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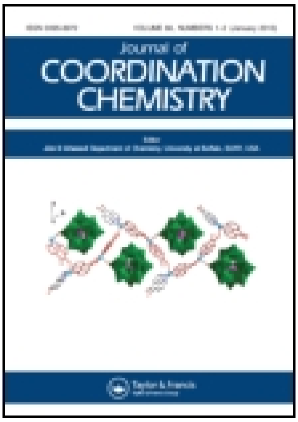

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Cis/trans equilibrium as the way to form Pd carbene catalyst from trans-isocyanide complex

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Accepted author version posted online: 23 Sep 2013.Published online: 06 Nov 2013.

To cite this article: Anton Yakimanskiy, Irina Boyarskaya & Vadim Boyarskiy (2013) Cis/trans equilibrium as the way to form Pd carbene catalyst from trans-isocyanide complex, Journal of Coordination Chemistry, 66:20, 3592-3601, DOI: 10.1080/00958972.2013.847185

To link to this article: http://dx.doi.org/10.1080/00958972.2013.847185

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 20, 3592–3601, http://dx.doi.org/10.1080/00958972.2013.847185

Cis/trans equilibrium as the way to form Pd carbene catalyst from *trans*-isocyanide complex

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(*Received 23 April 2013; accepted 21 August 2013*)

The behavior of Pd(II) *bis*-isocyanide complexes in solution was studied for examples of *bis*-(cyclohexylisocyanide)palladium(II) dichloride (**1**) and diiodide (**2**). The equilibrium between isomeric *cis*- and *trans*-forms of **1** was observed by NMR and IR spectroscopy. Complex **1** (which has the *cis*-configuration in the solid state) gives *cis*-/*trans*-isomeric mixture after dissolving in $CDCl_3$ for several days at room temperature. The effect of heating on the equilibration rate was considered. The studied equilibrium leads to a purely *cis*-structure of Pd carbene complex (**3**) that was synthesized via the interaction of *cis*-/*trans*-isomeric mixture of **1** with benzophenone hydrazone.

Keywords: Pd(II) Isocyanide complexes; Acyclic diaminocarbenes; *Cis/trans* equilibrium; Cross-coupling catalysts

1. Introduction

Acyclic diaminocarbene (ADC) palladium complexes are widely applied as catalysts of cross-coupling reactions [1, 2]. One method to obtain such catalysts is the interaction of palladium(II) *bis*-isocyanide complexes with nitrogen nucleophiles (scheme 1) [2, 3]. This caused a surge in interest to properties of these isocyanide complexes.

Palladium(II) liability to form square-planar complexes [4, 5], palladium(II) *bis*-isocyanide complexes exist as two isomers, with relative *cis*- (**A**) or *trans*- (**B**) arrangements of isocyanide fragments (scheme 2) [4, 5].

A number of dichloro(*bis*-isocyanide)palladium(II) complexes with different R possess *cis*-configuration in the solid state, confirmed by X-ray structural analysis (R = cyclohexyl, C_6H_{11} – [6]; R = tert-butyl, C_4H_9 – [7]; R = benzyl, C_7H_7 – [8]; R = phenyl, C_6H_5 – [9]). However, (*bis*-isocyanide)palladium(II) diiodides are reported to crystallize in the *trans*-form [10, 11].

The structures of several (*bis*-arylisocyanide)palladium(II) complexes in solution have been studied by Levelut *et al.* [12]. Analyzing IR and ^{1}H NMR spectroscopic data, the authors concluded that a mixture of two isomers was present in the solution, in contrast to

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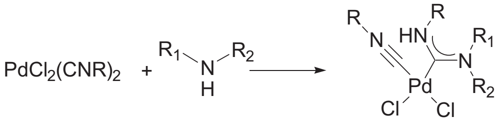
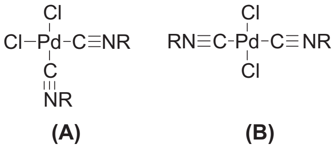


Scheme 1.



Scheme 2.

iodides which existed in the solution exclusively in their *trans*-form. The authors assumed the existence of a *cis-trans* equilibrium for chloride complexes in the solution.

However, the solution behavior of palladium halide complexes with aliphatic isocyanides has not been studied.

2. Results and discussion

The present paper is devoted to the structure and solution behavior of (*bis*-cyclohexylisocyanide)palladium(II) chloride **1**. This complex serves as a precursor for the synthesis of a number of ADC complexes which proved to be efficient catalysts in cross-coupling reactions [13–15], with TON up to 1.4 × 10^6 [13]. Palladium(II) iodide **2** (scheme 3) and its reactivity in the synthesis of ADC complexes are also studied.

2.1. *Complex 1 in solution*

^{1}H NMR study of **1** in $CDCl_3$ solution showed that only one signal of α-hydrogen of cyclohexyl ring is observed at 4.06 ppm just after dissolution of the original solid sample. In a few hours (at 25 °C), one more signal at 3.95 ppm arises in this range, indicating occurrence of the second isomer in the system. Since solid-state **1** is represented by the *cis*-form **1A** [6], the signal at 4.06 ppm may be assigned to **1A** and the other signal to the *trans*-form **1B**.

Analogous data were found in ^{13}C NMR spectra in $CDCl_3$, one signal of the α-carbon of the cyclohexyl ring at 56.4 ppm is observed for freshly dissolved complex and the second signal at 55.5 ppm appears later.

$(CyNC)_2PdCl_2$ $(CyNC)_2PdI_2$

1 **2**

Scheme 3.

The time behavior of **1** in $CDCl_3$ solution was studied at 22 °C. The intensity of the signal at 3.95 ppm in its ^{1}H NMR spectrum increased continuously for 5 days. The established 2 : 1 ratio of **1A** and **1B** signals did not change after that. This indicates that an equilibrium monomer ratio was attained under these conditions. The data are plotted below (figure 1). Thus, a gradual isomerization of **1A** proceeds in the system, and **1B** appears.

The reaction obeys the first-order kinetic equation $\ln C_{1A} = \ln C^{0}{}_{1A} - kt$ and $\ln C_{1B} = kt$ perfectly with $R^2 = 0.995$ for both curves. The calculated $k = 0.021 \pm 0.001\ s^{-1}$ (for both curves). Similar calculations for the formation of the *trans*-isomer resulted in the same k and C^0 values, the absolute term of the equation being normalized to 100. This means that no side processes take place. The coefficient k is the rate constant of the isomerization process.

The isomerization itself might proceed in different ways. An associative process could take place with the formation of an intermediate with an increased coordination number. The isomerization proceeds via this path with participation of the second molecule (*L* in scheme 4(a)). A dissociative process implies formation of an intermediate wdaggerith a reduced coordination number. In this case, the leaving group leaves the inner coordination sphere of the complex, and the new arrangement of ligands around the metal center occurs. A nucleophilic assistance of the solvent in the isomerization also might take place (scheme 4(b)). The first-order kinetic equation should be valid for such a process [4, 5]. For example, the isomerization of different palladium(II) and platinum(II) complexes in the solid phase proceeds intramolecularly [16].

The first-order kinetic equation proves that the isomerization takes place without participation of a second molecule of **1**.

The dissociative process proceeds with the formation of ions, requiring a polar solvent. The isomerization was studied in $CHCl_3$, which has rather low nucleophilicity and polarity (the dipole moment is close to 1D, the dielectric permittivity is <5). Indeed, the transformation of **1A** to **1B**, as observed above, is a rather slow process. We suggest that ligand exchange and, consequently, isomerization are accelerated by a base (nucleophilic agent).

In order to confirm this hypothesis, we used pyridine (a base that does not undergo nucleophilic addition to the isocyanide fragment of **1**). We varied the concentration of

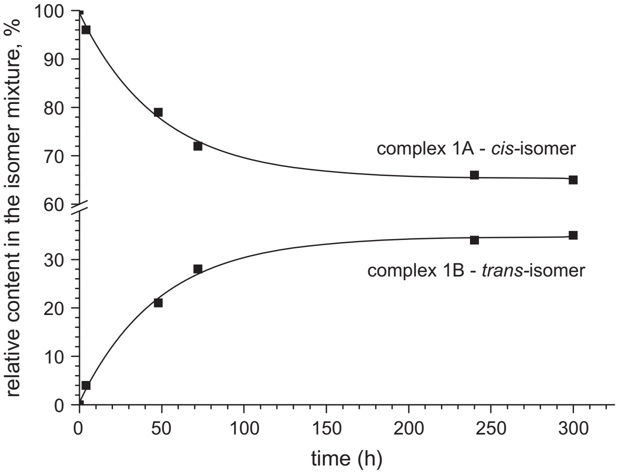
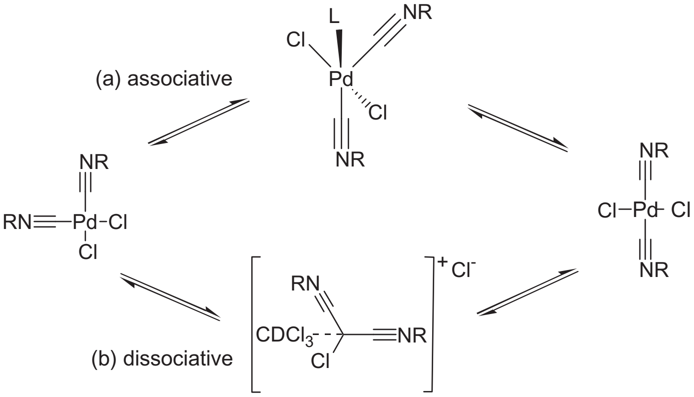


Figure 1. The relative content of **1A** and **1B** in the isomeric mixture as a function of time at room temperature.



Scheme 4.

pyridine in the system from 1 to 20 M%. Even at concentration of pyridine below 1 M%, the equilibrium was established almost immediately (in 3–5 min) at room temperature.

The effect of temperature on the isomerization rate was also investigated. A sample of the complex freshly dissolved in $CDCl_3$ (displaying one α-CH signal at 4.05 ppm) was heated to 50 °C. The equilibrium was established in 20–25 min, while only an insignificant (compared to the experimental accuracy) peak of the second isomer developed during this time at room temperature (figure 2).[†]

This reaction also obeys the first-order kinetic equation $\ln C_{1A} = \ln C^0{}_{1A} - kt$ and $\ln C_{1B} = kt$ ($R^2 = 0.992$ for both curves) and no changes in the overall equation were observed on heating, $k = 0.0036 \pm 0.0003\ s^{-1}$ (for both curves).

The reaction rate constant changes by a factor of 6 when the temperature increases by 30 °C. Thus, the rate of reaching the equilibrium in the system **1A**–**1B** is noticeably affected by the temperature. The activation enthalpy [4] (as a slope of the plot of $\ln(k/T)$ versus $(1/T)$) of the process was roughly estimated as 20.6 kJ/M.

The ratio of the isomerization products remained constant within the accuracy of the method with increasing temperature, evidencing a weak temperature effect on the equilibrium.

2.2. *IR study*

IR spectroscopic data are in a general agreement with the NMR results. Two intense bands of stretching vibrations of carbon–nitrogen triple bonds (2253 and 2235 cm^{-1}) with comparable intensities are observed in the IR spectra of KBr pellets of **1**, similar to the data reported [17]. This spectrum is a characteristic of **1A**, the aforementioned bands being assigned to symmetric and anti-symmetric vibrations of the CN triple bond in agreement with theoretical calculations. A pair of Pd–Cl vibration bands (336 and 316 cm^{-1}) and (less characteristic) Pd–C (1021 and 1032 cm^{-1}) bonds are present in the long-wave range as well. Complex **2** displays bands characteristic of the *trans*-isomer: $\nu_{CN} = 2225\ cm^{-1}$, $\nu_{Pd\text{–}I} = 219\ cm^{-1}$, $\nu_{Pd\text{–}C} = 1016\ cm^{-1}$.

[†] The experimental points measured during the first two minutes of the experiment are ignored. This is due to the time needed for the complete heating of the sample in the NMR tube.

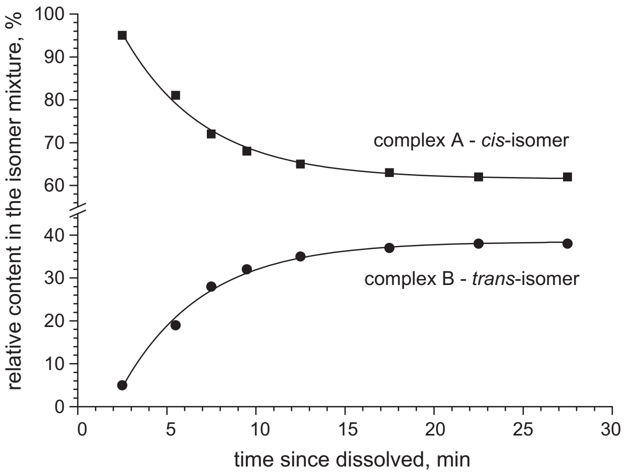


Figure 2. The relative content of **1A** and **1B** in the isomeric mixture as a function of time at 50 °C.

Using IR spectroscopy, the solution behavior of **1** in $CHCl_3$ and $CDCl_3$ solutions was compared. In both cases, a decrease in the intensity of the stretching vibration for the CN triple bond in the shorter-wavelength range (ν_{CN} = 2253 cm^{-1}) and a gradual development of a considerably more intense vibration band in the longer-wavelength range (ν_{CN} = 2232.8 cm^{-1}) were observed.

A series of IR spectra recorded for several days after dissolution of **1** in chloroform shows an isosbestic point, indicating the presence of equilibrium in a closed system. The equilibrium ratio of the isomers was established in three days. No further essential changes were observed in the spectrum.

Unfortunately, the stretching vibration band of the C–D bond in $CDCl_3$ overlaps with the CN triple bond vibrations, making it impossible for a quantitative comparison of the results derived from NMR and IR data in $CDCl_3$.

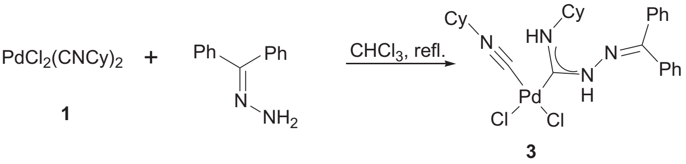
2.3. *Complex 1 as a precursor for ADC*

Knowledge of the configurations of carbene complexes is important for their use in catalysis, since *cis*-position of neutral ligands of a catalytically active species is most favorable for both oxidative addition and reductive elimination in cross-coupling reactions [18].

It was assumed on the basis of IR spectroscopic data [13] that the ADC complex **3** obtained from **1** upon addition of benzophenone-hydrazone, is the *cis*-isomer (scheme 5).

We found the geometry of **1**. Therefore, we synthesized **3** from **1** and used X-ray structural analysis to verify the assumption [13]. Indeed, **3** exists as *cis*-isomer in the solid state.

The crystallographic data and processing parameters, and bond lengths and angles for **3** are provided in Supplementary material; the plots for the structures can be found in figure 3.



Scheme 5.

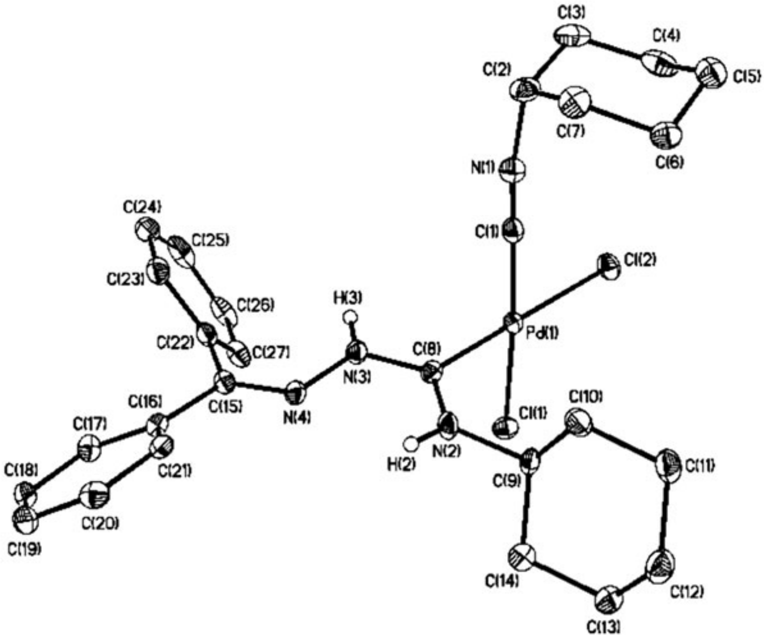


Figure 3. The view of **3** with the atom numbering scheme. Thermal ellipsoids are drawn with 50% probability. Most hydrogen labels are omitted for clarity.

Complex **3** is neutral. Both chlorides are in the inner coordination sphere. An almost undistorted square-planar geometry around palladium is completed with one diaminocarbene, one isocyanide (in the *cis*-position to the carbene), and two chlorides.

The Pd–C$_{carbene}$ distance [Pd–C8: 1.966(3) Å] is very close to that in related complexes, *cis*-[PdCl$_2${C(OMe)=NHMe}$_2$] 1.953–1.972 Å [13], *cis*-[PdCl$_2${C(=NHCy)NHNHC(=NHCy)}$_2$] 1.958–1.964 Å [19].

The carbene is roughly planar and the angles around carbene C8 are 119.1(3)–121.8(2)°, consistent with sp^2 hybridization. Two C–N bonds of the carbene fragment are [N(3)–C(8): 1.338(3); N(2)–C(8) 1.304(3)], between the single CN bond distance (1.469(10) Å in amines [20]) and double CN bond distance (1.279(8) Å in imines [20]). The N(2)–C(8) bond, corresponding to the isocyanide, is slightly longer than the newly formed N(3)–C(8) bond.

In the isocyanide ligand, the CN triple bond [C16–N3 1.142(3)] has a normal value (1.136–1.144 Å) and is similar to those observed in related isocyanide palladium complexes, e.g. *cis*-$[PdCl_2(CNR)_2]$ [*R* = Cy (1.128–1.142 Å), *t*Bu (1.108–1.149 Å), Xyl (1.145–1.156 Å)] [6, 21].

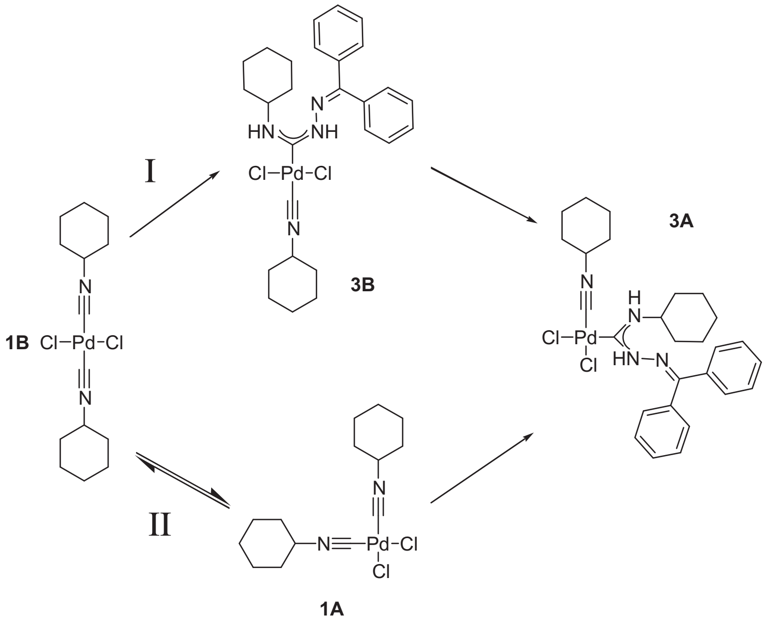
We obtained **3** from a freshly prepared solution of **1** (containing only **1A**) and from a solution of **1** where the equilibrium between **1A** and **1B** was already achieved. In both cases, we obtained the *cis*-product (**3A**) with an almost quantitative yield.

Thus, both **1A** and **1B** produced only the *cis*-isomer of the diaminocarbene product. Two explanations are possible. In the first case, **1B** produces the *trans*-product (**3B**), which isomerizes into a more stable *cis*-isomer (**3A**) under the reaction conditions (scheme 6, path I).

Another possibility is that the nucleophile is added only to **1A**, leading to a lack of **1A** in the system, and, hence, a gradual isomerization of **1B** into **1A**. These transformations occur till the complete consumption of **1** in the system (scheme 6, path II).

We investigated the system behavior using an originally *trans*-configured *bis*-isocyanide palladium(II) halide complex. To this end, (*bis*-cyclohexylisocyanide)palladium(II) iodide (**2**) was selected (*trans*-configuration is assigned for iodide complexes in solution [12]). The NMR and IR data obtained in the present paper also confirm that **2** in solution is the *trans*-isomer.

Complex **2** does not react with benzophenone hydrazone even under reflux in chloroform, while the reaction with **1** proceeds with a high rate at room temperature and even on cooling to −5 °C. The reason for this is, evidently, the mutual deactivation of one isocyanide ligand by the other, suggesting that the reaction of diaminocarbene complex formation does not proceed via path I depicted above (scheme 6).



Scheme 6.

3. Experimental

3.1. *Instruments and methods*

IR spectra were recorded in $CHCl_3$, $CDCl_3$, or KBr on a Shimadzu FTIR 8400S FTIR-spectrometer from 4000 to 400 cm^{-1} with 4 cm^{-1} resolution and on a Bruker Tensor-27 FTIR-spectrometer from 4000 to 200 cm^{-1} with 4 cm^{-1} resolution.

NMR spectra were registered on a Bruker-DPX 300 spectrometer with frequency of 300.13 MHz (^1H) and 75.04 (^{13}C) at room temperature (20–25 °C) and upon heating to 50 °C; the solvent was $CDCl_3$. NMR studies were performed at the Center for Magnetic Resonance, St. Petersburg State University.

X-ray structural analysis: Single crystals of $PdCl_2(CyNC)(CyNHCNHNCPh_2)$ were obtained by the isothermal crystallization method from a mixture of chloroform–methylene chloride–hexane. Single-crystal X-ray diffraction was carried out with a Bruker SMART 1000 CCD diffractometer [22] (graphite monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å, ω-scan technique, T = 120(2) K). A multi-scan absorption correction based on equivalent reflections (SADABS [23]) was applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL program package [24]. The hydrogen of NH was located from difference Fourier maps and involved in refinement in an isotropic approximation. The remaining hydrogens were positioned geometrically and included in the structure factor calculations in the riding approximation. The crystallographic details are summarized in the Supplementary material. The crystal structure has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 934968.

Mass-spectra of MeOH or MeCN solutions were measured on a Bruker micrOTOF spectrometer using electrospray ionization (ESI). The device was operated in the "positive ion" mode from the ratio *m*/*z* 50–3000. The following settings were applied: capillary voltage −4500 V (ESI^+–MS) and capillary exit ±(70–150) V. The sprayer pressure was 0.4 bar, and the flow rate was 4.0 μL/min.

3.2. *Synthesis*

3.2.1. Preparation of 1. $PdCl_2(CyNC)_2$ was prepared according to the procedure described [13] upon interaction of $PdCl_2(MeCN)_2$ with cyclohexyl-isocyanide (CyNC) in $CHCl_3$. The yield was 84%.

IR(KBr, selected bands, cm^{-1}): ν(C–H) 2936–2860 (m), ν(C≡N) 2261 (s), 2244 (s); ^1H NMR ($CDCl_3$, δ): 1.3–1.9 (m, 20H, CH_2); 3.95, 4.06 (s, 2H, CH); ^{13}C NMR ($CDCl_3$, δ): 22.5, 24.7, 31.8 (6C, CH_2); 55.6, 56.1 (2C, CH).

3.2.2. Preparation of 2. $PdI_2(CyNC)_2$ was obtained according to the modified procedure described [17]. 1 mM (395 mg) of **1** was dissolved in an excess of acetone (100 mL), and eightfold excess of KI (1.33 g, 8 mM) was added under stirring. The reaction mixture was stirred for 5 h under slight heating (40 °C). Upon completion of the reaction, acetone was removed on a rotary evaporator, and the mixture was washed with small portions of methylene chloride. The obtained bright-orange solution was filtered, partially distilled off on a rotary evaporator, and diluted with a small amount of diethyl ether. Then the solution was gradually evaporated. The product precipitated on the flask walls as large red-orange crystals. The yield was 87% (470 mg, 0.87 mM).

IR(KBr, selected bands, cm^{-1}): ν(C–H) 2932–2852 (m), ν(C≡N) 2224 (s); ^1H NMR ($CDCl_3$, δ): 1.49 (s, 8H, CH_2), 1.82–1.88 (m, 12H, CH_2), 4.05 (s, 2H, CH); ^{13}C NMR ($CDCl_3$, δ): 22.6 (4C, CH_2), 25.1 (2C, CH_2), 32.0 (4C, CH_2), 55.6 (2CN-CH), 118.7 (2CNCy).

3.2.3. Preparation of 3. The reaction was conducted according to the described procedure [13]. 80 mg (0.4 mM) benzophenone hydrazone was dissolved in 5 mL chloroform, and the solution of 159 mg (0.4 mM) of **1** in 10 mL chloroform was added upon stirring. The reaction mixture was stirred for 10 h. The pale-yellow solution was distilled to dryness on a rotary evaporator and then dissolved in a small amount of chloroform. The product was precipitated in an excess of diethyl ether. The precipitate was separated from the solution by centrifugation. A light-beige powder was obtained. The complex was recrystallized from a mixture of chloroform–diethyl ether–methylene chloride and isolated as a fine crystalline powder. The reaction yield was 83% (195 mg, 0.33 mM).

ESI^+-MS: Calculated for $C_{27}H_{34}N_4Cl_2Pd$: 590.12; found *m*/*z*: 591 [M]; IR: (KBr, selected bands, cm^{-1}): ν(C–H) 2934–2856 (m); ν(C≡N) 2226 (s); ν(N=CPh_2) 1636 (s); ν(N=$C_{carbene}$, N=C) 1557 (s); δ(C–H Ar) 702 (m); ^1H NMR ($CDCl_3$, δ): 8.91 (s, 1H, N–N**H**–C–NH); 8.32 (s, 1H, C-N**H**–N); 7.61–7.30 (m, 10H, Ar); 4.40 (1H, CH); 3.87 (1H, CH); 2.16–1.24 (m, 20H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 176.9 (NH–C–NH); 156.3 (CN); 135.7–128.2 (Ar); 58.7, 55.2 (CH), 33.5–22.3 (CH_2).

4. Conclusion

(*bis*-Cyclohexylisocyanide)palladium(II) chloride demonstrates a *cis*-*trans* equilibrium in solution with *cis*-configuration preferred in 2 : 1 *cis*-*trans* isomeric ratio. It is a slow process which is accelerated by heating and in the presence of nitrogen bases.

Nucleophilic addition of nitrogen nucleophiles with (*bis*-cyclohexylisocyanide)palladium (II) chloride complex proceed with participation of *cis*-(*bis*-cyclohexylisocyanide)palladium (II) chloride, and its continuous regeneration takes place due to the isomerization of *trans*-(*bis*-cyclohexylisocyanide)palladium(II) chloride into *cis*-(*bis*-cyclohexylisocyanide) palladium(II) chloride.

Supplementary material

Supplemental material for this article can be accessed http://dx.doi.org/10.1080/00958972.2013.847185.

Funding

The work was supported by the Russian Foundation for Basic Research [project number 11-03-00048-a] and by research grants of St. Petersburg State University (2011–2013).

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