 3, Table 4).

The elimination of pyridine coligand was confirmed by additional experiments on the introduction of pyridine additives into the reaction mass, which allowed revealing its inhibitory effect. It was found that the conversion depends linearly on the amount of added pyridine: 20 mol.% of pyridine reduces the conversion by almost half, while the same amount of 2,6-lutidine completely suppresses the catalysis.[61]

The low activity of complexes **5c—g**, **6b**,**c**, **7**, and **8** without the addition of Ac_2O can be explained by

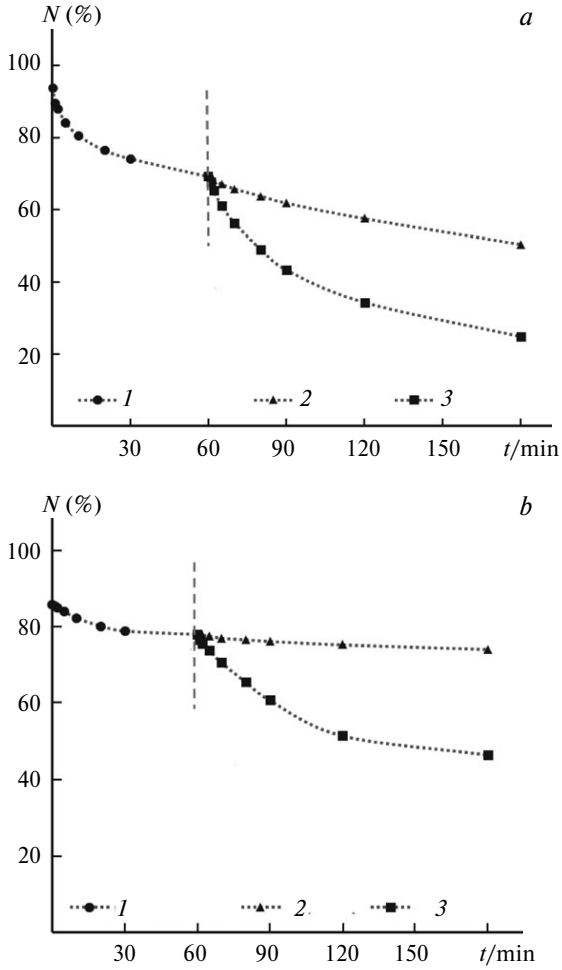


Fig. 3. Dependence of amount of the bound pyridine (*N*) in the reaction of complexes **5c** (*a*) and **5d** (*b*) with oxidant **2** on the time of heating without (*1*) and with either AcOH (*2*) or Ac_2O (*3*) added. The vertical line marks the time of introduction of additives.

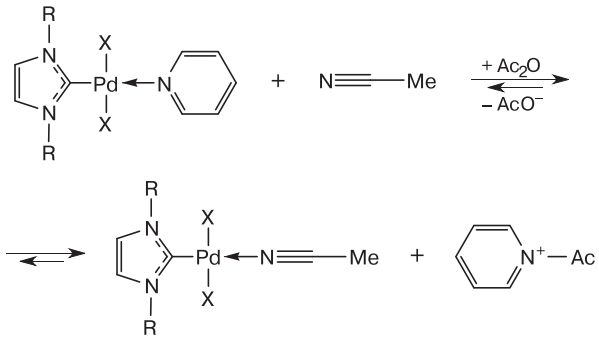
a combination of two factors: the steric bulkiness and inhibitory effect of pyridine. Apparently, Ac_2O stabilizes oxidant **2** and shifting the equilibrium towards the catalytically active form of Pd/NHC catalyst *via* the pyridine acylation (Scheme 6). An exception is the

Table 4. Effect of additives on the yield of product **3** in the reaction carried out in the presence of complexes **5c,d** within 20 h in CD_3CN at 80 °C

Entry	Additive (equiv.)	Yield of **3** (%)	
		5c	**5d**
1	Without additive	15	7
2	AcOH (10)	24	9
3	Ac_2O (10)	59	67

reaction carried out in an acetic acid medium (see Table 1, entry *1*). Apparently, acetic acid as the very polar solvent also facilitates the dissociation of the Pd—N bond.

Scheme 6



At the same time, sterically unhindered complexes **5a** and **6a** undergo their oxidation without a preliminary dissociation of the pyridine ligand. This was demonstrated by the corresponding changes in the NMR signals of the NHC ligand and bound pyridine, and therefore, there was no any induction period observed in the cases of catalysis by compounds **5a** and **6a**.

In summary, we have demonstrated a significant effect of the structure of Pd/NHC complex on the both catalytic activity and selectivity in the acetoxylation reaction. The higher activity of Pd/NHC complexes in comparison with palladium salts upon decreasing the reaction temperature, the high selectivity towards the disubstitution product (**4**) in the case of using dimeric complexes, and other observations allowed us to draw conclusion about a significant contribution of the NHC-connected mechanism to the catalysis in the considered reaction. On the other hand, the observed irreversible decomposition of the Pd complex does not lead to a complete deactivation of the catalytic system, but reduces the rate and selectivity of the process. Therefore, one can postulate that the acetoxylation reaction is catalyzed simultaneously by both molecular Pd/NHC complexes and "NHC-free" forms of palladium.

The regioselective syntheses of (2-acetoxyphenyl)-pyridine (**3**) and (2,6-diacetoxyphenyl)pyridine (**4**) catalyzed by Pd-PEPPSI (**6a**) and bridging (**10**) complexes based on 1,3-dimethylbenzimidazole were carried out in the yields of 84 and 94%, respectively.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 spectrometer (at the frequencies of 300 and 75 MHz, respectively) using residual signals of the deuterated solvent as the internal standards. High resolution mass spectra (HRMS) were recorded on a Bruker maXis Q-TOF spectrometer using electrospray ionization (ESI). Elemental analysis was performed using a Perkin Elmer 2400 analyzer (Germany). Gas chromatography—mass spectrometry (GC-MS) was carried out 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 reaction products were identified comparing their mass spectra with those of the reference samples and with spectra published in the NIST database. Diacetoxyiodobenzene **2**,[64] NHC salts (proligands),[53,65—74] their corresponding complexes **5a—g**, **6a—c**, **7**, and **8**,[51—53,68,75—80] as well as the necessary reference samples of cross-coupling products **3** and **4**[27] were obtained according to the known methods. The other reagents are commercially available.

Procedure for carrying out the acetoxylation reaction. 2-Phenylpyridine **1** (15.5 mg, 0.1 mmol), diacetoxyiodobenzene **2** (38.5 mg, 0.12 mmol), a 0.02 *M* solution (100 μL, 2 mol.%) of the Pd catalyst in MeCN, MeCN (100 μL), and Ac_2O (10 μL) were loaded into a screw-capped vial (V = 1.5 mL). The cap was closed, and the vial was heated and kept for 20 h at 90 °C. After cooling down, the products were analyzed by GC-MS.

Procedure for the acetoxylation reaction involving pretreated catalysts 5c,d and 6a. A 0.02 *M* solution (100 μL, 2 mol.%) of the corresponding palladium complex (**5c**, **6a**, or **5d**) in AcOH and Ac_2O (10 μL) were loaded into a screw-capped vial (V = 1.5 mL). The cap was tightly closed, and the vial was heated and kept for 20 h at 100 °C. After cooling down, AcOH and Ac_2O were evaporated *in vacuo*. 2-Phenylpyridine **1** (15.5 mg, 0.1 mmol), diacetoxyiodobenzene **2** (38 mg, 0.12 mmol), MeCN (200 μL), and Ac_2O (10 μL) were added to the residue. The tightly closed vial was heated and kept for 20 h at 90 °C. After cooling down, the products were analyzed by GC-MS.

Synthesis of compound 4 using catalyst 10. 2-Phenylpyridine **1** (62 mg, 0.4 mmol), diacetoxyiodobenzene **2** (154 mg, 0.48 mmol), catalyst **10** (4 mg, 1 mol.%), MeCN (800 μL), and Ac_2O (40 μL) were loaded into a screw-capped vial (V = 1.5 mL). The cap was tightly closed; the vial was heated, kept for 20 h at 90 °C and then cooled down, and the solvent as evaporated *in vacuo*. Product **4** was isolated using column chromatography on silica gel (the eluent was hexane—ethyl acetate = 8 : 5) as light yellow crystalline powder in the yield of 102 mg (94%). Found (%): C, 66.43; H, 4.85; N, 5.20. $C_{15}H_{13}NO_4$. Calculated (%): C, 66.41; H, 4.83; N, 5.16. ^{1}H NMR ($CDCl_3$), δ: 2.02 (s, 6 H, CH_3); 7.10 (d, 1 H, Ar, J = 8.2 Hz); 7.44 (dd, 1 H, Ar, J = 8.5 Hz, J = 7.9 Hz); 7.72 (td, 1 H, Ar, J = 7.7 Hz, J = 1.8 Hz); 8.69 (m, 1 H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 20.77, 120.84, 122.67, 125.27, 127.68, 129.54, 136.13, 149.26, 149.62, 152.46, 169.10.

Procedure for the oxidation of palladium complexes 5—8 and their corresponding NHC salts. Either complex **5—8** (0.01 mmol) or the corresponding NHC salt (0.01 mmol), diacetoxyiodobenzene **2** (38.5 mg, 0.12 mmol), MeCN (200 μL), and Ac_2O (10 μL) mixed in a screw-capped vial

(V = 1.5 mL). The cap was tightly closed, and the vial was heated, kept for 20 h at 90 °C, and then cooled down. Samples of the reaction mixture were analyzed by GC-MS.

Procedure for the ROESY experiment. An NMR ampoule was loaded with the corresponding complex **5—8** (0.01 mmol), pyridine (1 μL, 0.0125 mmol), and CD_3CN (600 μL). The ROESY NMR spectra were recorded at 343 K.

Procedure for the NMR experiments with either AcOH or Ac_2O added. An NMR ampoule was loaded with complex **5—8** (0.04 mmol), diacetoxyiodobenzene **2** (38.5 mg, 0.12 mmol), and CD_3CN (600 μL). The tightly closed ampoule was kept at 78 °C for 1 h, and within this period, it was periodically cooled to record NMR spectra of the resulting mixture at 273 K (recordings at 0, 1, 2, 5, 10, 20, 30, and 60 min). After 1 h, either AcOH (11 μL, 0.2 mmol) or Ac_2O (19 μL, 0.2 mmol) was added into the ampoule. The closed ampoule was kept at 78°C for 2 h, and within this period, it was periodically cooled to record NMR spectra of the resulting mixture at 273 K (recordings at 0, 1, 2, 5, 10, 20, 30, 60, and 120 min).

Procedure for the acetoxylation reaction with pyridine additions. 2-Phenylpyridine (15.5 mg, 0.1 mmol), diacetoxyiodobenzene **2** (38.5 mg, 0.12 mmol), a 0.02 M solution (100 μL, 2 mol.%) of catalyst **5—8** in MeCN, Ac_2O (10 μL), and the corresponding pyridine additive were loaded into a screw-capped vial (V = 1.5 mL). The cap was tightly closed, and the vial was heated, kept for 20 h at 90 °C, and cooling down. The products were analyzed by GC-MS.

The following mixtures were used as the said pyridine additives: 1) a 0.2 M solution (25 μL, 5 mol.%) of pyridine in MeCN and MeCN (75 μL); 2) a 0.2 M solution (50 μL, 10 mol.%) of pyridine in MeCN and MeCN (50 μL); 3) a 0.2 M solution (75 μL, 15 mol.%) of pyridine in MeCN and MeCN (25 μl); 4) a 0.2 M solution (100 μL, 20 mol.%) of pyridine in MeCN; 5) a 0.2 M solution (100 μL, 20 mol.%) of 2,6-lutidine in MeCN.

The authors are grateful to Prof. V. M. Chernyshev and the Academician of the Russian Academy of Sciences V. P. Ananikov for a fruitful discussion of the results reported herein and valuable comments, as well as to the Shared Research Center "Nanotechnologies" at the M. I. Platov South-Russian State Polytechnic University and the Shared Research Center at the N. D. Zelinskiy Institute of Organic Chemistry of the Russian Academy of Sciences for conducting analytical experiments.

This work was financially supported by the Russian Science Foundation (Project No. 19-73-10100).

No human or animal subjects were used in this research.

The authors declare no competing interests.

References

1. S. Moghimi, M. Mahdavi, A. Shafiee, A. Foroumadi, *Eur. J. Org. Chem.*, 2016, **2016**, 3282; DOI: 10.1002/ejoc.201600138.
2. Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.*, 2020, **120**, 1981; DOI: 10.1021/acs.chemrev.9b00634.
3. D.-D. Li, Y.-X. Cao, G.-W. Wang, *Org. Biomol. Chem.*, 2015, **13**, 6958; DOI: 10.1039/C5OB00691K.
4. D. Sarkar, A. V. Gulevich, F. S. Melkonyan, V. Gevorgyan, *ACS Catal.*, 2015, **5**, 6792; DOI: 10.1021/acscatal.5b01724.
5. B. Wang, C. Lin, Y. Liu, Z. Fan, Z. Liu, Y. Zhang, *Org. Chem. Front.*, 2015, **2**, 973; DOI: 10.1039/C5QO00144G.
6. Q. Zhang, Y. Wang, T. Yang, L. Li, D. Li, *Tetrahedron Lett.*, 2015, **56**, 6136; DOI: 10.1016/j.tetlet.2015.09.097.
7. J. Ding, Y. Guo, L.-Y. Shao, F.-Y. Zhao, D.-H. Liao, H.-W. Liu, Y.-F. Ji, *Chin. Chem. Lett.*, 2016, **27**, 1617; DOI: 10.1016/j.cclet.2016.04.007.
8. A. Maji, B. Bhaskararao, S. Singha, R. B. Sunoj, D. Maiti, *Chem. Sci.*, 2016, **7**, 3147; DOI: 10.1039/C5SC04060D.
9. H. Vu, F. W. Chen, X.-Q. Li, *ChemistrySelect*, 2019, **4**, 9465; DOI: 10.1002/slct.201902611.
10. A. L. García-Cabeza, R. Marín-Barrios, F. J. Moreno-Dorado, M. J. Ortega, H. Vidal, J. M. Gatica, G. M. Massanet, F. M. Guerra, *J. Org. Chem.*, 2015, **80**, 6814; DOI: 10.1021/acs.joc.5b01043.
11. N. Khatun, A. Banerjee, S. K. Santra, W. Ali, B. K. Patel, *RSC Adv.*, 2015, **5**, 36461; DOI: 10.1039/C5RA03462K.
12. S. Zhao, F.-J. Chen, B. Liu, B.-F. Shi, *Sci. China: Chem.*, 2015, **58**, 1302; DOI: 10.1007/s11426-015-5376-z.
13. F. Wang, Q. Hu, C. Shu, Z. Lin, D. Min, T. Shi, W. Zhang, *Org. Lett.*, 2017, **19**, 3636; DOI: 10.1021/acs.orglett.7b01559.
14. J. Li, Z. Yang, T. Yang, J. Yi, C. Zhou, *New J. Chem.*, 2018, **42**, 1581; DOI: 10.1039/C7NJ03989A.
15. F. Wang, Z. Lin, W. Yu, Q. Hu, C. Shu, W. Zhang, *RSC Adv.*, 2018, **8**, 16378; DOI: 10.1039/C8RA01974F.
16. V. Botla, A. Akudari, C. Malapaka, *Tetrahedron Lett.*, 2019, **60**, 115; DOI: 10.1016/j.tetlet.2018.11.071.
17. G.-J. Li, Y.-L. Pan, Y.-L. Liu, H.-F. Xu, J.-Z. Chen, *Org. Lett.*, 2019, **21**, 1740; DOI: 10.1021/acs.orglett.9b00306.
18. K. Padala, M. Jeganmohan, *Chem. Commun.*, 2013, **49**, 9651; DOI: 10.1039/C3CC45350B.
19. K. Padala, M. Jeganmohan, *Chem.—Eur. J.*, 2014, **20**, 4092; DOI: 10.1002/chem.201304646.
20. K. Raghuvanshi, K. Rauch, L. Ackermann, *Chem.—Eur. J.*, 2015, **21**, 1790; DOI: 10.1002/chem.201405071.
21. T. Okada, K. Nobushige, T. Satoh, M. Miura, *Org. Lett.*, 2016, **18**, 1150; DOI: 10.1021/acs.orglett.6b00268.
22. C.-a. Wang, N. Chatani, *Org. Chem. Front.*, 2020, **7**, 2955; DOI: 10.1039/D0QO00920B.
23. Z. Ye, W. Wang, F. Luo, S. Zhang, J. Cheng, *Org. Lett.*, 2009, **11**, 3974; DOI: 10.1021/ol901609t.
24. K. Kim, J. Hyun, J. Kim, H. Kim, *Asian J. Org. Chem.*, 2017, **6**, 907; DOI: 10.1002/ajoc.201700196.
25. C. Chen, Y. Pan, H. Zhao, X. Xu, J. Xu, Z. Zhang, S. Xi, L. Xu, H. Li, *Org. Chem. Front.*, 2018, **5**, 415; DOI: 10.1039/C7QO00844A.
26. C. Jin, G. Wang, X. Yang, W. Zhu, Y. Yang, *Tetrahedron Lett.*, 2018, **59**, 2042; DOI: 10.1016/j.tetlet.2018.04.034.
27. A. R. Dick, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.*, 2004, **126**, 2300; DOI: 10.1021/ja031543m.
28. D. C. Powers, M. A. L. Geibel, J. E. M. N. Klein, T. Ritter, *J. Am. Chem. Soc.*, 2009, **131**, 17050; DOI: 10.1021/ja906935c.

29. J. M. Racowski, A. R. Dick, M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 10974; DOI: 10.1021/ja9014474.
30. X.-F. Hou, Y.-N. Wang, I. Göttker-Schnetmann, *Organometallics*, 2011, **30**, 6053; DOI: 10.1021/om200484g.
31. A. Flores-Gaspar, Á. Gutiérrez-Bonet, R. Martin, *Org. Lett.*, 2012, **14**, 5234; DOI: 10.1021/ol3023819.
32. F. Tato, A. García-Domínguez, D. J. Cárdenas, *Organometallics*, 2013, **32**, 7487; DOI: 10.1021/om400981x.
33. S. P. Desai, M. Mondal, J. Choudhury, *Organometallics*, 2015, **34**, 2731; DOI: 10.1021/om501163m.
34. E. Bolbat, O. F. Wendt, *Eur. J. Org. Chem.*, 2016, **2016**, 3395; DOI: 10.1002/ejoc.201600322.
35. M. H. Majeed, P. Shayesteh, L. R. Wallenberg, A. R. Persson, N. Johansson, L. Ye, J. Schnadt, O. F. Wendt, *Chem.—Eur. J.*, 2017, **23**, 8457; DOI: 10.1002/chem.201700777.
36. M. H. Majeed, P. Shayesteh, A. R. Persson, L. R. Wallenberg, J. Schnadt, O. F. Wendt, *Eur. J. Inorg. Chem.*, 2018, **2018**, 4742; DOI: 10.1002/ejic.201800978.
37. N. Yuan, M. H. Majeed, É. G. Bajnóczi, A. R. Persson, L. R. Wallenberg, A. K. Inge, N. Heidenreich, N. Stock, X. Zou, O. F. Wendt, I. Persson, *Catal. Sci. Technol.*, 2019, **9**, 2025; DOI: 10.1039/C8CY02430H.
38. V. M. Chernyshev, A. V. Astakhov, I. E. Chikunov, R. V. Tyurin, D. B. Eremin, G. S. Ranny, V. N. Khrustalev, V. P. Ananikov, *ACS Catal.*, 2019, **9**, 2984; DOI: 10.1021/acscatal.8b03683.
39. K. E. Shepelenko, S. B. Soliev, A. S. Galushko, V. M. Chernyshev, V. P. Ananikov, *Inorg. Chem. Front.*, 2021, **8**, 1511; DOI: 10.1039/D0QI01411G.
40. O. N. Gorunova, I. M. Novitskiy, Y. K. Grishin, I. P. Gloriozov, V. A. Roznyatovsky, V. N. Khrustalev, K. A. Kochetkov, V. V. Dunina, *Organometallics*, 2018, **37**, 2842; DOI: 10.1021/acs.organomet.8b00363.
41. 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; DOI: 10.1021/acs.organomet.8b00124.
42. A. V. Astakhov, S. B. Soliev, E. G. Gordeev, V. M. Chernyshev, V. P. Ananikov, *Dalton Trans.*, 2019, **48**, 17052; DOI: 10.1039/C9DT03266E.
43. O. V. Khazipov, M. A. Shevchenko, D. V. Pasyukov, A. Y. Chernenko, A. V. Astakhov, V. A. Tafeenko, V. M. Chernyshev, V. P. Ananikov, *Catal. Sci. Technol.*, 2020, **10**, 1228; DOI: 10.1039/C9CY02041A.
44. V. M. Chernyshev, E. A. Denisova, D. B. Eremin, V. P. Ananikov, *Chem. Sci.*, 2020, **11**, 6957; DOI: 10.1039/D0SC02629H.
45. S. B. Soliev, A. V. Astakhov, D. V. Pasyukov, V. M. Chernyshev, *Russ. Chem. Bull.*, 2020, **69**, 683; DOI: 10.1007/s11172-020-2818-3.
46. A. Y. Chernenko, A. V. Astakhov, V. V. Kutyrev, E. G. Gordeev, J. V. Burykina, M. E. Minyaev, V. N. Khrustalev, V. M. Chernyshev, V. P. Ananikov, *Inorg. Chem. Front.*, 2021, **8**, 3382; DOI: 10.1039/d1qi00453k.
47. A. V. Astakhov, S. B. Soliev, V. M. Chernyshev, *Russ. Chem. Bull.*, 2020, **69**, 2073; DOI: 10.1007/s11172-020-3002-5.
48. I. E. Chikunov, G. S. Ranny, A. V. Astakhov, V. A. Tafeenko, V. M. Chernyshev, *Russ. Chem. Bull.*, 2018, **67**, 2003; DOI: 10.1007/s11172-018-2321-2.
49. A. Y. Chernenko, A. V. Astakhov, D. V. Pasyukov, P. V. Dorovatovskii, Y. V. Zubavichus, V. N. Khrustalev, V. M. Chernyshev, *Russ. Chem. Bull.*, 2018, **67**, 79; DOI: 10.1007/s11172-018-2040-8.
50. V. A. Glushkov, D. N. Babentzev, M. V. Dmitriev, I. A. Borisova, M. S. Denisov, *Russ. Chem. Bull.*, 2021, **70**, 122; DOI: 10.1007/s11172-021-3065-y.
51. A. Y. Chernenko, D. V. Pasyukov, A. V. Astakhov, V. A. Tafeenko, V. M. Chernyshev, *Russ. Chem. Bull.*, 2018, **67**, 1196; DOI: 10.1007/s11172-018-2201-9.
52. 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; DOI: 10.1039/C8SC01353E.
53. 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; DOI: 10.1021/acs.organomet.7b00184.
54. M. S. Denisov, M. V. Dmitriev, A. A. Gorbunov, V. A. Glushkov, *Russ. Chem. Bull.*, 2019, **68**, 2039; DOI: 10.1007/s11172-019-2664-3.
55. M. A. Shevchenko, Y. N. Tkachenko, A. V. Astakhov, O. V. Khazipov, R. V. Tyurin, D. V. Pasyukov, V. A. Tafeenko, O. A. Kravchenko, V. M. Chernyshev, *Russ. Chem. Bull.*, 2018, **67**, 1684; DOI: 10.1007/s11172-018-2277-2.
56. C. Chen, F.-S. Liu, M. Szostak, *Chem.—Eur. J.*, 2021, **27**, 4478; DOI: 10.1002/chem.202003923.
57. P. P. Nair, A. Jayaraj, C. A. Swamy, *ChemistrySelect*, 2022, **7**, e202103517; DOI: 10.1002/slct.202103517.
58. S. M. P. Vanden Broeck, F. Nahra, C. S. J. Cazin, *Inorganics*, 2019, **7**, 78; DOI: 10.3390/inorganics7060078.
59. D. V. Pasyukov, A. Yu. Chernenko, I. V. Lavrentev, V. A. Baidikova, M. E. Minyaev, O. A. Starovoitova, V. M. Chernyshev, *Russ. Chem. Bull.*, 2022, **71**, 993; DOI: 10.1007/s11172-022-3501-7.
60. V. M. Chernyshev, O. V. Khazipov, D. B. Eremin, E. A. Denisova, V. P. Ananikov, *Coord. Chem. Rev.*, 2021, **437**, 213860; DOI: 10.1016/j.ccr.2021.213860.
61. M. H. Emmert, A. K. Cook, Y. J. Xie, M. S. Sanford, *Angew. Chem., Int. Ed.*, 2011, **50**, 9409; DOI: 10.1002/anie.201103327.
62. N. R. Babij, E. O. McCusker, G. T. Whiteker, B. Canturk, N. Choy, L. C. Creemer, C. V. D. Amicis, N. M. Hewlett, P. L. Johnson, J. A. Knobelsdorf, F. Li, B. A. Lorsbach, B. M. Nugent, S. J. Ryan, M. R. Smith, Q. Yang, *Org. Process Res. Dev.*, 2016, **20**, 661; DOI: 10.1021/acs.oprd.5b00417.
63. A. K. Cook, M. S. Sanford, *J. Am. Chem. Soc.*, 2015, **137**, 3109; DOI: 10.1021/jacs.5b00238.
64. M. S. Yusubov, G. A. Zholobova, I. L. Filimonova, K.-W. Chi, *Russ. Chem. Bull.*, 2004, **53**, 1735; DOI: 10.1007/s11172-005-0027-8.
65. S. Gardner, T. Kawamoto, D. P. Curran, *J. Org. Chem.*, 2015, **80**, 9794; DOI: 10.1021/acs.joc.5b01682.

66. T. Rehm, M. Rothemund, A. Bär, T. Dietel, R. Kempe, H. Kostrhunova, V. Brabec, J. Kasparkova, R. Schobert, *Dalton Trans.*, 2018, **47**, 17367; DOI: 10.1039/C8DT03360A.
67. K. T. Greeson, N. G. Hall, N. D. Redeker, J. C. Marcischak, L. V. Gilmore, J. A. Boatz, T. C. Le, J. R. Alston, A. J. Guenthner, K. B. Ghiassi, *J. Mol. Liq.*, 2018, **265**, 701; DOI: 10.1016/j.molliq.2018.06.016.
68. C. J. Adams, M. Lusi, E. M. Mutambi, A. Guy Orpen, *Chem. Commun.*, 2015, **51**, 9632; DOI: 10.1039/C5CC02924D.
69. R. Kore, R. Srivastava, *J. Mol. Catal. A: Chem.*, 2011, **345**, 117; DOI: 10.1016/j.molcata.2011.06.003.
70. A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523; DOI: 10.1016/S0040-4020(99)00927-8.
71. A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12742; DOI: 10.1021/ja973241o.
72. G. Grieco, O. Blacque, H. Berke, *Beilstein J. Org. Chem.*, 2015, **11**, 1656; DOI: 10.3762/bjoc.11.182.
73. M. Pompeo, R. D. J. Froese, N. Hadei, M. G. Organ, *Angew. Chem., Int. Ed.*, 2012, **51**, 11354; DOI: 10.1002/anie.201205747.
74. G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, *J. Org. Chem.*, 2001, **66**, 7729; DOI: 10.1021/jo010613+.
75. L. G. Pezük, B. Şen, F. E. Hahn, H. Türkmen, *Organometallics*, 2019, **38**, 593; DOI: 10.1021/acs.organomet.8b00882.
76. C. J. O´Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem.—Eur. J.*, 2006, **12**, 4743; DOI: 10.1002/chem.200600251.
77. Y. Shi, Z. Cai, Y. Peng, Z. Shi, G. Pang, *J. Chem. Res.*, 2011, **35**, 161; DOI: 10.3184/174751911X12983924042406.
78. K.-A. Green, P. T. Maragh, K. Abdur-Rashid, A. J. Lough, T. P. Dasgupta, *Eur. J. Inorg. Chem.*, 2014, **2014**, 3600; DOI: 10.1002/ejic.201402317.
79. E. Lee, J. Lee, D. V. Yandulov, *Eur. J. Inorg. Chem.*, 2017, **2017**, 2058; DOI: 10.1002/ejic.201700034.
80. A. V. Astakhov, O. V. Khazipov, E. S. Degtyareva, V. N. Khrustalev, V. M. Chernyshev, V. P. Ananikov, *Organometallics*, 2015, **34**, 5759; DOI: 10.1021/acs.organomet.5b00856.

Received February 22, 2022;
in revised form March 30, 2022;
accepted March 31, 2022