ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Facile Hydrolysis of Nickel(II) Complexes with N-Heterocyclic Carbene Ligands

Alexander V. Astakhov,[†] Oleg V. Khazipov,[†] Evgeniya S. Degtyareva,[‡] Victor N. Khrustalev,[§] Victor M. Chernyshev,[†] and Valentine P. Ananikov*[,†,‡]

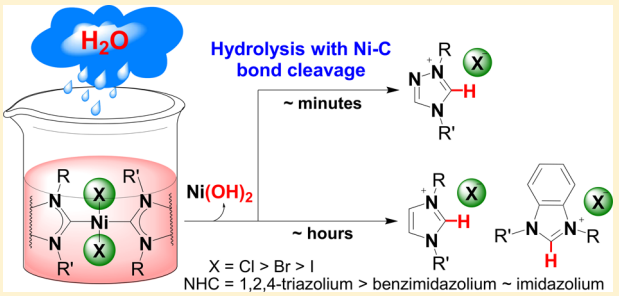
[†]Platov South-Russian State Polytechnic University (NPI), Prosveschenya 132, Novocherkassk 346428, Russia

[‡]Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow 119991, Russia

[§]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str., 28, Moscow 119991, Russia

Supporting Information

ABSTRACT: Metal complexes with N-heterocyclic carbene ligands (NHC) are ubiquitously used in catalysis, where the stability of the metal−ligand framework is a key issue. Our study shows that Ni-NHC complexes may undergo facile decomposition due to the presence of water in organic solvents (hydrolysis). The ability to hydrolyze $Ni(NHC)_2X_2$ complexes decreases in the order of NHC = 1,2,4-triazolium > benzimidazolium ≈ imidazolium. Depending on the ligand and substituents, the half reaction time of the complex decomposition may change from several minutes to hours. The nature of the halogen is also an important factor, and the ability for decomposition of the studied complexes decreases in the order of Cl > Br > I. NMR and MS monitoring revealed that Ni-NHC complexes in the presence of water undergo hydrolysis with Ni−$C_{carbene}$ bond cleavage, affording the corresponding *N,N′*-dialkylated azolium salts and nickel(II) hydroxide. These findings are of great importance for designing efficient and recyclable catalytic systems, because trace water is a common contaminant in routine synthetic applications.



INTRODUCTION

Ni-catalyzed reactions have underwent outstanding growth in recent years and have had a paramount impact on the development of organic synthesis.[1−6] In many cases, Ni-catalyzed transformations have achieved high performance and demonstrated efficient practical applications in industry and fine organic synthesis. Moreover, in several cases, Ni was an inexpensive replacement for demanding and expensive catalysts. Ni complexes have shown unique reactivity and facilitated the development of novel catalytic transformations. Ni-mediated cross-coupling reactions, especially those involving alkyl halides, and atom-economic addition reactions are parts of an established toolbox of contemporary organic synthesis.[1−4] Excellent recent developments have been made in C−H bond functionalization reactions,[5a] carbonyl reduction to alcohols,[5b] and the synthesis of biologically active heterocyclic compounds.[5c] Particularly useful are nickel complexes with N-heterocyclic carbene ligands (NHC ligands), which are easy to prepare and are now widely used for C−C bond formation.[1,3,4b,5a,d] Ni-NHC complexes have also mediated regioselective reductive coupling[6] and stereospecific alkyl−alkyl cross-coupling reactions, employing an enantioselective nickel catalyst.[4b] Ni-NHC catalysts have been successfully applied to reduce carbon dioxide over water under electrocatalytic conditions.[2d]

Over the past few years, a growing number of environmentally friendly synthetic methodologies propose water or aqueous organic solvents for the implementation of metal-catalyzed organic reactions.[7] In this regard, hydrolytic stability becomes an essential requirement for organometallic catalysts. It is commonly accepted that the majority of metal complexes with NHC ligands are highly stable and quite resistant to hydrolysis, which is an important advantage of NHC ligands over phosphine ligands for metal catalysts in aqueous media.[7e,8]

However, the question of the hydrolytic stability of Ni(II)-NHC complexes has not been considered in detail. When reproducing a number of procedures published in the literature for the preparation of Ni(II) complexes with NHC ligands generated from *N,N′*-dialkyl-1,2,4-triazolium salts, we discovered that the yields of the target products highly depended on the degree of dryness of the solvents and reagents. Moreover, in many cases, we were unable to obtain the target products when isolating the Ni(II) triazolium NHC complexes by dilution of reaction mixtures with water, as can be carried out in the synthesis of Ni(II) complexes with imidazolium and benzimidazolium NHCs.[9] Thus, we were puzzled by the problem of the hydrolytic stability of Ni(II) complexes with NHC ligands.

Received: October 12, 2015

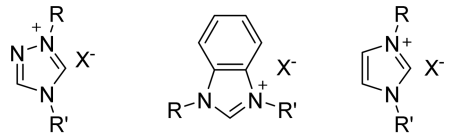
DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX

In this work, we investigate the hydrolytic stability of Ni(II) complexes with NHC ligands generated from *N*,*N*′-dialkylated salts of 1,2,4-triazole, benzimidazole, and imidazole, three classes of heterocyclic systems used for the preparation of metal NHC catalysts.

RESULTS AND DISCUSSION

Synthesis of the Complexes. An overview of the ligand precursors used in this study is shown in Table 1. The 1,2,4-triazolium and (benz)imidazolium salts were prepared by the direct alkylation of a number of *N*-substituted 1,2,4-triazoles, imidazoles, and benzimidazoles. These quaternization reactions are commonly performed in refluxing acetone or acetonitrile. The salts were obtained in good yields as white to yellowish solids, and most of them were hygroscopic. These carbene precursors were characterized by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HRMS).

Table 1. Overview of the Ligand Precursors Used in This Study



1a-e 2a-d 3a,b

	R	R′	X		R	R′	X
1a	Me	Me	I	**2a**	Me	Et	I
1b	Bu	Bu	Br	**2b**	Bu	Me	I
1c	Bn	Me	I	**2c**	Bn	Bu	Br
1d	Bu	Bn	Br	**2d**	Bu	Bu	Br
1e	Bn	Bn	CI	**3a**	Me	Me	I
				3b	Me	Bu	CI

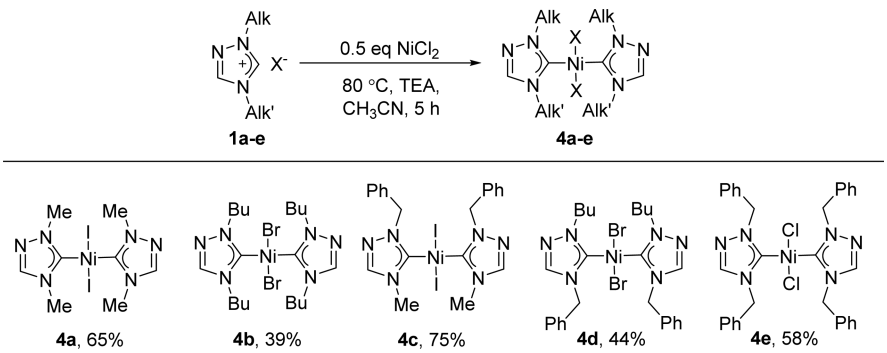
Nickel complexes **4a−e** with 1,2,4-triazole carbenes were synthesized by heating triazolium salts **1a−e** with anhydrous $NiCl_2$ in dry acetonitrile (Scheme 1).[10] The highest yields (65−75%) were observed for the well-crystallized iodine-containing complexes **4a**,**c**, while the yields of highly soluble chlorine- and bromine-containing complexes were in the range of 39−58%. Complexes with benzimidazole (**5a−d**) and imidazole ligands (**6a**,**b**) were prepared by the fusion of salts **2a−d** and **3a**,**b** with anhydrous nickel(II) acetate in molten tetrabutylammonium bromide or iodide at 130−160 °C under vacuum, according to the known procedure (Scheme 2, Methods A,B).[9] Alternatively, complexes **5b**,**d** were obtained by the reaction of NHC species, generated from the corresponding azolium salts in the presence of NaH in THF, with the pyridine complex of $NiCl_2$ (Scheme 2, Method C). The yields of compounds **4−6** decreased significantly when the solvents or reagents were insufficiently dried. Furthermore, we were unable to obtain imidazolium complexes **6** containing Cl^- or Br^- as ligands by fusion of the corresponding *N*,*N*-dialkylimidazolium chlorides or bromides with nickel acetate. In these cases, only starting compounds were isolated from the reaction mixtures. However, reaction of the same reagents in the presence of I^- anions resulted in the successful formation of NHC complexes containing iodide ligands. Thus, melting 1-butyl-3-methyl-1*H*-imidazol-3-ium chloride, nickel(II) acetate, and an excess of tetrabutylammonium iodide afforded complex **6b** in 55% yield. These results allowed us to assume that Ni(II) imidazolium carbene complexes with iodine ligands are more thermodynamically stable than analogous complexes with chlorine or bromine ligands. Possibly, in the reactions of imidazolium salts with nickel acetate, the equilibrium is shifted to the right in the case of complexes with iodine ligands and to the left in the case of complexes with chlorine or bromine ligands (Scheme S1 in the Supporting Information).

All of the obtained complexes were fully characterized by ^{1}H and ^{13}C NMR and elemental analysis. According to the spectral data, the complexes were obtained in the form of *trans* isomers. Similar to what was previously observed for *trans*-NHC complexes with unsymmetrical ligands,[9b,10,11] two sets of NMR signals were obtained for all of the complexes, except for **5d** and **6a** due to *syn*/*anti* isomerization. Specific shifts in the ^{13}C NMR resonances at δ 171−189 ppm of metal-bonded C atoms were observed for all of these compounds.

The structures of complexes **4e** and **5c**,**d** were confirmed by single-crystal X-ray diffraction analyses (Figures 1−3).

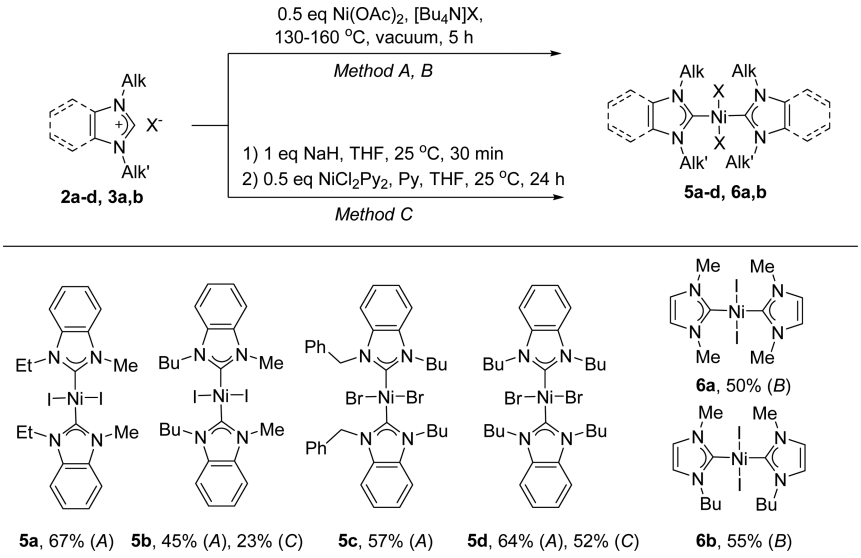
In the crystal structure, the molecule of **4e** is located in a special position with C_{2h} symmetry and is consequently disordered over two sites. Unlike the case for **4e**, the molecules of **5c**,**d** in the crystal lie on an inversion center. In all compounds, the coordination geometry around the nickel(II) center is nearly perfectly square planar, with the coordination of two NHC ligands and two halogenides in *trans* positions. Due to the virtual symmetry, the bond angles at the Ni atom in **4e** are strictly equal to 90°, whereas they are very close to this value in **5c**,**d**. The Ni−Hal and Ni−C bond distances are within the range reported for other nickel NHC complexes, but those of Ni−$C_{carbene}$ for **5c**,**d** are expectedly shorter than that found in **4e**. The triazole (for **4e**) or benzimidazole (for **5c**,**d**) rings are oriented nearly perpendicular to the coordination plane of the Ni atom with dihedral angles of 71.6(6)° (in the case of **4e**) and 76.79(5) and 82.42(5)° (in the case of **5c**,**d**), which is a

Scheme 1. Synthesis of Compounds 4a−e



DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX

Scheme 2. Synthesis of Compounds 5a–d and 6a,b



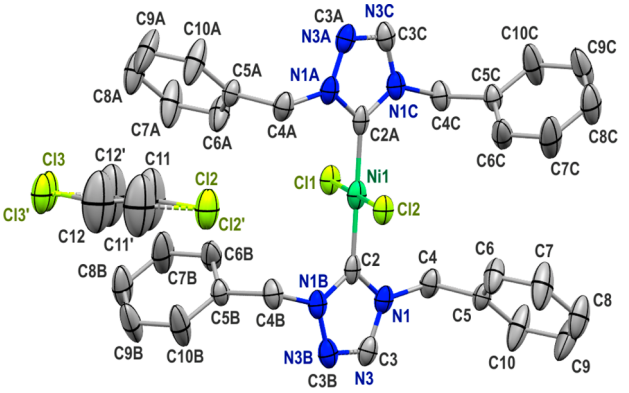


Figure 1. Molecular structure of the solvate of compound **4e** with 1,2-dichloroethane. Thermal ellipsoids are shown at the 50% probability level. Dashed lines indicate the alternative positions of the disordered fragments. Selected bond lengths (Å) and angles (deg): Ni1–Cl1 2.1922(17), Ni1–C2 1.919(8), N1–C2 1.349(7); Cl1–Ni1–C2 90.0, N1–C2–N1B 103.1(7).

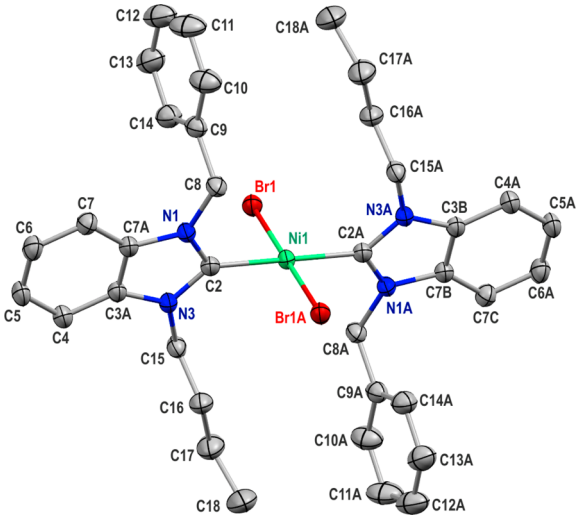


Figure 2. Molecular structure of compound **5c**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ni1–Br1 2.3082(3), Ni1–C2 1.899(2), N1–C2 1.355(3), C2–N3 1.358(3); Br1–Ni1–C2 89.57(7), N1–C2–N3 106.16(19).

characteristic feature of carbene complexes that relieves steric strain.

For all NHC ligands in **4e** and **5c,d**, the N-substituent wingtips dangle *anti* to each other. All molecules in the crystals are arranged at van der Waals distances.

Stability of Ni-NHC Complexes in the Presence of Water. We established that Ni(II) complexes with triazolium carbenes are unstable in the presence of water (aqueous acetonitrile, THF, ethanol, acetone) and decompose even at room temperature. Solutions of compounds **4a–e** in aqueous acetonitrile discolored almost completely within a few minutes after heating at 70 °C. Figure 4 shows the influence of water addition to the solution of compound **4b** in acetonitrile. A bluish green nickel(II) hydroxide, the structure of which was confirmed by XRF and XRD analyses, precipitated from the solutions. Proligands **1a–e** were isolated in high yields (Table 2) from these solutions after precipitation of nickel hydroxide (the structures were confirmed by ^{1}H and ^{13}C NMR and HRMS experiments). Therefore, hydrolysis of these Ni(II)-NHC complexes readily took place according to the reaction shown in Scheme 3.

Benzimidazolium and imidazolium complexes of Ni(II) also underwent hydrolysis (Scheme 3); however, their hydrolytic resistance is appreciably higher. For example, the starting complexes were isolated in 12–30% yields in addition to the formed proligands **2a,b,d** after heating complexes **5a,b,d** at 70 °C in 90% v/v aqueous acetonitrile for 24 h (Table 2). The hydrolytic resistance of complexes **6c,d** with bulky substituted imidazolium ligands (Chart 1) is even higher. For these complexes no decomposition was observed in aqueous THF at room temperature within 24 h, which is consistent with the published data for compound **6d**.[11b] Heating of these compounds at 70 °C in 90% v/v aqueous THF (10% water and 90% THF) for 24 h initiated slow hydrolysis (compounds **6c,d** are insoluble in acetonitrile).

We performed kinetic experiments to estimate the hydrolytic ability of complexes **4–6** in aqueous acetonitrile. The progress of the reactions was monitored by NMR ^{1}H spectroscopy (see Figure 5). The kinetics of the hydrolytic reactions were

DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX–XXX

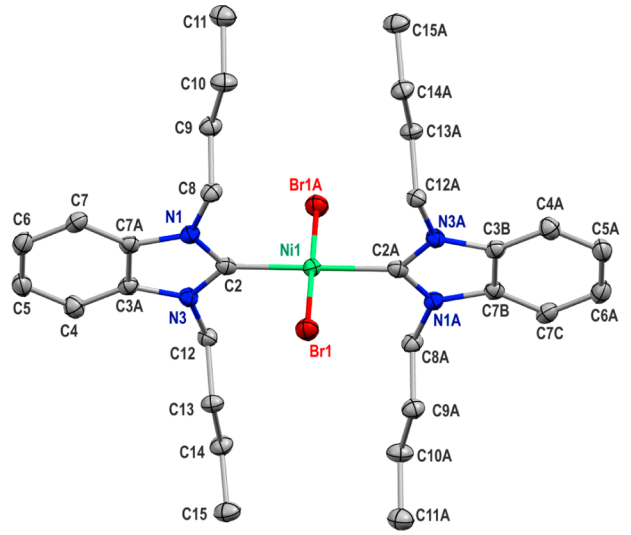


Figure 3. Molecular structure of compound **5d**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ni1−Br1 2.3005(4), Ni1−C2 1.903(3), N1−C2 1.354(4), C2−N3 1.359(3); Br1−Ni1−C2 89.08(8), N1−C2−N3 105.9(2).

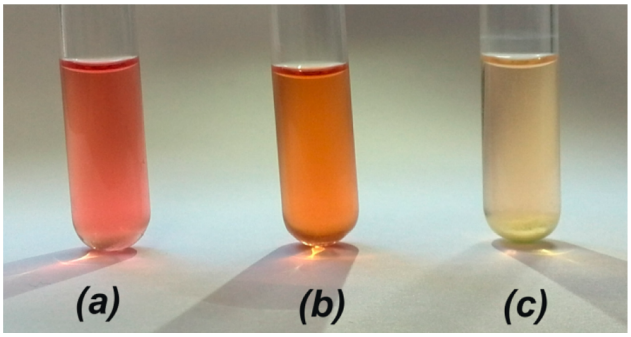


Figure 4. Photos of solutions of complex **4b** (1.3×10^{-2} M) in dry acetonitrile (a), in 90% v/v aqueous acetonitrile (10% water and 90% acetonitrile) after 10 min at 25 °C (b), and in 90% v/v aqueous acetonitrile after 10 min at 70 °C (c). Metal complex decomposition and precipitation of nickel hydroxide readily took place.

monitored by following the signals of the α protons of *N*-alkyl groups in the starting complexes **4**−**6** (or methyl groups in compound **6c**) and the proligands **1**−**3** formed during hydrolysis. Due to the large excess of water in the reaction mixtures, all of the studied reactions were first order with respect to the concentration of the complex. Pseudo-first-order rate constants (k), half reaction times (t_{50}), and times for 99% conversion (t_{99}) of the Ni(II)-NHC complexes are presented in Table 3.

The kinetic data obtained show that the hydrolytic resistance of benzimidazolium and imidazolium complexes **5** and **6** is sufficiently higher than that of triazolium complexes **4**. It is also important to mention that the nature of the coordinated halogen has an appreciable effect on the hydrolytic stability, which increases in the order Cl < Br < I. For example, the rate constant for the hydrolysis of compound **4e** (X = Cl) is ∼30 times higher than that of **4a,c** (X = I). The hydrolysis of bromide complexes is several times faster than that of analogous iodide complexes. The hydrolytic stability of imidazole complexes with *N*-aryl-substituted ligands **6c,d** is sufficiently higher than that with the *N*-alkyl-substituted

Table 2. Decomposition of the Ni-NHC Complexes in the Presence of Water

complex	t, h	complex decomposed (complex remaining),[a] %	proligand formed (proligand isolated),[b] %
4a	10	99 (trace)	99 (84)
4b	3	99 (trace)	99 (91)
4c	10	99 (trace)	99 (88)
4d	3	99 (trace)	99 (79)
4e	0.5	99 (trace)	99 (81)
5a	24	70 (30)[c]	70 (61)
5b	24	72 (28)[c]	72 (63)
5c	24	99 (trace)	99 (83)
5d	24	88 (12)[c]	88 (67)
5d	60	99 (trace)	99 (82)
6a	48	99 (trace)	99 (88)
6b	48	99 (trace)	99 (86)[d]

[a]The amount of decomposed Ni-NHC complex as determined by NMR (the amount of remaining complex is shown in parentheses). [b]The amount of free proligand formed after hydrolysis of the Ni-NHC complex (the isolated yield of the proligand is given in parentheses). [c]Isolated yield. [d]Yield of 3-butyl-1-methyl-1*H*-imidazol-3-ium iodide (**3c**).

Scheme 3. Hydrolysis of Ni(II)-NHC Complexes

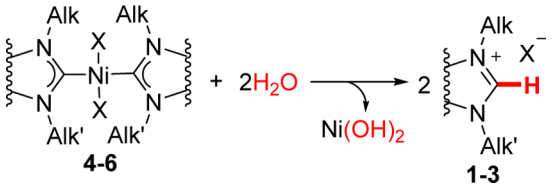
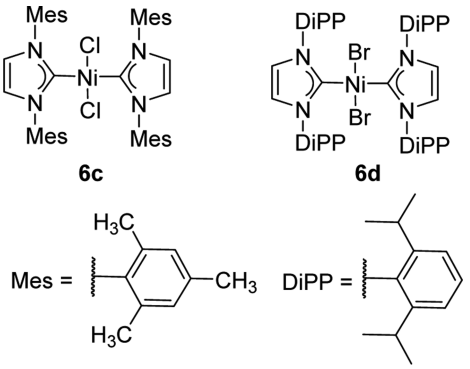


Chart 1. Structures of Ni(II)-NHC Complexes 6c,d



complexes **6a,b**. The reason for this higher stability is unclear but is likely due to a combination of steric and electronic factors.

It should be noted that hydrolysis with cleavage of the metal−$C_{carbene}$ bond is considered an atypical reaction for the majority of NHC metal complexes.[1,7e,8,10−12] An analogous reaction was described for Ag(I)-NHC complexes, for which the metal−carbon bond energy is relatively small.[13] However, to the best of our knowledge, such a hydrolysis reaction of Ni(II)-NHC complexes has not been described in the literature.

CONCLUSIONS

To summarize, the ability of Ni(II) complexes with NHC ligands to hydrolyze under mild conditions with Ni−$C_{carbene}$ bond cleavage was demonstrated for the first time. The

DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX

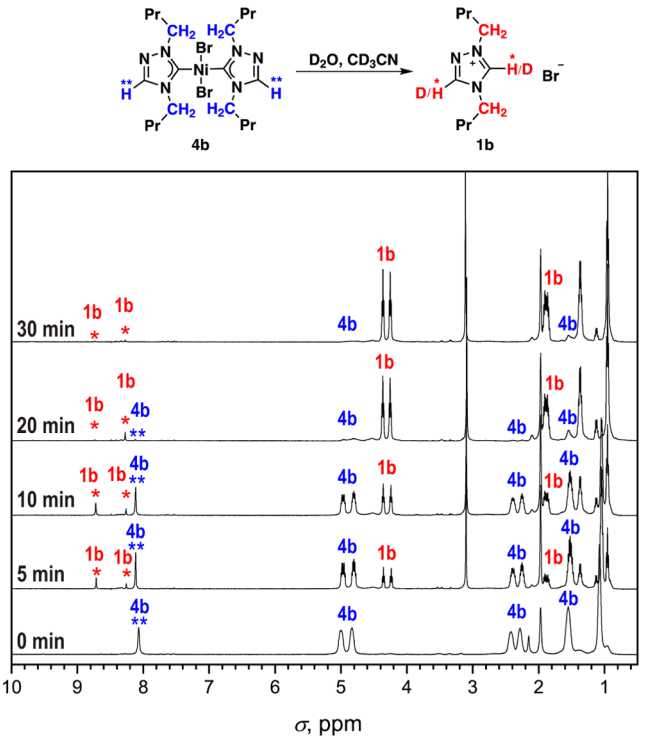


Figure 5. Time-dependent ^{1}H NMR spectral changes of the reaction mixture during hydrolysis of **4b** in CD_3CN diluted with D_2O (10% v/v) at 70 °C. The CH signals of **1b** marked by asterisks disappear gradually due to a known process of H/D exchange.

Table 3. Pseudo-First-Order Rate Constants (k), Half-Reaction Times (t_{50}), and Times for 99% Conversion (t_{99}) of Ni(II)-NHC Complexes in 90% v/v Aqueous Acetonitrile at 70 ± 1 °C

complex	k, 10^3 min^{-1}	t_{50}	t_{99}
4a	11.2 ± 0.9	1 h	6 h 50 min
4b	48.1 ± 1.0	14 min	1 h 40 min
4c	8.5 ± 0.7	1 h 20 min	9 h
4d	122.1 ± 21.5	6 min	35 min
4e	271.3 ± 41.9	3 min	20 min
5a	0.78 ± 0.07	14 h 45 min	98 h
5b	0.81 ± 0.08	14 h 20 min	95 h
5c	3.49 ± 0.23	3 h 20 min	22 h
5d	1.44 ± 0.11	8 h	53 h
6a	3.29 ± 0.08	3 h 30 min	23 h 20 min
6b	1.94 ± 0.01	6 h	39 h 30 min
6c[a]	0.27 ± 0.03	43 h	288 h 30 min

[a]The experiment was performed in 90% v/v aqueous THF (10% water and 90% THF), since the complex was insoluble in acetonitrile.

hydrolytic ability depends on the nature of the NHC ligand and is enhanced with an increase in the π deficiency of heterocyclic ligands: NHC = 1,2,4-triazolium > benzimidazolium ≈ imidazolium. Furthermore, the hydrolytic ability is influenced by the nature of the coordinated halogen: Cl > Br > I.

The stability of Ni(II)-NHC complexes and their ability to hydrolyze should be kept in mind for the synthesis of these complexes as well as their applications in catalytic reactions. Decomposition of Ni-NHC complexes due to the presence of water may affect the activity and selectivity of catalytic reactions. The key issue concerns the recovery and reuse of the catalysts, where decomposition during the reaction and workup is a critical factor.

EXPERIMENTAL SECTION

General Information. Melting points were determined in open capillary tubes in a Thiele apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 instrument at 500 and 125 MHz, respectively, in DMSO-d_6, CD_3CN, or $CDCl_3$ and using TMS as an internal standard. High-resolution mass spectra (HRMS) were obtained on a TOF MS instrument using electrospray ionization (ESI) in positive ion mode (interface capillary voltage 4500 V). Powder XRD measurements were taken on an ARL X'TRA instrument using monochromatic Cu Kα radiation as the incident beam, operating at 40 kV/40 mA. XRD diffraction patterns were obtained by continuous scanning in a 2θ range of 15−80° with a 2θ step size of 0.01° and a scan step time of 1 s. Elemental analyses were performed using a PerkinElmer 2400 elemental analyzer.

1-Butyl-1,2,4-triazole, 1-benzyl-1,2,4-triazole, 1-methylbenzimidazole, 1-butylbenzimidazole, and compounds **6c,d** were obtained by known methods.[14,15]

General Procedure for the Preparation of 1,4-Dialkyl-1,2,4-triazolium Halides 1a−e. A mixture of 1-substituted 1,2,4-triazole (0.01 mol), alkyl halide (0.02 mol), and acetonitrile (15 mL) was heated under reflux for 36 h (5 h in case of MeI or BnBr); the volatiles were then removed under reduced pressure, and the crude product was washed with anhydrous diethyl ether (10 mL) or recrystallized and dried in vacuo.

*1,4-Dimethyl-4H-1,2,4-triazol-1-ium Iodide (**1a**).* Yield: 1.664 g (74%) of colorless hygroscopic crystals. Mp: 121−123 °C (lit. mp 121−123 °C).[16a] ^{1}H NMR (CD_3CN, 500 MHz): δ 3.98 (s, 3H, CH_3), 4.10 (s, 3H, CH_3), 8.78 (s, 1H, 3-H), 9.88 (s, 1H, 5-H). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 34.5, 39.1, 143.0, 145.0. HRMS (ESI): calcd for $C_4H_8N_3^+$ [M − I$^-$]$^+$ 98.0713, found 98.0713.

*1,4-Dibutyl-4H-1,2,4-triazol-1-ium Bromide (**1b**).* Yield: 1.919 g (73%) of yellowish hygroscopic crystals. Mp: 63−65 °C (oil).[16b] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.97−1.00 (m, 6H, $2CH_3$), 1.37−1.48 (m, 4H, $2CH_2$), 1.97−2.06 (m, 4H, $2CH_2$), 4.54 (t, J = 7.5 Hz, 2H, CH_2), 4.62 (t, J = 7.2 Hz, 2H, CH_2), 9.50 (s, 1H, CH), 11.62 (s, 1H, CH). ^{1}H NMR (CD_3CN, 500 MHz): δ 0.95−0.98 (m, 6H, $2CH_3$), 1.36−1.43 (m, 4H, $2CH_2$), 1.91−1.98 (m, 4H, $2CH_2$), 4.39 (t, J = 7.4 Hz, 2H, CH_2), 4.45 (t, J = 7.2 Hz, 2H, CH_2), 9.08 (s, 1H, CH), 10.83 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 13.3, 13.4, 19.3, 30.7, 32.0, 48.4, 52.5, 142.5, 144.5 (2 signals are overlapped). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 12.70, 12.71, 18.98, 19.00, 30.3, 31.2, 47.8, 52.0, 142.4, 144.3. HRMS (ESI): calcd for $C_{10}H_{20}N_3^+$ [M − Br$^-$]$^+$ 182.1652, found 182.1655.

*1-Benzyl-4-methyl-4H-1,2,4-triazol-1-ium Iodide (**1c**).* Yield: 2.078 g (69%) of colorless hygroscopic crystals. Mp: 123−125 °C (lit. mp 122−124 °C).[16a] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.21 (s, 3H, CH_3), 5.69 (s, 2H, CH_2), 7.41−7.42 (m, 3H, Ph), 7.58−7.59 (m, 2H, Ph), 8.86 (s, 1H, CH), 11.20 (s, 1H, CH). ^{1}H NMR (CD_3CN, 500 MHz): δ 3.96 (s, 3H, CH_3), 5.65 (s, 2H, CH_2), 7.45−7.46 (m, 3H, Ph), 7.53−7.55 (m, 2H, Ph), 8.77 (s, 1H, CH), 10.06 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 35.8, 56.6, 129.4, 129.6, 129.8, 131.4, 143.1, 144.6. ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 34.6, 55.6, 129.1, 129.3, 132.5, 142.7, 145.4 (2 signals are overlapped). HRMS (ESI): calcd for $C_{10}H_{12}N_3^+$ [M − I$^-$]$^+$ 174.1026, found 174.1030.

*4-Benzyl-1-butyl-4H-1,2,4-triazol-1-ium Bromide (**1d**).* Yield: 2.310 g (78%) of colorless hygroscopic crystals. Mp: 125−127 °C. ^{1}H and ^{13}C{^{1}H} NMR spectra ($CDCl_3$, 500 and 125 MHz, correspondingly) are analogous to those published in the literature.[16c] ^{1}H NMR (CD_3CN, 500 MHz): δ 0.93 (t, J = 7.4 Hz, 3H, CH_3), 1.31−1.39 (m, 2H, CH_2), 1.86−1.92 (m, 2H, CH_2), 4.36 (t, J = 7.2 Hz, 2H, CH_2), 5.50 (s, 2H, CH_2Ph), 7.46−7.52 (m, 5H, Ph), 8.79 (s, 1H, CH), 9.81 (s, 1H, CH). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 12.7, 19.0, 30.2, 51.4, 52.3, 129.2, 129.4, 129.5, 132.6, 144.1 (2 signals are overlapped). HRMS (ESI): calcd for $C_{13}H_{18}N_3^+$ [M − Br$^-$]$^+$ 216.1495, found 216.1498.

DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX

*1,4-Dibenzyl-4H-1,2,4-triazol-1-ium Chloride (**1e**).* Yield: 2.373 g (83%) of colorless hygroscopic crystals. Mp: 178−181 °C (lit. mp 178−181 °C).[16a] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.63 (s, 2H, CH_2), 5.79 (s, 2H, CH_2), 7.30−7.33 (m, 6H, Ph), 7.49−7.51 (m, 2H, Ph), 7.63−7.64 (m, 2H, Ph), 9.32 (s, 1H, CH), 12.20 (s, 1H, CH). ^{1}H NMR (CD_3CN, 500 MHz): δ 5.49 (s, 2H, CH_2), 5.56 (s, 2H, CH_2), 7.43−7.51 (m, 10H, Ph), 8.78 (s, 1H, CH), 9.96 (s, 1H, CH). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 5.62 (s, 2H, CH_2), 5.68 (s, 2H, CH_2), 7.39−7.49 (m, 8H, Ph), 7.56−7.58 (m, 2H, Ph), 9.52 (s, 1H, CH), 10.78 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 51.9, 56.1, 129.2, 129.3, 129.4, 129.6, 129.8, 131.9, 132.4, 143.0, 144.2 (2 signals are overlapped). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 51.6, 55.8, 129.1, 129.26, 129.27, 129.35, 129.38, 129.6, 132.4, 132.5, 142.2, 144.5. ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 51.0, 55.3, 129.3, 129.36, 129.39, 129.5, 133.7, 134.2, 143.4, 145.5 (signals are partially overlapped). HRMS (ESI): calcd for $C_{16}H_{16}N_3^+$ [M − Cl^-]$^+$ 250.1339, found 250.1339.

General Procedure for the Preparation of 1,3-Dialkylimidazolium and 1,3-Dialkylbenzimidazolium Halides 2a−d and 3a. A mixture of 1-alkylimidazole or 1-alkylbenzimidazole (0.01 mol), the appropriate alkyl halide (0.02 mol), and acetone (20 mL) was heated under reflux for 5 h. Then, volatiles were removed under reduced pressure, and the residue obtained was washed with diethyl ether (10 mL) and dried under vacuum.

*1-Ethyl-3-methyl-1H-benzo[d]imidazol-3-ium Iodide (**2a**).* Yield: 2.650 g (92%) of colorless crystals. Mp: 191−193 °C (lit. mp 191−194 °C).[16d] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.79 (t, J = 7.3 Hz, 3H, CH_3), 4.31 (s, 3H, CH_3), 4.66 (q, J = 7.3 Hz, 2H, CH_2), 7.68−7.70 (m, 2H, Ar), 7.75−7.77 (m, 2H, Ar), 11.05 (s, 1H, NCH). ^{1}H NMR (CD_3CN, 500 MHz): δ 1.63 (t, J = 7.3 Hz, 3H, CH_3), 4.12 (s, 3H, CH_3), 4.56 (q, J = 7.3 Hz, 2H, CH_2), 7.70−7.74 (m, 2H, Ar), 7.89−7.94 (m, 2H, Ar), 9.60 (s, 1H, NCH). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.56 (t, J = 7.2 Hz, 3H, CH_3), 4.10 (s, 3H, CH_3), 4.54 (q, J = 7.2 Hz, 2H, CH_2), 7.70−7.72 (m, 2H, Ar), 8.03−8.11 (m, 2H, Ar), 9.77 (br. s, 1H, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 13.8, 33.5, 42.6, 113.3, 113.4, 126.8, 126.9, 131.2, 132.3, 141.5. ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 14.7, 33.8, 42.5, 113.96, 114.04, 126.9, 131.2, 132.3, 142.8 (2 signals are overlapped). HRMS (ESI): calcd for $C_{10}H_{13}N_2^+$ [M − I^-]$^+$ 161.1073, found 161.1074.

*3-Butyl-1-methyl-1H-benzo[d]imidazol-3-ium Iodide (**2b**).* Yield: 2.815 g (89%) of colorless crystals. Mp: 161−162 °C.[16e] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.00 (t, J = 7.4 Hz, 3H, CH_3), 1.45−1.53 (m, 2H, CH_2), 2.05−2.11 (m, 2H, CH_2), 4.32 (s, 3H, CH_3), 4.61 (t, J = 7.4 Hz, 2H, CH_2), 7.68−7.71 (m, 2H, Ar), 7.78−7.85 (m, 2H, Ar), 10.90 (s, 1H, NCH). ^{1}H NMR (CD_3CN, 500 MHz): δ 0.99 (t, J = 7.4 Hz, 3H, CH_3), 1.41−1.49 (m, 2H, CH_2), 1.98−2.02 (m, 2H, CH_2), 4.12 (s, 3H, CH_3), 4.52 (t, J = 7.3 Hz, 2H, CH_2), 7.69−7.73 (m, 2H, Ar), 7.89−7.97 (m, 2H, Ar), 9.64 (s, 1H, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 12.8, 19.3, 30.8, 33.6, 47.0, 113.37, 113.43, 126.8, 126.9, 131.4, 132.3, 141.7. HRMS (ESI): calcd for $C_{12}H_{17}N_2^+$ [M − I^-]$^+$ 189.1386, found 189.1388.

*1-Benzyl-3-butyl-1H-benzo[d]imidazol-3-ium Bromide (**2c**).* Yield: 2.830 g (82%) of colorless crystals. Mp: 162−164 °C.[16f] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.99 (t, J = 7.4 Hz, 3H, CH_3), 1.44−1.51 (m, 2H, CH_2), 2.04−2.10 (m, 2H, CH_2), 4.63 (t, J = 7.4 Hz, 2H, CH_2), 5.93 (s, 2H, CH_2), 7.31−7.37 (m, 3H, Ar), 7.53−7.74 (m, 6H, Ar), 11.58 (s, 1H, NCH). ^{1}H NMR (CD_3CN, 500 MHz): δ 1.00 (t, J = 7.4 Hz, 3H, CH_3), 1.42−1.49 (m, 2H, CH_2), 1.99−2.05 (m, 2H, CH_2), 4.53 (t, J = 7.4 Hz, 2H, CH_2), 5.84 (s, 2H, CH_2), 7.39−7.45 (m, 3H, Ar), 7.56−7.57 (m, 2H, Ar), 7.64−7.67 (m, 2H, Ar), 7.81−7.82 (m, 1H, Ar), 7.93−7.94 (m, 1H, Ar), 10.38 (s, 1H, NCH). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.95 (t, J = 7.4 Hz, 3H, CH_3), 1.34−1.42 (m, 2H, CH_2), 1.91−1.97 (m, 2H, CH_2), 4.54−4.57 (m, 2H, CH_2), 5.82 (s, 2H, CH_2), 7.37−7.44 (m, 3H, Ar), 7.54−7.57 (m, 2H, Ar), 7.64−7.70 (m, 2H, Ar), 7.98−8.00 (m, 1H, Ar), 8.13−8.15 (m, 1H, Ar), 10.12 (br. s, 1H, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 12.8, 19.4, 30.6, 47.2, 50.5, 113.7, 113.8, 126.9, 128.5, 129.0, 129.1, 131.4, 131.8, 133.6, 141.9 (2 signals are overlapped). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 13.9, 19.6, 30.9, 47.1, 50.4, 114.4, 127.1, 127.2, 128.7, 129.2, 129.4, 131.3, 131.8, 134.5, 142.9 (2 signals are overlapped). HRMS (ESI): calcd for $C_{18}H_{21}N_2^+$ [M − Br^-]$^+$ 265.1699, found 265.1700.

*1,3-Dibutyl-1H-benzo[d]imidazol-3-ium Bromide (**2d**).* Yield: 2.680 g (86%) of colorless crystals. Mp: 144−145 °C (lit. mp 140−142 °C).[16g] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.00 (t, J = 7.4 Hz, 6H, $2CH_3$), 1.44−1.51 (m, 4H, $2CH_2$), 2.03−2.09 (m, 4H, $2CH_2$), 4.65 (t, J = 7.4 Hz, 4H, $2CH_2$), 7.66−7.69 (m, 2H, Ar), 7.72−7.74 (m, 2H, Ar), 11.54 (s, 1H, NCH). ^{1}H NMR (CD_3CN, 500 MHz): δ 0.97−1.00 (m, 6H, $2CH_3$), 1.40−1.48 (m, 4H, $2CH_2$), 1.98−2.04 (m, 4H, $2CH_2$), 4.54−4.57 (m, 4H, $2CH_2$), 7.68−7.70 (m, 2H, Ar), 7.94−7.96 (m, 2H, Ar), 10.35 (s, 1H, NCH). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 0.94 (t, J = 7.4 Hz, 6H, $2CH_3$), 1.32−1.40 (m, 4H, $2CH_2$), 1.89−1.95 (m, 4H, $2CH_2$), 4.52−4.55 (m, 4H, $2CH_2$), 7.70−7.72 (m, 2H, Ar), 8.12−8.14 (m, 2H, Ar), 10.00 (br. s, 1H, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 12.8, 19.3, 30.8, 47.0, 113.5, 126.7, 131.6, 141.8. ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): δ 13.9, 19.6, 31.0, 46.9, 114.2, 127.0, 131.6, 142.6. HRMS (ESI): calcd for $C_{15}H_{23}N_2^+$ [M − Br^-]$^+$ 231.1856, found 231.1854.

*1,3-Dimethyl-1H-imidazol-3-ium Iodide (**3a**).* Yield: 1.880 g (84%) of yellowish hygroscopic crystals. Mp: 78−80 °C (lit. mp 81−83 °C).[16h] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.50 (s, 6H, $2CH_3$), 7.15 (s, 2H, 2CH), 9.00 (s, 1H, NCH). ^{13}C{^{1}H} NMR ($CDCl_3$, 500 MHz): δ 36.8, 123.4, 136.2. HRMS (ESI): calcd for $C_5H_9N_2^+$ [M − I^-]$^+$ 97.0760, found 97.0759.

General Procedure for the Synthesis of Compounds 4a−e. A mixture of compound **1a−e** (8 mmol), 0.520 g (4 mmol) of anhydrous $NiCl_2$, and 2.024 g (20 mmol) of Et_3N in dry acetonitrile (100 mL) was heated under reflux for 5 h. Then, the solvent and Et_3N were removed under reduced pressure, and the residue obtained was chromatographed on a silica gel column, with neat $CHCl_3$ as eluent.

*Bis(2,4-dimethyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)-diiodonickel(II) (**4a**).* Yield: 1.321 g (65%) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 4.20 and 4.24 (both s, 6H, $2CH_3$), 4.34 and 4.38 (both s, 6H, $2CH_3$), 7.76 and 7.77 (both s, 2H, 2CH). ^{1}H NMR (CD_3CN, 500 MHz) (mixture of *syn* and *anti* isomers): δ 4.19 and 4.20 (both s, 6H, $2CH_3$), 4.30 and 4.32 (both s, 6H, $2CH_3$), 8.04 and 8.05 (both s, 2H, 2CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 35.10, 35.15, 39.74, 39.79, 143.07, 143.09, 179.28, 179.31. Anal. Calcd for $C_8H_{14}N_6I_2Ni$: C, 18.96; H, 2.78; N, 16.58. Found: C, 18.72; H, 2.75; N, 16.76.

*Dibromo[bis(2,4-dibutyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)]-nickel(II) (**4b**).* Yield: 0.911 g (39%) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 1.07−1.09 (m, 12H, $4CH_3$), 1.56−1.58 (m, 8H, $4CH_2$), 2.29−2.38 (m, 8H, $4CH_2$), 4.81−5.03 (m, 8H, four CH_2), 7.76 (s, 2H, 2CH). ^{1}H NMR (CD_3CN, 500 MHz) (mixture of *syn* and *anti* isomers): δ 1.07−1.09 (m, 12H, $4CH_3$), 1.54−1.56 (m, 8H, $4CH_2$), 2.25−2.35 and 2.35−2.50 (both m, 8H, $4CH_2$), 4.82−4.84 and 4.99−5.01 (both m, 8H, $4CH_2$), 8.07 (s, 2H, 2CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 13.7, 13.8, 20.1, 20.2, 31.65, 31.68, 32.25, 32.29, 48.45, 48.53, 52.7, 52.8, 141.65, 141.68, 172.41, 172.44 (signals are partially overlapped). Anal. Calcd for $C_{20}H_{38}Br_2N_6Ni$: C, 41.34; H, 6.59; N, 14.46. Found: C, 41.19; H, 6.68; N, 14.59.

*Bis(2-benzyl-4-methyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)-diiodonickel(II) (**4c**).* Yield: 1.979 g (75%) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 4.20 and 4.24 (both s, 6H, $2CH_3$), 5.95 and 6.01 (both s, 4H, $2CH_2$), 7.31−7.61 (m, 10H, 2Ph), 7.771 and 7.773 (both s, 2H, two CH). ^{1}H NMR (CD_3CN, 500 MHz) (mixture of *syn* and *anti* isomers): δ 4.23 and 4.26 (both s, 6H, two CH_3), 6.00 and 6.03 (both s, 4H, two CH_2), 7.34−7.66 (m, 10H, 2Ph), 8.08 and 8.09 (both s, 2H, 2CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 35.41, 35.44, 56.6, 128.3, 128.4, 128.6, 128.7, 129.2, 129.3, 134.7, 134.8, 143.7, 143.8, 179.9, 180.0 (signals are partially overlapped). Anal. Calcd for $C_{20}H_{22}I_2N_6Ni$: C, 36.46; H, 3.37; N, 12.75. Found: C, 36.63; H, 3.19; N, 13.00.

*Bis(4-benzyl-2-butyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)-dibromonickel(II) (**4d**).* Yield: 1.146 g (44%) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 0.96

DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX

and 1.10 (both t, J = 7.2 Hz and J = 7.1 Hz, 6H, $2CH_3$), 1.42−1.49 and 1.57−1.65 (both m, 4H, $2CH_2$), 2.23−2.29 and 2.31−2.37 (both m, 4H, $2CH_2$), 4.91 and 5.03 (both t, J = 7.3 Hz and J = 7.3 Hz, 4H, $2CH_2$), 6.01 and 6.23 (both s, 4H, $2CH_2$), 7.35−7.58 (m, 12H, 2Ph and 2CH). ^{1}H NMR (CD_3CN, 500 MHz) (mixture of *syn* and *anti* isomers): δ 0.95 and 1.10 (both t, J = 7.3 Hz and J = 7.3 Hz, 6H, $2CH_3$), 1.40−147 and 1.56−1.63 (both m, 4H, $2CH_2$), 2.20−2.26 and 2.31−2.37 (both m, 4H, $2CH_2$), 4.91 and 5.03 (both t, J = 7.3 Hz and J = 7.3 Hz, 4H, $2CH_2$), 6.04 and 6.24 (both s, 4H, $2CH_2$), 7.36−7.66 (m, 10H, 2Ph), 7.93 and 7.95 (both s, 2H, 2CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 13.7, 13.8, 20.1, 20.2, 31.7, 31.8, 52.3, 52.4, 52.8, 52.9, 128.8, 128.9, 129.0, 129.2, 129.3, 134.38, 134.41, 141.5, 141.6, 172.8, 172.9 (signals are partially overlapped). Anal. Calcd for $C_{26}H_{34}Br_2N_6Ni$: C, 48.11; H, 5.28; N, 12.95. Found: C, 47.95; H, 5.35; N, 12.85.

*Dichlorobis(2,4-dibenzyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)-nickel(II) (**4e**).* Yield: 1.459 g (58%) of orange crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 5.99 and 6.03 (both s, 4H, $2CH_2$), 6.09 and 6.13 (both s, 4H, $2CH_2$), 7.31−7.35 (m, 20H, 4Ph), 7.44 and 7.54 (both s, 2H, 2CH). ^{1}H NMR (CD_3CN, 500 MHz) (mixture of *syn* and *anti* isomers): δ 6.05−6.22 (m, 8H, $4CH_2$), 7.35−7.56 (m, 20H, 4Ph), 8.02 (br s, 2H, 2CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 52.1, 56.3, 128.2, 128.66, 128.71, 129.2, 134.7, 135.6, 142.0, 170.6 (signals are partially overlapped). HRMS (ESI): calcd for $C_{32}H_{30}ClN_6Ni^+$ $[M - Cl^-]^+$ 591.1578, found 591.1568. Anal. Calcd for $C_{32}H_{30}Cl_2N_6Ni$: C, 61.18; H, 4.81; N, 13.38. Found: C, 61.38; H, 4.98; N, 13.49.

General Procedure for the Synthesis of Compounds 5a−d and 6a,b. *Method A.* A mixture of compound **2a−d** (8 mmol), anhydrous $Ni(OAc)_2$ (0.708 g, 4 mmol), and tetrabutylammonium bromide or iodide (4 g) was dried under vacuum at 80 °C for 1 h and then slowly heated to 130 °C (bromide salts) or 160 °C (iodide salts); the molten mixture that formed was stirred at this temperature for 5 h under vacuum. Then, the solid mixture was cooled to 20 °C and triturated with water (∼30 mL). The insoluble reddish product was collected by filtration, washed with water, recrystallized from acetonitrile, and dried under vacuum.

Method B. A mixture of 8 mmol of compound **3a,b**, anhydrous $Ni(OAc)_2$ (0.708 g, 4 mmol), and tetrabutylammonium iodide (12 g) was dried under vacuum at 80 °C for 1 h and then heated slowly to 160 °C; the molten mixture that formed was stirred at this temperature for 5 h under vacuum. Then, the solid mixture was cooled to 20 °C and triturated with water (∼30 mL). The insoluble reddish product was collected by filtration, washed with water, and dried under vacuum.

Method C. A mixture of compound **2b,d** (4 mmol) and NaH (60% dispersion in paraffin oil, 0.176 g, 4.4 mmol) in dry THF (30 mL) was magnetically stirred for 30 min at 25 °C. Then, a solution of $[NiCl_2Py_2]$ (0.576 g, 2 mmol) in pyridine (3.0 mL) was added to the reaction mixture. The mixture was stirred at room temperature for 24 h, and then the solvent was removed under vacuum. The residue obtained was treated with water (20 mL), and an insoluble reddish product was collected by filtration, washed with water, recrystallized from acetonitrile, and dried under vacuum.

*Bis(1-ethyl-3-methyl-1,3-dihydro-2H-benzimidazol-2-ylidene)-diiodonickel(II) (**5a**).* Yield: 1.703 g (67%, Method A) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 1.85−1.88 (m, 6H, $2CH_3$), 4.49 and 4.50 (both s, 6H, $2CH_3$), 5.17−5.22 (m, 4H, $2CH_2$), 7.18−7.22 (m, 4H, Ar), 7.29−7.32 (m, 4H, Ar). The ^{13}C NMR spectrum of **5a** could not be obtained due to low solubility. Anal. Calcd for $C_{20}H_{24}N_4I_2Ni$: C, 37.95; H, 3.82; N, 8.85. Found: C, 38.14; H, 3.94; N, 8.74.

*Bis(1-butyl-3-methyl-1,3-dihydro-2H-benzimidazol-2-ylidene)-diiodonickel(II) (**5b**).* Yield: 1.252 g (45%, Method A), 0.317 g (23%, Method C) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 1.11 and 1.15 (both t, J = 7.3 Hz and J = 7.3 Hz, 6H, $2CH_3$), 1.64−1.70 (m, 4H, $2CH_2$), 2.34−2.41 (m, 4H, $2CH_2$), 4.51 and 4.52 (both s, 6H, $2CH_3$), 5.03−5.08 (m, 4H, $2CH_2$), 7.18−7.19 (m, 4H, Ar), 7.27−7.29 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 13.9, 14.0, 20.76, 20.78, 30.7, 31.0, 34.6, 34.8, 48.6, 48.7, 109.15, 109.23, 109.60, 109.63, 121.9, 122.0, 135.5, 136.3, 189.0, 189.1 (signals are partially overlapped). HRMS (ESI): calcd for $C_{24}H_{32}IN_4Ni^+$ $[M - I^-]^+$ 561.1020, found 561.1005. Anal. Calcd for $C_{24}H_{32}N_4I_2Ni$: C, 41.83; H, 4.68; N, 8.13. Found: C, 41.88; H, 4.76; N, 8.32.

*Bis(1-benzyl-3-butyl-1,3-dihydro-2H-benzimidazol-2-ylidene)-dibromonickel(II) (**5c**).* Yield: 1.713 g (57%, Method A) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 0.87−0.90 and 1.15−1.18 (both m, 6H, $2CH_3$), 1.39−1.45 and 1.71−1.77 (both m, 4H, $2CH_2$), 2.32−2.37 and 2.45−2.50 (both m, 4H, $2CH_2$), 5.15−5.18 and 5.26−5.28 (both m, 4H, $2CH_2$), 6.46 and 6.69 (both s, 4H, $2CH_2$), 6.94−7.68 (m, 18H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 13.7, 14.1, 20.6, 20.9, 31.7, 31.8, 48.4, 52.8, 53.3, 109.7, 109.8, 110.8, 111.0, 122.15, 122.24, 127.7, 127.8, 127.9, 128.0, 128.6, 128.8, 134.7, 135.0, 135.2, 135.3, 135.4, 135.7, 184.4, 184.5 (signals are partially overlapped). Anal. Calcd for $C_{36}H_{40}N_4Br_2Ni$: C, 57.87; H, 5.40; N, 7.50. Found: C, 58.15; H, 5.31; N, 7.36.

*Dibromobis(1,3-dibutyl-1,3-dihydro-2H-benzimidazol-2-ylidene)-nickel(II) (**5d**).* Yield: 1.734 g (64%, Method A), 0.703 g (52%, Method C) of red-brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) (mixture of *syn* and *anti* isomers): δ 1.12 (t, J = 7.4 Hz, 12H, $4CH_3$), 1.67−1.74 (m, 8H, $4CH_2$), 2.38−2.44 (m, 8H, $4CH_2$), 5.29 (t, J = 7.4 Hz, 8H, $4CH_2$), 7.17−7.19 (m, 4H, Ar), 7.31−7.33 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) (mixture of *syn* and *anti* isomers): δ 14.1, 20.9, 31.7, 48.4, 109.9, 122.0, 135.0, 183.4. HRMS (ESI): calcd for $C_{30}H_{44}BrN_4Ni^+$ $[M - Br^-]^+$ 597.2097, found 597.2088. Anal. Calcd for $C_{30}H_{44}N_4Br_2Ni$: C, 53.05; H, 6.53; N, 8.25. Found: C, 53.24; H, 6.42; N, 8.34.

*Bis(1,3-dimethyl-1,3-dihydro-2H-imidazol-2-ylidene)diiodonickel-(II) (**6a**).* Yield: 1.010 g (50%, Method B) of red crystals. The physical and spectral characteristics of the product obtained are identical with those described in the literature.[17]

*Bis(1-butyl-3-methyl-1,3-dihydro-2H-imidazol-2-ylidene)-diiodonickel(II) (**6b**).* Yield: 1.298 g (55%, Method B) of reddish brown crystals. The physical and spectral characteristics of the product obtained are identical with those described in the literature.[9a]

General Procedure for the Hydrolysis of Nickel(II) Complexes 4−6. A mixture of the compound **4−6** (0.1 mmol), water (2 mL), and CH_3CN (18 mL) was heated to 70 °C (see Table 2). A bluish green powder of $Ni(OH)_2$ that precipitated during the synthesis was filtered out, and the filtrate was evaporated under reduced pressure to afford a white or yellowish solid of compound **1a−e**, **2a−d**, **3a** or 1-butyl-3-methyl-1*H*-imidazol-3-ium iodide (**3c**). The physical and spectral characteristics of the products obtained are identical with those described above for **1a−e**, **2a−d**, and **3a**. The characteristics of compound **3c** are identical with those described in the literature.[9a]

Hydrolysis Kinetics. Kinetic experiments on the hydrolysis of compounds **4a−e** were carried out in NMR tubes. D_2O (70 μL) was added to a solution of compound **4a−e** (10.0 mg) in 600 μL of CD_3CN (THF-d_8 for **6c**). The resulting mixture was shaken and thermostated at 70 ± 1 °C. At certain intervals, the mixture was centrifuged, and its ^{1}H NMR spectrum was recorded.

Kinetic experiments on the hydrolysis of compounds **5a−d** and **6a,b** were performed in 5 mL screw-top glass vials. A magnetically stirred solution of the corresponding Ni complex (5 mg) in a mixture of CH_3CN (3 mL) and water (0.35 mL) was thermostated at 70 ± 1 °C for an appropriate amount of time. Then, the solvent was removed quickly under reduced pressure, and the solid obtained was dissolved in 600 μL of $CDCl_3$. The solution was centrifuged, and its ^{1}H NMR spectrum was recorded.

The relative concentrations of starting complex **4−6** and the corresponding proligands formed during hydrolysis were determined from the integral intensities of the signals of α protons of *N*-alkyl groups.

X-ray Crystal Structure Determination of 4e and 5c,d. Data were collected on a Bruker SMART APEX-II CCD diffractometer (λ(Mo Kα) radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the SADABS program.[18] For details, see the Supporting Information. The structures were solved by

DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX

direct methods and refined by the full-matrix least-squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The crystal of **4e** contained a solvate dichloroethane molecule occupying a special position on the mirror plane. The solvate molecule was disordered over two sites with equal occupancies. All hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters (U_{iso}(H) = 1.5[U_{eq}(C)] for the CH_3 groups and U_{iso}(H) = 1.2[U_{eq}(C)] for the other groups). All calculations were carried out using the SHELXTL program.[19] Crystallographic data for **4e** and **5c**,**d** have been deposited with the Cambridge Crystallographic Data Center. CCDC 1426180 (**4e**), CCDC 1426181 (**5c**), and CCDC 1426182 (**5d**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, + 44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk; web, www.ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00856.

NMR spectra for the synthesized compounds and details of the X-ray structure determinations (PDF)
Crystallographic data for **4e** (CIF)
Crystallographic data for **5c** (CIF)
Crystallographic data for **5d** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for V.P.A.: val@ioc.ac.ru.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Russian Science Foundation (grant no. 14-23-00078). Technical assistance by Dr. Chizhov A. O. and Mr. Fakhrutdinov A. N. is gratefully acknowledged. The authors also thank the Shared Research Center "Nanotechnologies" of the Platov South-Russian State Polytechnic University and the Department of Structural Studies of Zelinsky Institute of Organic Chemistry for analytical services.

■ REFERENCES

(1) (a) Henrion, M.; Ritleng, V.; Chetcuti, M. J. *ACS Catal.* **2015**, *5*, 1283−1302. (b) Han, F.-S. *Chem. Soc. Rev.* **2013**, *42*, 5270−5298. (c) Haynes, M. T.; Jackson, E. P.; Montgomery, J. In *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2014; pp 371−396. (d) Prakasham, A. P.; Ghosh, P. *Inorg. Chim. Acta* **2015**, *431*, 61−100.

(2) (a) Hu, X. *Chem. Sci.* **2011**, *2*, 1867−1886. (b) Ren, P.; Vechorkin, O.; von Allmen, K.; Scopelliti, R.; Hu, X. *J. Am. Chem. Soc.* **2011**, *133*, 7084−7095. (c) Vechorkin, O.; Godinat, A.; Scopelliti, R.; Hu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 11777−11781. (d) Thoi, V. S.; Chang, C. J. *Chem. Commun.* **2011**, *47*, 6578−6580. (e) Orlov, N. V.; Chistyakov, I. V.; Khemchyan, L. L.; Ananikov, V. P.; Beletskaya, I. P.; Starikova, Z. A. *J. Org. Chem.* **2014**, *79*, 12111−12121. (f) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596−1636.

(3) (a) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299−309. (b) Ananikov, V. P. *ACS Catal.* **2015**, *5*, 1964−1971.

(4) (a) Glorius, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 8347−8349. (b) Tollefson, E. J.; Hanna, L. E.; Jarvo, E. R. *Acc. Chem. Res.* **2015**, *48*, 2344−2353. (c) Ananikov, V. P.; Gayduk, K. A.; Starikova, Z. A.; Beletskaya, I. P. *Organometallics* **2010**, *29*, 5098−5102. (d) Kashin, A. S.; Ananikov, V. P. *J. Org. Chem.* **2013**, *78*, 11117−11125.

(5) (a) Johnson, S. A. *Dalton Trans.* **2015**, *44*, 10905−10913. (b) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48*, 1995−2003. (c) Kurahashi, T.; Matsubara, S. *Acc. Chem. Res.* **2015**, *48*, 1703−1716. (d) Tobisu, M.; Chatani, N. *Acc. Chem. Res.* **2015**, *48*, 1717−1726.

(6) (a) Standley, E. A.; Tasker, S. Z.; Jensen, K. L.; Jamison, T. F. *Acc. Chem. Res.* **2015**, *48*, 1503−1514. (b) Jackson, E. P.; Malik, H. A.; Sormunen, G. J.; Baxter, R. D.; Liu, P.; Hengbin, W.; Shareef, A.-R.; Montgomery, J. *Acc. Chem. Res.* **2015**, *48*, 1736−1745. (c) Ananikov, V. P.; Khokhlova, E. A.; Egorov, M. P.; Shakharov, A. M.; Zlotin, S. G.; Kucherov, A. V.; Kustov, L. M.; Gening, M. L.; Nifantiev, N. E. *Mendeleev Commun.* **2015**, *25*, 75−82.

(7) (a) Li, B.; Dixneuf, P. H. *Chem. Soc. Rev.* **2013**, *42*, 5744−5767. (b) Gu, Y.; Jérôme, F. *Chem. Soc. Rev.* **2013**, *42*, 9550−9570. (c) García-Álvarez, R.; Crochet, P.; Cadierno, V. *Green Chem.* **2013**, *15*, 46−66. (d) Gonsalvi, L.; Bertini, F.; Guerriero, A.; Mellone, I. In *Organometallics and Related Molecules for Energy Conversion Green Chemistry and Sustainable Technology*; Wong, W.-Y., Ed.; Springer: New York, 2015; pp 395−419. (e) Levin, E.; Ivry, E.; Diesendruck, Ch. E.; Lemcoff, N. G. *Chem. Rev.* **2015**, *115*, 4607−4692.

(8) (a) Velazquez, H. D.; Verpoort, F. *Chem. Soc. Rev.* **2012**, *41*, 7032−7060. (b) Schaper, L.-A.; Hock, S. J.; Herrmann, W. A.; Kuhn, F. E. *Angew. Chem., Int. Ed.* **2013**, *52*, 270−289. (c) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−496.

(9) (a) McGuinness, D. S.; Mueller, W.; Wasserscheid, P.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. *Organometallics* **2002**, *21*, 175−181. (b) Huynh, H. V.; Holtgrewe, C.; Pape, T.; Koh, L. L.; Hahn, E. *Organometallics* **2006**, *25*, 245−249.

(10) Dash, C.; Shaikh, M. M.; Butcher, R. J.; Ghosh, P. *Dalton Trans.* **2010**, *39*, 2515−2524.

(11) (a) Zhang, D.; Zhou, S.; Li, Zh.; Wang, Q.; Weng, L. *Dalton Trans.* **2013**, *42*, 12020−12030. (b) Hameury, S.; de Frémont, P.; Breuil, P.-A. R.; Olivier-Bourbigou, H.; Braunstein, P. *Organometallics* **2015**, *34*, 2183−2201.

(12) Henrion, M.; Oertel, A. M.; Ritleng, V.; Chetcuti, M. J. *Chem. Commun.* **2013**, *49*, 6424−6426.

(13) Hindi, K. M.; Siciliano, T. J.; Durmus, S.; Panzner, M. J.; Medvetz, D. A.; Reddy, D. V.; Hogue, L. A.; Hovis, C. E.; Hilliard, J. K.; Mallet, R. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *J. Med. Chem.* **2008**, *51*, 1577−1583.

(14) (a) Astleford, B. A.; Goe, G. L.; Keay, J. G.; Scriven, E. F. V. *J. Org. Chem.* **1989**, *54*, 731−732. (b) Saif, M. J.; Flower, K. R. *Transition Met. Chem.* **2013**, *38*, 113−118. (c) Gupta, S.; Chatterjee, A.; Das, S.; Basu, B.; Das, B. *J. Chem. Eng. Data* **2013**, *58*, 1−6.

(15) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422−3427.

(16) (a) Becker, H. G. O.; Hoffmann, G.; Gwan, K. M.; Knüpfer, L. *J. Prakt. Chem.* **1988**, *330*, 325−337. (b) Abenhaïm, D.; Díez-Barra, E.; de la Hoz, A.; Loupy, A.; Sánchez-Migallón, A. *Heterocycles* **1994**, *38*, 793−802. (c) Gnanamgari, D.; Moores, A.; Rajaseelan, E.; Crabtree, R. H. *Organometallics* **2007**, *26*, 1226−1230. (d) Alfaia, A. J. I.; Calado, A. R. T.; Reis, J. C. R. *Eur. J. Org. Chem.* **2000**, *2000*, 3627−3631. (e) Jishkariani, D.; Hall, C. D.; Demircan, A.; Tomlin, B. J.; Steel, P. J.; Katritzky, A. R. *J. Org. Chem.* **2013**, *78*, 3349−3354. (f) Kishore, R.; Das, S. K. *J. Mol. Struct.* **2013**, *1053*, 38−47. (g) Huang, W.; Guo, J.; Xiao, Y.; Zhu, M.; Zou, G.; Tang, J. *Tetrahedron* **2005**, *61*, 9783−9790. (h) Benac, B. L.; Burgess, E. M.; Arduengo, A. J., III *Org. Synth.* **1986**, *64*, 92.

(17) Herrmann, W. A.; Gerstberger, G.; Spiegler, M. *Organometallics* **1997**, *16*, 2209−2212.

(18) Sheldrick, G. M. *SADABS, v. 2.03, Bruker/Siemens Area Detector Absorption Correction Program*; Bruker AXS, Madison, WI, 2003.

(19) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

DOI: 10.1021/acs.organomet.5b00856
Organometallics XXXX, XXX, XXX−XXX