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Bisisocyanide Complexes of Zn(II) Halides: Synthesis, Structure, and Application in the Catalysis of Isocyanides Reaction with Secondary Amines

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Abstract—Isocyanide zinc complexes $[ZnX_2(CNR)_2]$ (X = Cl, Br, I; R = Xyl, Cy, Bu^t) have been prepared via the interaction of the corresponding zinc halides ZnX_2 and isocyanide CNR in toluene at 100°C (yield 64–77%) and characterized by the data of elemental analysis, mass spectrometry, IR and NMR spectroscopy, and X-ray diffraction analysis. The zinc complexes $[ZnBr_2(CNR)_2]$ (R = Xyl, Cy) have been used as catalysts for the synthesis of formamidines $R^1N{=}CHNR^2_2$ [R^1 = Xyl, Cy; $R^2_2 = Et_2$, $(CH_2)_4$, $(CH_2CH_2)_2NMe$, Me + CH_2Ph] from isocyanides CNR^1 and secondary amines HNR^2_2 in bulk (yield 92–98%).

Keywords: isocyanide, zinc complex, nucleophilic addition, reactivity, formamidine
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Isocyanide complexes are known for nearly all transition metals. They are widely used as precursors in the synthesis of other complexes and organometal compounds as well as catalysts [1]. Moreover, isocyanide complexes are intermediates in most metal-promoted and metal-catalyzed reactions of isocyanides [1]. Whereas the isocyanide complexes of transition metals of the second and third decades have been well studied, structure and properties of these complexes of 3*d*-metals (including zinc) have been scarcely investigated.

Only a few examples of zinc complexes with isocyanides have been described. Bisisocyanide complexes of zinc(II) dihalides $[ZnBr_2(CNBu\text{-}t)_2]$ [2], $[ZnI_2(CNPr\text{-}i)_2]$ [3], and $[ZnI_2(CNBu\text{-}t)_2]$ [3] have been prepared via the interaction of $ZnBr_2$ [2] or $\{ZnI_2[(SCNMe_2)_2]_2\}$ [3] and the corresponding isocyanide. The mixed complexes $[Zn(EAr)_2(CNBu\text{-}t)_2]$ and $[Zn_2(\mu\text{-}EAr)_2(EAr)_2(CNBu\text{-}t)_2]$ (E = S, Se; Ar = 2,4,6-tri-*tert*-butylphenyl) are formed in the reaction between $Zn(EAr)_2$ and CNBu-*t*, the type of the resulting complex being determined by the $Zn(EAr)_2$: CNBu-*t* ratio [4]. Binuclear complexes containing the Zn–Zn bond $[Zn_2(CNR)_6][BAr_4]_2$ {R = Ph, *t*-Bu, Ar = $B[C_6H_3(CF_3)_2]_4$} can be obtained via the interaction of $[Zn_2(THF)_6][BAr]_2$ with CNR [5].

Despite being poorly studied, isocyanide zinc complexes have been successfully used in the laboratory practice during the recent 5 years: as catalysts for the synthesis of 2,4,5-substituted oxazoles from carboxylic acids and isocyanides [2], for the manufacture of zinc analog of calomel electrode [5], and for structure elucidation of intermediates of organic transformations [6–8]. In this work, we discuss the data in the synthesis of new isocyanide complexes of zinc(II) and the study of Zn(II)-catalyzed nucleophilic addition of secondary amines to isocyanides.

Isocyanide zinc complexes $[ZnX_2(CNR)_2]$ (X = Cl, Br, I; R = Xyl, Cy, *t*-Bu) **2a**–**2c**, **3a**–**3c**, and **4a**–**4c** were prepared via the procedure adopted from [2]: the interaction of zinc halide with isocyanide in toluene at 100°C during 10 min (Scheme 1). The target complexes **2a**–**2c**, **3a**–**3c**, and **4a**–**4c** were recrystallized from a dichloromethane–hexane mixture (4 : 1 by volume), their yield being 64–77%. Complexes **2a**, **2c**, **3a**–**3c**, and **4a**–**4c** were colorless crystalline substances, and compound **2b** was yellowish oil.

The new complexes **2a**–**2c**, **3a**, **3b**, and **4a**, **4b** were characterized by the data of elemental analysis, mass spectrometry, IR, ^1H NMR, and ^{13}C–$\{^1H\}$ NMR spectroscopy. The structure of known compounds **3c** [2] and **4c** [3] was confirmed by the set of physico-

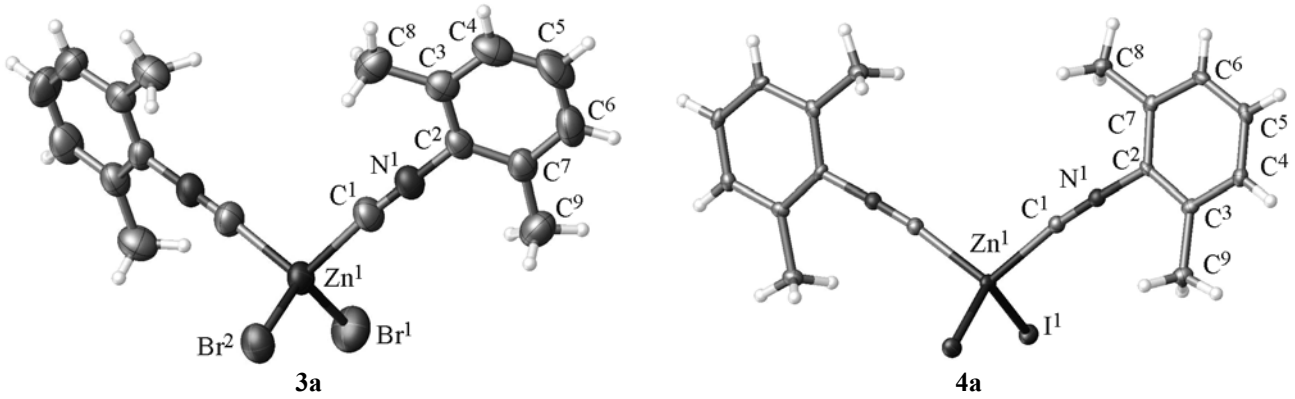


Fig. 1. General view of molecules of complexes **3a** and **4a**.

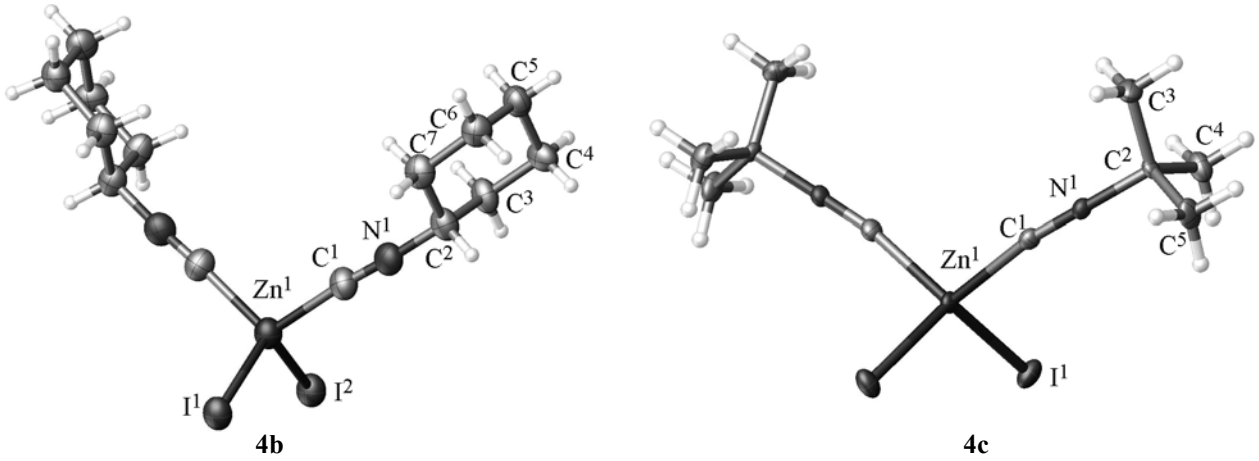
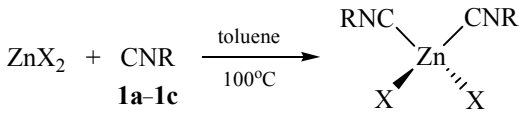


Fig. 2. General view of molecules of complexes **4b** and **4c**.

chemical data. Structure of complexes **3a** and **4a**–**4c** was elucidated by means of single-crystal X-ray diffraction analysis.

The elemental analysis data for complexes **4a**–**4c** were in good agreement with the calculated values. The poor agreement for the elemental analysis data of complexes **2a**–**2c** and **3a**–**3c** was due to their high hygroscopicity. Mass spectra of complexes **2**–**4** contained the peaks corresponding to the products of fragmentation with elimination of the halide ion $[M - X]^+$. IR spectra of complexes **2**–**4** contained a single strong absorption band of the ν(C≡N) stretching vibrations at 2206–2237 cm^{-1}. The band position was in good agreement with the reference data for isocyanide complexes of zinc [2]. The increase in the frequency of the ν(CN) absorption in comparison to the free isocyanide [ν(CN) 2114 cm^{-1} [9]) evidenced the increase in the electrophilic character of the isocyanide carbon atom and indirectly reflected the increase in the reactivity with respect to nucleophiles [10].

Scheme 1.



X = Cl, R = Xyl (**2a**), Cy (**2b**), *t*-Bu (**2c**); X = Br, R = Xyl (**3a**), Cy (**3b**), *t*-Bu (**3c**); X = I, R = Xyl (**4a**), Cy (**4b**), *t*-Bu (**4c**).

The solid-state structure of complexes **3a** and **4a**–**4c** was confirmed by means of single-crystal X-ray diffraction analysis (Figs. 1 and 2). The XRD data for the complexes revealed the practically non-distorted tetrahedral structure: the CZnC and CZnX angles were 104.9°–108.3° and 102.1°–109.5°, respectively (cf. the table). The C≡N bond length equaled 1.140(3)–1.151(15) Å, coinciding with the data for other isocyanide complexes [11–14].

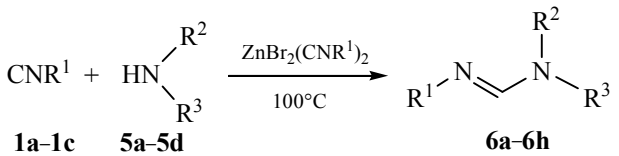
Reactivity and chemical properties of the free isocyanide and its complexes are different due to the

Selected bond lengths and bond angles in the molecules of compounds **3a** and **4a**–**4c**

Bond, angle	**3a**	**4a**	**4b**	**4c**
		d, Å		
$Zn^1–X^1$	2.3332(7)	2.5579(3)	2.5714(17)	2.5703(4)
$Zn^1–X^2$	2.3523(6)	2.5579(3)	2.5724(18)	2.5703(4)
$Zn^1–C^1$	2.085(3)	2.078(3)	2.058(11)	2.061(3)
$C^1–N^1$	1.140(3)	1.143(3)	1.151(15)	1.145(5)
$N^1–C^2$	1.402(3)	1.404(3)	1.470(14)	1.475(4)
		ω, deg		
$X^1Zn^1X^2$	117.78(3)	120.251(19)	112.58(8)	116.32(2)
$X^1Zn^1C^1$	106.45(8)	107.10(7)	109.5(3)	114.08(10)
$X^2Zn^1C^1$	110.20(8)	107.84(7)	109.5(3)	102.13(10)
$C^1Zn^1C^2$	104.93(15)	105.87(14)	106.6(7)	108.26(19)
$C^1N^1C^2$	178.6(3)	176.3(3)	176.6(12)	173.8(3)
$Zn^1C^1N^1$	174.1(2)	172.0(2)	175.3(10)	169.4(3)

structure changes resulting from the coordination of the isocyanide to the metal site [15]. The coordination at a metal site in high oxidation state (and, hence, lacking electrons) imparts electrophilic properties to the coordinated carbon atom of isocyanide [16], whereas the carbon atom of a free isocyanide is rather nucleophilic [17]. Hence, the coordination opens the possibility of performing nucleophilic addition of weak nucleophiles (that normally do not react with isocyanides) at the triple C≡N bond [16, 18]. For example, acyclic diaminocarbene complexes successfully used as catalysts of cross-coupling reactions can be obtained using kinetically inert metal centers of 4*d*- and 5*d*-elements such as palladium(II) and platinum(II) [19–22]. In the case of kinetically labile metal centers of 3*d*-elements, nucleophilic coupling of CNR with amines is followed by decoordination of the diaminocarbene ligand and its isomerization in formamidine [23]. To verify the suggested electrophilic activation of isocyanides in the zinc complexes, we studied their interaction with secondary amines. Heating the complex **3b** with equimolar amount of pyrrolidine **5b** (100°C, 1 h) led to the formation of *N*-(purrolidin-1-ylmethylene)cyclohexylamine **6e** in a preparatory yield (91%).

Scheme 2.



1a–**1c** **5a**–**5d** **6a**–**6h**

1, R^1 = Xyl (**a**), Cy (**b**); **5**, $R^2 = R^3$ = Et (**a**), R^2, R^3 = –$(CH_2)_4$– (**b**), R^2, R^3 = –$(CH_2)_2N(Me)(CH_2)_2$– (**c**), R^2 = Me, R^3 = Bn (**d**); **6**, R^1 = Xyl, $R^2 = R^3$ = Et (**a**), R^2, R^3 = –$(CH_2)_4$– (**b**), R^2, R^3 = –$(CH_2)_2N(Me)(CH_2)_2$– (**c**), R^2 = Me, R^3 = Bn (**d**); R^1 = Cy, $R^2 = R^3$ = Et (**e**), R^2, R^3 = –$(CH_2)_4$– (**f**), R^2, R^3 = –$(CH_2)_2N(Me)(CH_2)_2$– (**g**), R^2 = Me, R^3 = Bn (**h**).

The catalytic interaction of secondary amines **5a**–**5d** and isocyanides CNR **1a**, **1b** in the presence of 1 mol % of the corresponding isocyanide complex $[ZnBr_2(CNR)_2]$ **3** [R = Xyl (**3a**), Cy (**3b**), 100°C, 1 h] led to the formation of formamidines **6a**–**6h** in a preparatory yield 92–98% (Scheme 2). Acyclic (**5a**, **5d**) and cyclic secondary amines (**5b**, **5c**) were found to be equally reactive in the interaction. Moreover, we demonstrated the use of isocyanides with aliphatic (R = Cy) as well as aromatic (R = Xyl) substituents. At the same time, *tert*-butylisocyanide **1c** was found to be inactive in the reaction: the reaction mixture after heating amines **5a**–**5d** with CNBu-*t* {1 mol % $[ZnBr_2(CNBu\text{-}t)_2]$, 100°C, 1 h} contained only the starting isocyanide and the amine. The coupling of amines **5a**–**5d** with isocyanides **1** was zinc-catalyzed, as confirmed the experiment showing no interaction between amine **5b** with isocyanides **1a**, **1b** at 100°C during 1 h. The structure of compounds **6f** [24] and **6e** [25] was confirmed by the comparison of their spectral

parameters with the reference data; compounds **6a–6d, 6g, 6h** have not been described earlier, and their structure was elucidated from the data of mass spectrometry as well as ^{1}H and ^{13}C–{^{1}H} NMR spectroscopy.

Earlier, a single example of zinc-catalyzed reaction of isocyanide CNBu-*t* and primary amine NH_2Bu-*t* ($ZnCl_2$, 16 mol %, 105–110°C, 48 h) affording *t*-BuN=CHNHBu-*t* isolated as the picrate in low yield (18%) has been described [26]. The copper(I)-catalyzed (0.2 mol % CuCl) coupling of isocyanides CNR (R = Cy, *n*-Bu, Ph) with primary (cyclohexylamine, *n*-butylamine, aniline) and secondary (piperidine, piperazine, methylphenylamine) amines (3.3 equiv.) giving the corresponding formamidines in 20–97% yield has been studied as well [23]. The suggested mechanism includes the reaction of isocyanide and amine in coordination sphere of copper(I).

In summary, in this study we prepared a series of zinc(II) isocyanide complexes $[ZnX_2(CNR)_2]$ (X = Cl, Br, I; R = Xyl, Cy, *t*-Bu) and demonstrated the possibility of the addition of such nucleophiles as amines to their triple CN bond. It was shown that the reaction of isocyanides CNR and secondary amines catalyzed by the $[ZnBr_2(CNR)_2]$ complexes (1 mol %) occurred in bulk and led to the formation of formamidines in preparatory yields (92–98%). The obtained data are in good agreement with the earlier report [23] and evidence the coordination of isocyanide at the Zn(II) center accompanied by its electrophilic activation and the promotion of the reaction with amines.

EXPERIMENTAL

The applied chemicals were purchased from Aldrich and used as received. Mass spectrometry analysis was performed using a Bruker micrOTOF (Bruker Daltonics) spectrometer (electrospray ionization; methanol as solvent). The *m*/*z* values are reported for the most common isotopes. IR spectra were recorded using a Shimadzu 8400S spectrophotometer (4000–400 cm^{-1}, KBr). ^{1}H and ^{13}C–{^{1}H} NMR spectra were recorded at room temperature using a Bruker Avance II+ [400.13 (^{1}H), 100.61 MHz (^{13}C)] spectrometer in $CDCl_3$.

X-ray diffraction studies were performed using Agilent Technologies Excalibur Eos and Agilent Technologies Supernova single-crystal diffractometers equipped with planar detector of the reflected beam Atlas CCD. The measurements were performed at 100 K using monochromatic radiation (MoK_α, CuK_α). Unit cell parameters were refined by least-squares method. The structures were solved via the direct method using SHELXL software [27] from OLEX2 package [28]. Correction for extinction was introduced using CrysAlisPro software package [29]. Positions of hydrogen atoms of the organic molecules were determined using SHELX package, with U_{iso}(H) = 1.5U_{eq}(C), and C–H 0.96 Å for CH_3 groups, 1.2U_{eq}(C) and C–H 0.97 Å for CH_2 groups, 1.2*U*eq(C) and C–H 0.93 Å for CH groups. The crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC 1552947–1552950).

Synthesis of zinc bisisocyanide complexes. The corresponding isocyanide (1.7 mmol) was added to a stirred suspension of ZnX_2 (0.7 mmol) in toluene (5 mL) heated to 100°C. The mixture was stirred during 10 min, and the solvent was distilled off at a reduced pressure (30 mbar, 20°C). The product was recrystallized from a dichloromethane–*n*-hexane mixture (4 : 1 v/v). Due to the high hygroscopicity of complexes **2a**–**2c** and **3a**–**3c**, their elemental data were not satisfactory.

Dichlorobis(2,6-dimethylphenylisocyanide)zinc (2a). Yield 0.21 g (77%). IR spectrum, ν, cm^{-1}: 2990 m (C–H), 2208 s (CN). ^{1}H NMR spectrum, δ, ppm: 2.52 s (6H, CH_3), 7.22 d (2H, *m*-CH, *J* = 7.7 Hz), 7.36 t (1H, *p*-CH, *J* = 7.7 Hz). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 18.73, 123.69, 128.33, 131.24, 136.88, 145.01. Mass spectrum, *m*/*z*: 361.0478 $[M - Cl]^+$.

Dichlorobis(cyclohexylisocyanide)zinc (2b). Yield 0.16 g (64%). IR spectrum, ν, cm^{-1}: 2943 m (C–H), 2237 s (CN). ^{1}H NMR spectrum, δ, ppm: 1.30–2.10 m (20H, CH_2), 3.80–4.05 m (2H, CH). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 22.60, 24.54, 31.54, 54.38, 132.77. Mass spectrum, *m*/*z*: 317.0775 $[M - Cl]^+$.

Dichlorobis(*tert*-butylisocyanide)zinc (2c). Yield 0.15 g (71%). IR spectrum, ν, cm^{-1}: 2992 m (C–H), 2235 s (CN). ^{1}H NMR spectrum, δ, ppm: 1.59 s (9H, CH_3). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 29.7, 58.5, 131.2. Mass spectrum, *m*/*z*: 265.0466 $[M - Cl]^+$.

Dibromobis(2,6-dimethylphenylisocyanide)zinc (3a). Yield 0.24 g (71%). IR spectrum, ν, cm^{-1}: 3064 m (C–H), 2206 s (CN). ^{1}H NMR spectrum, δ, ppm: 2.52 s (6H, CH_3), 7.20 d (2H, *m*-CH, *J* = 7.7 Hz), 7.34 t (1H, *p*-CH, *J* = 7.7 Hz). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 18.77, 123.65, 128.41, 131.33, 136.61,

144.91. Mass spectrum, *m*/*z*: 404.9948 [M − Br]$^+$. X-ray diffraction: monoclinic crystals, space group $P2_1/m$, $C_{18}H_{18}N_2Br_2Zn$, M 487.53, a 7.8126(3), b 16.2361(4), c 8.6878(3) Å, α 90°, β 115.695(4)°, γ 90°, V 993.04(5) Å^3, Z 2, d 1.630 mg/mm^3.

Dibromobis(cyclohexylisocanide)zinc (3b). Yield 0.21 g (69%). IR spectrum, ν, cm^{-1}: 2951 m (C–H), 2236 s (CN). ^{1}H NMR spectrum, δ, ppm: 1.30–2.10 m (20H, CH_2), 3.76–4.12 m (2H, CH). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 22.06, 24.50, 31.55, 54.34, 132.63. Mass spectrum, *m*/*z*: 361.0239 [M − Br]$^+$.

Dibromobis(*tert*-butylisocyanide)zinc (3c). Yield 0.21 g (77%). Spectral data coincided with the reference ones [2].

Diiodobis(2,6-dimethylphenylisocyanide)zinc (4a). Yield 0.30 g (75%). IR spectrum, ν, cm^{-1}: 2987 m (C–H), 2209 s (CN). ^{1}H NMR spectrum, δ, ppm: 2.53 s (6H, CH_3), 7.21 d (2H, *m*-CH, J = 7.7 Hz), 7.38 t (1H, *p*-CH, J = 7.7 Hz). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 18.81, 123.57, 128.45, 131.37, 136.79, 142.9. Mass spectrum, *m*/*z*: 452.9824 [M − I]$^+$. Found, %: C 37.14; H 3.08; N 4.81. $C_{18}H_{18}N_2ZnI_2$. Calculated, %: C 37.18; H 3.12; N 4.82. X-ray diffraction: monoclinic crystals, space group $C2/c$, $C_{18}H_{18}N_2I_2Zn$, M 581.51, a 24.7730(14), b 8.13738(16), c 13.4028(8) Å, α 90°, β 131.626(10)°, γ 90°, V 2019.60(17) Å^3, Z 4, d 1.913 mg/mm^3.

Diiodobis(cyclohexylisocyanide)zinc (4b). Yield 0.28 g (74%). IR spectrum, ν, cm^{-1}: 2946 m (C–H), 2233 s (CN). ^{1}H NMR spectrum, δ, ppm: 1.30–2.10 m (20H, CH_2), 3.72–4.21 m (2H, CH). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 22.43, 24.31, 31.29, 54.71, 133.10. Mass spectrum, *m*/*z*: 409.0140 [M − I]$^+$. Found, %: C 31.22; H 4.08; N 5.16. $C_{14}H_{22}N_{22}ZnI_2$. Calculated, %: C 31.28; H 4.13; N 5.21. X-ray diffraction: orthorhombic crystals, space group $Pmn2_1$, $C_{14}H_{22}N_2I_2Zn$, M 537.51, a 14.2463(4), b 10.4337(3), c 5.97379(15) Å, α 90°, β 90°, γ 90°, V 887.96(4) Å^3, Z 2, d 2.010 mg/mm^3.

Diiodo(*tert*-butylisocyanide)zinc (4c). Yield 0.26 g (76%). IR spectrum, ν, cm^{-1}: 2989 m (C–H), 2230 s (CN). ^{1}H NMR spectrum, δ, ppm: 1.57 s (9H, CH_3). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 29.71, 58.58, 129.54. Mass spectrum, *m*/*z*: 356.9812 [M − I]$^+$. Found, %: C 24.71; H 3.69; N 5.72. $C_{10}H_{18}N_2ZnI_2$. Calculated, %: C 24.74; H 3.74; N 5.77. X-ray diffraction: orthorhombic crystals, space group $Pccn$, $C_{10}H_{18}N_2I_2Zn$, M 485.43, a 10.6932(6), b 13.7106(8), c 11.3132(7) Å, α 90°, β 90°, γ 90°, V 1658.62(17) Å^3, Z 4, d 1.944 mg/mm^3.

Reaction of isocyanide complex with amine. A mixture of [$ZnBr_2(CNCy)_2$] **3b** (0.100 g, 0.2 mmol) and pyrrolidine **5b** (0.018 mL, 0.2 mmol) was heated during 1 h at 100°C. After that, 0.5 mL of water was added to the mixture, and the product was extracted with diethyl ether (3×5 mL). The extracts were combined, and the solvent was distilled off at a reduced pressure. The product was purified by chromatography on silica gel eluting with diethyl ether. Yield of formamidine **6f** 91%. Structure and purity of the product were confirmed by the data of ^{1}H NMR spectroscopy in comparison with the reference data [24].

Reaction of isocyanides with amines in the presence of catalytic amount of zinc complexes. **Synthesis of formamidines.** A mixture of isocyanide **1a** or **1b** (0.80 mmol), the corresponding isocyanide complex **3a** or **3b** (0.008 mmol, 1 mol %), and secondary amine **5a**–**5d** (0.8 mmol) was heated at 100°C during 1 h. The reaction mixture was then cooled to ambient and suspended in diethyl ether (10 mL), the zinc compounds were centrifuged off, and the supernatant was evaporated at a reduced pressure (30 mbar, 20°C). Formamidines **6a**–**6h** were isolated as oily substances with 92–98% yield, without further purification.

***N*'-(2,6-Dimethylphenyl)-*N*,*N*-diethylformamidine (6a).** Yield 0.16 g (97%). ^{1}H NMR spectrum, δ, ppm: 1.25 t (6H, CH_3, J = 7.0 Hz), 2.17 s (6H, CH_3), 3.03–4.51 m (4H, CH_2), 6.84 t (1H, *p*-CH, J = 7.0 Hz), 7.02 d (2H, *m*-CH, J = 7.5 Hz), 7.24 s (1H, N=CHN). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 14.64, 18.71, 46.33, 121.86, 127.73, 129.89, 150.54, 152.01. Mass spectrum, *m*/*z*: 205.1714 [M + H]$^+$.

2,6-Dimethyl-*N*-(pyrrolidin-1-ylmethylene)aniline (6b). Yield 0.17 g (98%). ^{1}H NMR spectrum, δ, ppm: 1.95–2.00 m (4H, CH_2), 2.18 s (6H, CH_3), 3.45–3.55 m (4H, CH_2), 6.84 t (1H, *p*-CH, J = 7.5 Hz), 7.01 d (2H, *m*-CH, J = 7.5 Hz), 7.43 s (1H, N=CHN). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm: 18.73, 25.11, 47.00, 121.86, 127.70, 129.76, 148.58, 150.43. Mass spectrum, *m*/*z*: 203.1552 [M + H]$^+$.

2,6-Dimethyl-*N*-[(4-methylpiperazin-1-yl)methylene]aniline (6c). Yield 0.18 g (97%). ^{1}H NMR spectrum, δ, ppm: 2.15 s (6H, CH_3), 2.36 s (3H, CH_3), 2.48–2.59 m (4H, CH_2), 3.49–3.58 m (4H, CH_2), 6.84 t (1H, *p*-CH, J = 7.5 Hz), 7.01 d (2H, *m*-CH, J = 7.5 Hz),

7.19 s (1H, N=CHN). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 18.88, 46.10, 46.35, 46.71, 54.91, 56.39, 127.78, 128.63, 129.50, 149.72, 152.24. Mass spectrum, *m*/*z*: 232. 1824 $[M + H]^+$.

***N*-Benzyl-*N*'-(2,6-dimethylphenyl)-*N*-methylformamidine (6d).** Yield 0.18 g (92%). ^1H NMR spectrum, δ, ppm: 2.23 s (6H, CH_3), 3.01 s (3H, CH_3), 4.00–5.18 m (2H, CH_2), 6.90 t (1H, *p*-CH, *J* = 7.5 Hz), 7.08 d (2H, *m*-CH, *J* = 7.5 Hz), 7.22–7.45 m (6H, CH_{Ar} + N=CHN). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 18.90, 39.87, 57.42, 127.12, 127.43, 128.61, 129.33, 132.17, 133.37, 138.12, 147.27, 151.81. Mass spectrum, *m*/*z*: 253.1713 $[M + H]^+$.

***N*-[(4-Methylpiperazin-1-yl)methylene]cyclohexaneamine (6g).** Yield 0.16 g (95%). ^1H NMR spectrum, δ, ppm: 1.02–1.91 m (10H, CH_2), 2.25 s (3H, CH_3), 2.30–2.35 m (4H, CH_2), 2.75–2.82 m (1H, CH), 3.19–3.28 m (4H, CH_2), 7.29 s (1H, N=CHN). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 24.87, 25.66, 34.08, 44.87, 45.30, 46.94, 55.28, 55.96, 66.72, 154.12. Mass spectrum, *m*/*z*: 210.1984 $[M + H]^+$.

***N*-Benzyl-*N*-methyl-*N*'-cyclohexylformamidine (6h).** Yield 0.18 g (96%). ^1H NMR spectrum, δ, ppm: 1.13–1.83 m (10H, CH_2), 2.78 s (3H, CH_3), 2.95 t.t (1H, CH, *J* = 10.5, 4.0 Hz), 4.34 s (2H, CH_2), 7.19–7.37 m (5H, CH_{Ar}), 7.57 s (1H, N=CHN). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm: 24.82, 25.73, 34.29, 36.14, 54.76, 64.63, 127.95, 128.10, 128.62, 138.02, 153.21. Mass spectrum, *m*/*z*: 231.1838 $[M + H]^+$.

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