

Synthesis, Characterization and Crystal Structure of New 2-Morpholinoethyl-Substituted Bis-(NHC)Pd(II) Complexes and the Catalytic Activity in the Direct Arylation Reaction

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Abstract This paper contains the synthesis of the new 2-morpholinoethyl substituted bis-(NHC)Pd(II) complexes and their catalytic activity in direct arylation reaction. The new bis-(NHC)Pd(II) complexes have been prepared from Ag(I)NHC complexes by using transmetallation method. The new bis-(NHC)Pd(II) complexes have been characterized by using ¹H NMR, ¹³C NMR, FTIR spectroscopy

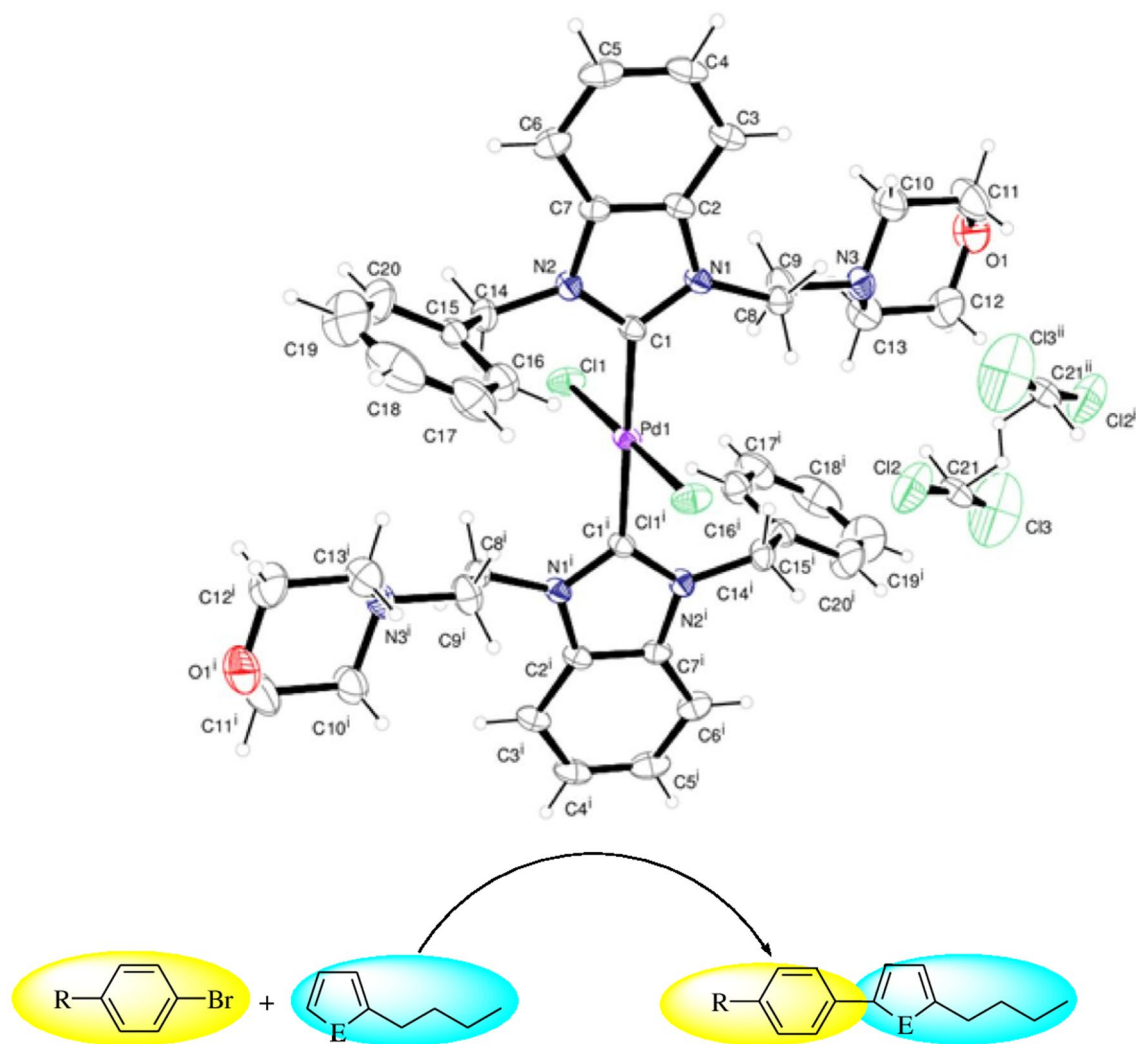
and elemental analysis techniques. Molecular and crystal structure of the complex **1a** and its ligand (*N*-benzylbenzimidazole) were obtained by single crystal X-ray diffraction method. The new bis-(NHC)Pd(II) complexes exhibit activity in the reaction after being examined as catalysts in the direct arylation (C–H activation) reaction.

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Graphical Abstract



Keywords *N*-Heterocyclic carbenes · Bis-(NHC) Pd(II) · Single crystal X-ray diffraction · Direct arylation · Butylfuran · Butylthiophene

1 Introduction

The *N*-heterocyclic carbenes (NHCs) were known as unstable and non-isolable intermediates when first discovered by Wanzlick [1] and Öfele [2] in 1968. However, after the report on the extraordinary stability, isolation, and storability of crystalline NHC IAd by Arduengo et al. in 1991 [3–5], numerous studies have been reported on the NHC as ligands in organic and organometallic chemistry [6]. These ligands with strong σ -donor and weak π -acceptor properties can form stable complexes with almost all transition metals [7–9].

In recent years NHC ligands have an important place in transition-metal chemistry due to their unique complexation properties, synthetic versatility and highly adjustable properties [10]. Metal-NHC complexes, especially Ag(I)-NHC complexes have attracted continuous attention [11]. They are used as suitable carbene transfer reagents for other metal–carbene complexes (as Pd, Ru, Ni, Rh, and Ir) which are not always easily found [12–16]. Also, biomedical applications of Ag-NHC complexes such as antimicrobial, anticancer and antitumor agents have been researched [17–19].

Pd-NHC complexes are considered to be one of the most important classes of metal-NHC complexes. The pioneering participation from the groups of Nolan [20], Herrmann [21, 22], Glorius [23] and Organ [24] have been mentioned in this topic. Metal-NHC complexes have found wide application area that including olefin metathesis, hydrosilylation, and Pd-catalyzed

cross-coupling reactions [25]. Bis-(NHC)Pd(II)dihalide complexes are efficient catalysts for different C–C and C–N coupling reactions [26, 27]. Usually accepted that the chelate effect revealed on their metal complexes presents extra stability for the generation of durable metal complexes, which are extremely desirable for catalytic applications, especially those requiring harsh reaction conditions [28].

The palladium catalyzed direct arylation of isoxazoles [29], the reaction of the five-membered heteroaromatic ring with aryl halides via C–H bond activation, has been firstly reported by Nakamura et al in 1982 [30–39]. One of the most important methods in modern organic chemistry is palladium-catalyzed carbon–carbon (C–C) cross-coupling reactions since direct (C–H) arylation has taken attention as an alternative C–C coupling reaction in recent years [37, 40]. Recently, reactions of the C–H activation via organopalladium intermediate species have become multipurpose [41, 42]. Palladium catalytic systems are rather widespread owing to their selectivity, high activity, versatility, and efficiency. Also, different catalytic systems for the C–H bond transformations have been improved for the eco-friendly synthesis method [43–45].

In recent years, numerous studies have been published on the metal-NHC complexes containing direct arylation, transfer hydrogenation, Suzuki–Miyaura and Heck reactions [46–54]. Our study contains the synthesis of the new series of 2-morpholinoethyl-substituted bis-(NHC)Pd(II) complexes and their structural and spectroscopic characterization. The structure of **1a** was confirmed by the single-crystal X-ray diffraction method. Also, the catalytic activities of the bis-(NHC)Pd(II) complexes have been investigated that they are more efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran and 2-*n*-butylthiophene with aryl bromide.

2 Experimental

All synthesis involving bis-(NHC)Pd(II) complexes **1a–f** were carried out under an inert atmosphere in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: Et₂O (Na/K alloy), CH₂Cl₂ (P₄O₁₀), hexane, toluene (Na).

All other reagents were commercially available from Aldrich Chemical Co. and used without further purification. Melting points were identified in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were saved in the range 400–4000 cm^{−1} on Perkin Elmer Spectrum 100 FT-IR

spectrometer. Proton (¹H) and Carbon (¹³C) NMR spectra were recorded using either a Varian AS 300 Merkur spectrometer operating at 300 MHz (¹H), 75.47 MHz (¹³C) in CDCl₃ with tetramethylsilane as an internal reference. All reactions were observed on an Agilent 6890 N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). Elemental analyses were performed by İnönü University Scientific and Technological Research Center (Malatya, Turkey).

Single crystal X-ray diffraction data set of the complex **1a** and its ligand (*N*-benzylbenzimidazole) were collected at room temperature on a Rigaku-Oxford Xcalibur EOS diffractometer using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). The data were collected and integrated using CrysAlis^{Pro} software [55]. Utilizing OLEX2 [56], the structures were solved by direct methods in SHELXT [57] and refined by full-matrix least-squares on *F*² in SHELXL [58]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms of the ligand were found in the difference map and refined freely. For the complex, all hydrogen atoms were placed in geometrically idealized positions (C–H = 0.93–0.97 Å, Cl–H = 1.630–1.707 Å). Crystallographic data is summarized in Table 1.

2.1 Synthesis of bis[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene]dichloropalladium(II), **1a**

PdCl₂(PhCN)₂ (0.078 g, 0.3 mmol) was added to a solution of chloro[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I) (288 mg, 0.6 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 24 h at room temperature in the dark conditions. Then filtered through Celite and the solvents were evaporated under vacuum to afford the product as a light yellow solid. The crude product was recrystallized from dichloromethane/diethyl ether (1:3) at room temperature. Yield: 0.172 g (70%). m.p.: 205–206 °C; ν_(CN): 1452.6 cm^{−1}. Anal. Calc. for C₄₀H₄₆N₆O₂PdCl₂: C: 58.58; H: 5.65; N: 10.25. Found: C: 59.41; H: 6.13; N: 9.82. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 2.42 (t, 8H, *J*: 4.2 Hz, –NCH₂CH₂O–); 3.11 (m, 4H, –NCH₂CH₂NC₄H₈O); 3.48 (m, 8H, –NCH₂CH₂O–); 5.00 (t, 4H, *J*: 4.5 Hz, –NCH₂CH₂NC₄H₈O–); 6.18 (s, 4H, –CH₂C₆H₅–); 7.03–7.35 (m, 18H, Ar–H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 52.1 (–NCH₂CH₂O–); 54.3 (–NCH₂CH₂NC₄H₈O); 58.0 (–NCH₂CH₂O–); 66.9 (–NCH₂CH₂NC₄H₈O–); 67.3 (–C₆H₄CH₂–); 111.0, 111.7, 111.9, 124.2, 128.1, 133.0, 133.2, 134.1, 134.2, 134.5, and 137.6 (Ar–C); 181.6 (2-CH).

Table 1 Crystal data and structure refinement data of complex **1a** and *N*-benzylbenzimidazole

	<i>N</i> -benzylbenzimidazole	1a
Empirical formula	C ₁₄ H ₁₂ N ₂	C ₄₁ H ₄₈ Cl ₄ N ₆ O ₂ Pd
Formula weight	208.26	905.05
Crystal description, colour	Prismatic, colourless	Prismatic, colourless
Crystal size (mm)	0.359 × 0.286 × 0.260	0.191 × 0.171 × 0.104
Temperature (K)	294 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group, <i>Z</i>	<i>P</i> 121/ <i>n</i> 1, 4	<i>P</i> -1, 1
<i>a</i> (Å)	6.2199 (6)	9.9679 (7)
<i>b</i> (Å)	8.2758 (8)	10.6355 (7)
<i>c</i> (Å)	21.406 (2)	12.4128 (9)
α (°)	90	73.424 (6)
β (°)	97.260 (10)	72.786 (6)
γ (°)	90	62.099 (7)
Volume (Å ³)	1093.05 (19)	1093.94 (15)
ρ_{calc} (mg m ⁻³)	1.266	1.374
μ (mm ⁻¹)	0.076	0.709
<i>F</i> (000)	440	466
θ Range for data collection (°)	3.12–28.46	3.04–25.68
Index ranges		
<i>h</i>	–8 to 6	–12 to 6
<i>k</i>	–10 to 10	–12 to 12
<i>l</i>	–28 to 27	–15 to 14
Reflections collected	4373	7184
Independent reflections	1436 [R (int) = 0.0259]	3372 [R (int) = 0.0369]
Completeness	99.78%	99.83%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1436/0/193	3372/6/259
Goodness-of-fit on <i>F</i> ²	1.006	1.055
Final <i>R</i> indices [I > 2 σ (I)]	<i>R</i> ₁ = 0.049, <i>wR</i> ₂ = 0.087	<i>R</i> ₁ = 0.062, <i>wR</i> ₂ = 0.110
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.096, <i>wR</i> ₂ = 0.104	<i>R</i> ₁ = 0.081, <i>wR</i> ₂ = 0.138

2.2 Synthesis of Bis[1-(3-methylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene] dichloropalladium(II), **1b**

The synthesis of **1b** was carried out in the same way as that described for **1a**, but chloro[1-(3-methylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I) (296 mg, 0.6 mmol) was used instead of chloro[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I). Yield: 0.188 g, (74%). m.p.: 254–256 °C; ν_{CN} : 1456.7 cm⁻¹. Anal. Calc. for C₄₂H₅₀N₆O₂PdCl₂: C: 59.47; H: 5.94; N: 9.91. Found: C: 59.61; H: 6.01; N: 9.93. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 2.30 (s, 6H, –C₆H₄–CH₃); 2.99 (t, 8H, *J*: 4.5 Hz, –NCH₂CH₂O–); 3.36 (t, 4H, *J*: 7.6 Hz, –NCH₂CH₂NC₄H₈O–); 3.64 (t, 8H, *J*: 4.5 Hz, –NCH₂CH₂O–); 4.89 (t, 4H, *J*: 7.6 Hz, –NCH₂CH₂NC₄H₈O–); 6.14 (s, 4H, –CH₂C₆H₄–); 7.03–7.39 (m, 16H, Ar–H). ¹³C

NMR (75 MHz, CDCl₃, δ , ppm); 45.7 (–C₆H₄–CH₃); 52.8 (–NCH₂CH₂O–); 53.8 (–NCH₂CH₂NC₄H₈O–); 57.7 (–NCH₂CH₂O–); 66.8 (–NCH₂CH₂NC₄H₈O–); 67.1 (–C₆H₄CH₂–); 110.4, 110.7, 111.5, 123.0, 127.8, 128.6 and 129.3 (Ar–C); 181.8 (2-CH).

2.3 Synthesis of Bis[1-(4-methylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene] dichloropalladium(II), **1c**

The synthesis of **1c** was carried out in the same way as that described for **1a**, but chloro[1-(4-methylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I) (296 mg, 0.6 mmol) was used instead of chloro[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I). Yield: 0.198 g, (78%). m.p.: 249–251 °C; ν_{CN} :

1448.1 cm^{-1} . Anal. Calc. for $\text{C}_{42}\text{H}_{50}\text{N}_6\text{O}_2\text{PdCl}_2$: C: 59.47; H: 5.94; N: 9.91. Found: C: 59.53; H: 5.88; N: 9.82. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 2.36 (s, 6H, $-\text{C}_6\text{H}_4-\text{CH}_3$); 2.42 (t, 8H, J : 4.2 Hz, $-\text{NCH}_2\text{CH}_2\text{O}-$); 3.11 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 3.47 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{O}-$); 4.99 (t, 4H, J : 4.5 Hz, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 6.20 (s, 4H, $-\text{CH}_2\text{C}_6\text{H}_4-$); 7.02–7.18 (m, 16H, Ar-**H**). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 21.2 ($-\text{C}_6\text{H}_4-\text{CH}_3$); 52.1 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 54.2 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 57.6 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 66.8 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 67.4 ($-\text{C}_6\text{H}_4\text{CH}_2-$); 110.4, 111.4, 111.6, 123.1, 127.7 and 129.3 (Ar-**C**); 181.8 (2-**CH**).

2.4 Synthesis of Bis[1-(2,3,4,5,6-pentamethylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene]dichloropalladium(II), **1d**

The synthesis of **1d** was carried out in the same way as that described for **1a**, but chloro[1-(2,3,4,5,6-pentamethylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I) (330 mg, 0.6 mmol) was used instead of chloro[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I). Yield: 0.207 g, (72%). m.p.: 248–250 $^\circ\text{C}$; ν_{CN} : 1456.7 cm^{-1} . Anal. Calc. for $\text{C}_{50}\text{H}_{66}\text{N}_6\text{O}_2\text{PdCl}_2$: C: 62.53; H: 6.93; N: 8.75. Found: C: 62.64; H: 7.02; N: 8.67. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 2.30 (s, 6H, $-\text{C}_6-\text{CH}_3$); 2.38–2.40 (s, 30H, $-\text{C}_6-(\text{CH}_3)_5$); 2.42 (s, 8H, $-\text{NCH}_2\text{CH}_2\text{O}-$); 2.60 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 3.50 (s, 8H, $-\text{NCH}_2\text{CH}_2\text{O}-$); 3.78 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 5.12 (s, 4H, $-\text{CH}_2\text{C}_6(\text{CH}_3)_5-$); 7.35–7.47 (m, 8H, Ar-**H**). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 16.9–17.6 ($-\text{C}_6-(\text{CH}_3)_4$); 17.3 ($-\text{C}_6-\text{CH}_3$); 51.3 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 51.7 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 54.0 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 65.8 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 66.8 ($-\text{C}_6(\text{CH}_3)_5\text{CH}_2-$); 127.9, 133.1, 134.3, 134.5, 134.9 and 135.9 (Ar-**C**); 182.0 (2-**CH**).

2.5 Synthesis of Bis[1-(3,4,5-trimethoxybenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene]dichloropalladium(II), **1e**

The synthesis of **1e** was carried out in the same way as that described for **1a**, but chloro[1-(3,4,5-trimethoxybenzyl)-3-(2-morpholinoethyl)-2-ylidene]silver(I) (342 mg, 0.6 mmol) was used instead of chloro[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I). Yield: 0.210 g, (70%). m.p.: 225–238 $^\circ\text{C}$; ν_{CN} : 1455.2 cm^{-1} . Anal. Calc. for $\text{C}_{46}\text{H}_{58}\text{N}_6\text{O}_8\text{PdCl}_2$: C: 55.23; H: 5.84; N: 8.40. Found: C: 55.38; H: 5.72; N: 8.21. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 2.42 (t, 8H, J : 4.2 Hz, $-\text{NCH}_2\text{CH}_2\text{O}-$); 3.12 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 3.51 (s, 8H,

$-\text{NCH}_2\text{CH}_2\text{O}-$); 3.86 (s, 6H, $-\text{C}_6\text{H}_2\text{OCH}_3$); 3.89 (s, 12H, $-\text{C}_6\text{H}_2(\text{OCH}_3)_2$); 5.01 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 6.13 (s, 4H, $-\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3-$). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 52.3 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 54.2 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 56.4 ($-\text{C}_6\text{H}_2\text{OCH}_3$); 56.7 ($-\text{C}_6\text{H}_2(\text{OCH}_3)_2$); 57.8 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 60.8 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 66.8 ($-\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_3-$); 131.1, 133.3, 133.9, 134.9, 135.0, 153.4 and 153.8 (Ar-**C**); 181.7 (2-**CH**).

2.6 Synthesis of Bis[1-butyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene]dichloropalladium(II), **1f**

The synthesis of **1f** was carried out in the same way as that described for **1a**, but chloro[1-butyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I) (267 mg, 1.2 mmol) was used instead of chloro[1-benzyl-3-(2-morpholinoethyl)benzimidazol-2-ylidene] silver(I). Yield: 0.178 g, (79%). m.p.: 237–238 $^\circ\text{C}$; ν_{CN} : 1454.8 cm^{-1} . Anal. Calc. for $\text{C}_{34}\text{H}_{50}\text{N}_6\text{O}_2\text{PdCl}_2$: C: 54.29; H: 6.70; N: 11.17. Found: C: 55.48; H: 6.95; N: 10.83. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 1.08 (m, 6H, $-(\text{CH}_2)_3-\text{CH}_3$); 1.60 (m, 4H, $-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_3$); 2.25 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{C}_2\text{H}_5$); 2.67 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{O}-$); 3.25 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 3.72 (m, 8H, $-\text{NCH}_2\text{CH}_2\text{O}-$); 4.88 (t, 4H, J : 7.8 Hz, $-\text{CH}_2-\text{C}_3\text{H}_7$); 5.01 (t, 4H, J : 6.6 Hz, $-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 7.29–7.49 (m, 8H, Ar-**H**). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 14 ($-(\text{CH}_2)_3-\text{CH}_3$); 20.5 ($-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_3$); 32.2 ($-\text{CH}_2-\text{CH}_2-\text{C}_2\text{H}_5$); 48.2 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 54.2 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}$); 58.0 ($-\text{NCH}_2\text{CH}_2\text{O}-$); 58.2 ($-\text{CH}_2-\text{C}_3\text{H}_7$); 67.4 ($-\text{NCH}_2\text{CH}_2\text{NC}_4\text{H}_8\text{O}-$); 110.5, 110.8, 111.4, 122.8, 123.7, 134.2 and 134.7 (Ar-**C**); 181.4 (2-**CH**).

2.7 General Method for Direct Arylation of Furan and Thiophene with Aryl Bromides

The aryl bromide derivatives (4-bromo acetophenone, 4-bromoanisole and 4-bromo toluene) (1 mmol) and heteroaryl derivatives (2-*n*-butylfuran and 2-*n*-butylthiophene) (2 mmol), KOAc (1 mmol) and bis-(NHC)Pd(II) complexes **1a–f** (0.003 mmol) were dissolved in *N,N*-dimethylacetamide (DMAc) (2 mL) in a small Schlenk tube under argon as described in the literature [46]. The reaction mixture was stirred in an oil bath at 130 $^\circ\text{C}$ for 1 h then was cooled to room temperature and the solvent was removed under vacuum. The obtained residue was purified by column chromatography (silica gel 60–120 mesh) by using diethyl ether/*n*-hexane (1:5) as eluent to afford the pure product. The purity of the compounds was checked by gas chromatography (GC) and gas chromatography-mass

spectrometry (GC-MS). Conversions were calculated by taking into account the conversion of aryl bromides to products.

3 Results and Discussion

3.1 Synthesis of Bis-NHCPd(II) Complexes (**1a–f**)

The *N*-benzylbenzimidazole is synthesized by using benzimidazole and benzyl chloride [59, 60] (Fig. 1). The synthetic route for unsymmetrically 2-morpholinoethyl-substituted bis-(NHC)Pd(II) complexes defined in this study was illustrated in Scheme 1. The new bis-(NHC)Pd(II) complexes **1a–f** were prepared from the synthesized Ag(I) NHC complexes via transmetallation method. The air and moisture stable the new bis-(NHC)Pd(II) complexes were soluble in solvents such as toluene, dichloromethane, and chloroform. The new bis-(NHC)Pd(II) complexes **1a–f** were prepared by mixing chloro[1-alkyl-3-(2-morpholinoethyl) benzimidazol-2-ylidene] silver(I) with 0.5 equivalents of PdCl₂(PhCN)₂ in dichloromethane (20 mL), then the reaction mixture was stirred at room temperature for 24 h in dark condition. The new bis-(NHC)Pd(II) complexes were obtained as a light yellow solid in 78 to 79% yield. The formations of the nonsymmetrical substituted complexes were confirmed by FT-IR, ¹H NMR and ¹³C NMR spectroscopic methods and elemental analysis techniques. These spectra are consistent with the proposed formulate. In the ¹³C NMR spectra, the Pd–C_{carbene} resonances of this new bis-(NHC)

Pd(II) complexes in the ¹³C NMR spectra appeared highly downfield shifted at δ 181.6, 181.8, 181.8, 182.0, 181.7 and 181.4 ppm for **1a–f**, respectively. The results of the elemental analysis, which is one of the analytical techniques used to prove the synthesis of compounds, were evaluated and it was observed that the calculated values were very close to the found values. The FT-IR data clearly indicated the presence of ν(CN) at 1452.6, 1456.7, 1448.1, 1456.7, 1455.2 and 1454.8 cm^{−1} for the new bis-(NHC)Pd(II) complexes (**1a–f**), respectively. Also, we obtained an appropriate single crystal for complex **1a**.

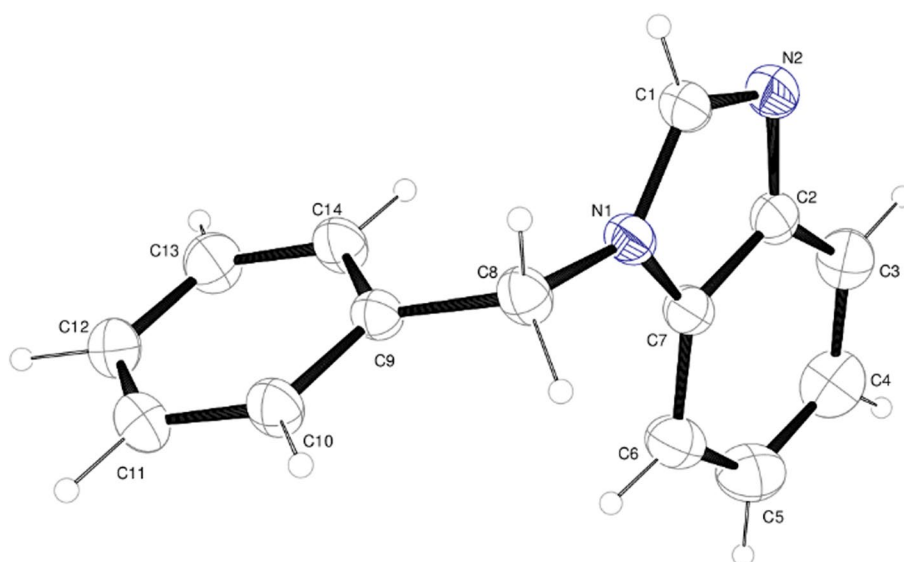
3.2 Direct Arylation of 2-*n*-butylfuran and 2-*n*-butylthiophene with Various Aryl Bromides

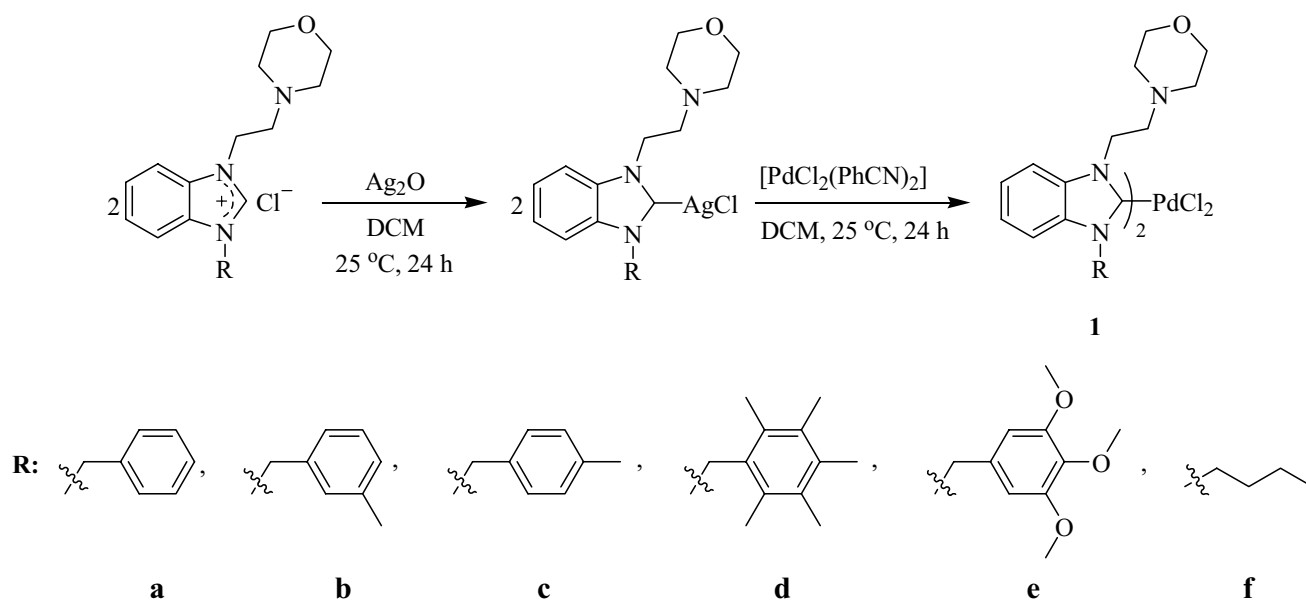
We carried out some experiments for the parameters of direct arylation reaction of para-substituted aryl bromides with 2-*n*-butylthiophene and 2-*n*-butylfuran in the presence of **1a–f** as the catalyst. The best reaction conditions consisted of at the temperature: 130 °C, base: KOAc, time: 1 h, solvent: DMAc and catalyst loading: 3 mmol% in the literature [46].

Conversions of the products for 2-*n*-butylthiophene are between 63 and 99% and for 2-*n*-butylfuran are between 59 and 96% (Tables 2, 3). When 4-bromoacetophenone was used, the best conversion was obtained. However, when we used 4-bromoanisole, it was obtained at low conversion (Tables 2, 3).

Initially, we investigated the binding of 2-*n*-butylthiophene with 4-bromoacetophenone, 4-bromoanisole and

Fig. 1 The molecular structure of the *N*-benzylbenzimidazole, showing the atom labeling. Displacement ellipsoids are drawn at the 25% probability level





Scheme 1 Synthesis of bis-(NHC)Pd(II) Complexes **1a–f**

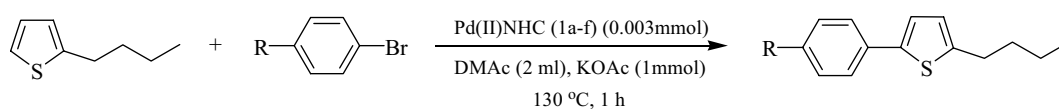
4-bromotoluene by using complexes **1a–f** as the catalyst. When the effects of **1a–f** in the formation of the products **2**, **3** and **4** were analyzed, conversions of 99–91, 63–89 and 82–93% were observed respectively (Table 2). The use of 4-bromoacetophenone with 2-*n*-butylthiophene gave the desired coupling product for different complexes (1b, 1d, and 1f) as catalysts in better excellent conversion than the others, such as 95, 99 and 95%, respectively (Table 2). Then, we investigated the binding of 2-*n*-butylfuran with 4-bromoacetophenone, 4-bromoanisoie, and 4-bromotoluene with complexes **1a–f** as the catalyst. When the effects of **1a–f** in the formation of product **5**, **6** and **7** were analyzed, conversions of 86–96, 59–81 and 83–93% were observed respectively (Table 3). The best results were obtained when 2-*n*-butylthiophene with 4-bromoacetophenone were used (Table 3). Finally, 2-*n*-butylfuran was bound with 4-bromoanisoie to give the arylated products **6** in fewer conversions. When 4-bromoacetophenone and 4-bromotoluene with 2-*n*-butylfuran were utilized in the direct arylation reaction, conversions of the products (**5** and **7**) were obtained and observed to be better than the product **6** (Table 3). When compared to similar studies [53, 61], published recently, bis-(NHC)Pd(II) complexes that we have synthesized to appear highly active catalysts.

3.3 Structure Description of the Complex **1a**

The results of the single crystal X-ray diffraction analysis illustrate that complex **1a** crystallizes with a disordered

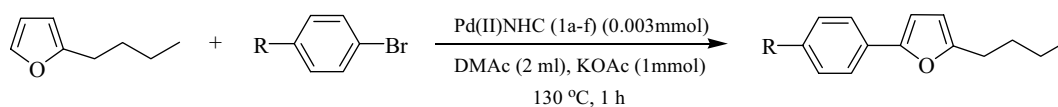
dichloromethane solvent molecule in the triclinic space group *P* 1. As depicted in Fig. 2, the asymmetric unit has one-half-molecule and it is completed with a twofold symmetry axis [symmetry code: 1–*x*, 1–*y*, 1–*z*]. The structure shows a distorted *square-planar* geometry in a *trans* configuration around the metal center. The Pd–C bond length [2.016 (1) Å] is compatible with the many other *trans*-Pd(II) complexes, whereas it is longer than the *cis*-configuration ones [62–65]. In the study of Huynh et al., these results show that the carbene ligands are more weakly bound to the Pd-center in the *trans*-form [66]. The planes of the *N*-benzylbenzimidazole are almost perpendicular [74.65(2)°] to the Pd/C1/C1'/C1/C1' plane. All other bond lengths and angles are shown in Tables 4 and 5, mostly consistent with the Pd(II) complex studies in the literature [67, 68].

In the crystal structure, molecules are linked by intermolecular C–H...O hydrogen bond [H...O = 2.46 Å, C–O = 3.353(2) Å, C–H...O = 161°, symmetry code: 1 + *x*, –1 + *y*, 1 + *z*] to form an infinite chain along the *ab* plane. This hydrogen bond also generates *R*₂²(16) ring motif (Fig. 3). Moreover, there is a strong C–H...*pi* interaction between the C13 atom of the morpholine ring and the benzene ring of the benzimidazole moiety [Cg: C2/C3/C4/C5/C6/C7; C13–Cg 3.697(3) Å, H13A...Cg 2.81 Å, C13–H13A...Cg 152°, symmetry code: –*x*, 1–*y*, 1–*z*], which is responsible for the 2D supramolecular network and stabilization of the crystal structure.

Table 2 Bis-(NHC)Pd(II) catalysed direct arylation of 2-*n*-butylthiophene by using aryl bromides

Entry	Ar-Br	Pd(II)NHC	Product	% Conv.
1		1a		91
2		1b		95
3		1c		91
4		1d		99
5		1e		92
6		1f		95
7		1a		82
8		1b		78
9		1c		63
10		1d		89
11		1e		82
12		1f		79
13		1a		87
14		1b		82
15		1c		83
16		1d		87
17		1e		92
18		1f		93

Reaction conditions: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), bis-(NHC)Pd(II)(0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h, product purity was checked by GC and NMR, conversions were calculated according to aryl bromide

Table 3 Bis-(NHC)Pd(II) catalyzed direct arylation of 2-*n*-butylfuran by using aryl bromides


Entry	Ar-Br	Pd(II)NHC	Product	% Conv.
1		1a	 5	96
2		1b		93
3		1c		88
4		1d		91
5		1e		86
6		1f		92
7		1a	 6	74
8		1b		78
9		1c		81
10		1d		62
11		1e		71
12		1f		59
13		1a	 7	93
14		1b		83
15		1c		87
16		1d		84
17		1e		92
18		1f		85

Reaction conditions: 2-*n*-Butylfuran (2 mmol), aryl bromide (1 mmol), bis-(NHC)Pd(II)(0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h, product purity was checked by GC and NMR, conversions were calculated according to aryl bromide

Fig. 2 The molecular structure of the complex **1a**, showing the atom labeling. Displacement ellipsoids are drawn at the 25% probability level

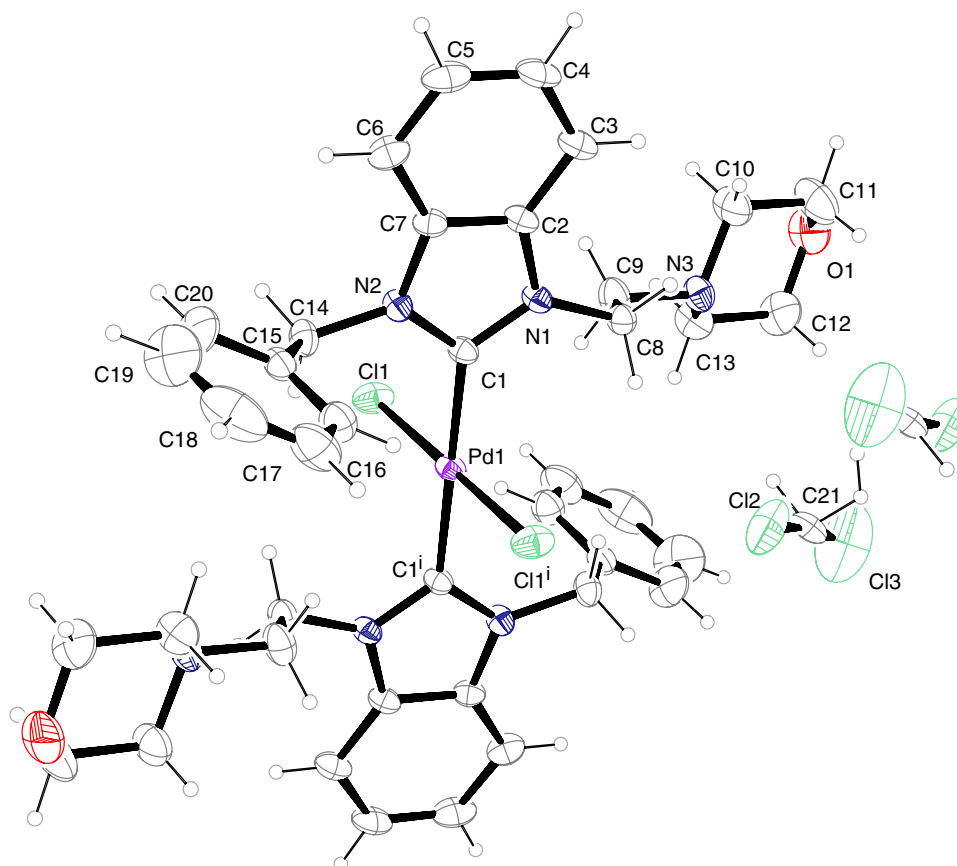


Table 4 Selected bond length (Å) of **1a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	C1	2.0156 (1)	N1	C1	1.3467 (1)	N2	C7	1.3888 (1)
Pd1	Cl1	2.3052 (2)	N1	C2	1.3848 (1)	N2	C14	1.4606 (1)
O1	C11	1.4184 (1)	N1	C8	1.4643 (1)	N3	C9	1.4419 (1)
O1	C12	1.4095 (1)	N2	C1	1.3486 (1)	N3	C10	1.4659 (1)
						N3	C13	1.4725 (1)

Table 5 Selected bond angles (°) of **1a**

Atom	Atom	Atom	Angles (°)	Atom	Atom	Atom	Angles (°)
Cl1	Pd1	C1	89.26 (1)	C1	N1	C8	125.09 (1)
Cl1	Pd1	C1 ⁱ	90.74 (1)	C2	N1	C8	124.34 (1)
Pd1	C1	N1	127.12 (1)	C1	N2	C7	111.10 (1)
Pd1	C1	N2	126.66 (1)	C1	N2	C14	125.00 (1)
N1	C1	N2	106.21 (1)	C9	N3	C10	110.87 (1)
				C9	N3	C13	111.56 (1)

ⁱSymmetry code: 1-x, 1-y, 1-z

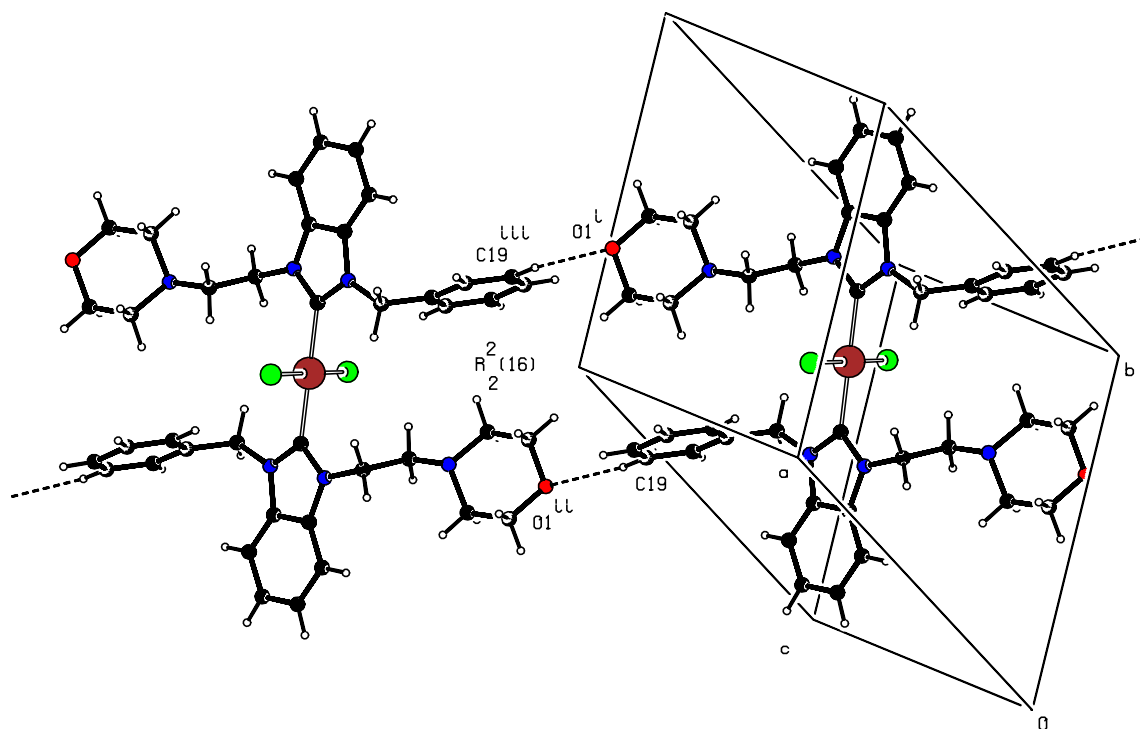


Fig. 3 Hydrogen bonding of the molecules in the crystal structure and formation of the $R_2^2(16)$ ring motif [symmetry codes: (i) $1-x, 1-y, 1-z$, (ii) $1+x, -1+y, 1+z$, (iii) $2-x, -y, 2-z$]

4 Conclusions

As a result, we reported the synthesis of the new 2-morpholinoethyl substituted bis-(NHC)Pd(II) complexes **1a–f**. The bis-(NHC)Pd(II) complexes were prepared via the Ag(I)NHC complexes transmetallation route. The catalytic activities of this new 2-morpholinoethyl substituted bis-(NHC)Pd(II) complexes have been examined that they are more efficient and stable catalysts for the direct arylation reactions of 2-*n*-butylfuran and 2-*n*-butylthiophene with aryl bromide. The crystal structures determination of the complex **1a** and its ligand (*N*-benzylbenzimidazole) were performed by single crystal X-ray diffraction method. The bis-(NHC)Pd(II) complex **1a** has a distorted *square planar* geometry in the *trans* configuration. The crystal structure is stabilized by the intermolecular C–H⋯O hydrogen bonds and the C–H⋯π interaction (Tables 4, 5).

5 Supplementary

Crystallographic data as .cif files for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 1542124 for complex **1a** and 1542126 for *N*-benzylbenzimidazole. Copies of the data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge

Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK. fax: (+44) 1223-336-033, email: deposit@ccdc.cam.ac.uk.

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