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Note

Synthesis and structural characterization of *cis* isomer of 1,2,3-triazol-5-ylidene based palladium complexes

Rajendran Saravanakumar, Venkatachalam Ramkumar, Sethuraman Sankararaman*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

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ABSTRACT

A palladium complex (**3**) of abnormal *N*-heterocyclic carbene (NHC) namely, 4-(hydroxymethyl)-3-methyl-1-phenyl-1*H*-1,2,3-triazol-5-ylidene was prepared *via* silver carbene transmetalation method and characterized by spectroscopic and single crystal XRD data. Single crystal analysis revealed the structure of the complex **3** to be a *cis* isomer. The synthesis of palladium complex **6** *via* silver carbene transmetalation method led to a mixture of *cis*–*trans* isomers. In this case *trans* isomer was formed as major product. We have reported earlier the synthesis and structural characterization of *trans* isomer (*trans*-**6**). However, the presence of *cis* isomer was not recognized until the crude reaction mixture was recrystallized from acetonitrile. Pure *cis* isomer (*cis*-**6**) was obtained by washing the *cis*–*trans* mixture with acetonitrile followed by slow evaporation of acetonitrile solution at 35 °C. Structure of *cis* (*cis*-**6**) isomer was unambiguously established by single crystal XRD data.

1. Introduction

Chemistry of *N*-heterocyclic carbenes (NHCs) has gained momentum after the isolation of free *N*-heterocyclic carbene by Arduengo and coworkers in 1991 [1] as it is evident from number of publications that have appeared over past two decades on properties and application of NHCs [2–7]. NHCs have been used as organocatalysts in various organic transformations [8]. More important is their use as ligands in organometallic chemistry. NHCs have been used as efficient ligands for transition metals and other group metals [9–12]. Most significantly, a number of NHC-metal complexes have been successfully used as catalyst for various reactions such as cross coupling reactions [13], olefin metathesis [14], hydrogenation [15,16], C–H activation [17,18], click reaction [19,20] etc. The remarkable stability and performance of NHC-metal complexes have been attributed to strong σ-donating and weak π-acceptor property of NHCs and strong metal-carbene bond [21]. Imidazole based NHCs have been well established compared to other NHCs such as 1,2,4-triazolylidenes, pyrazolylidenes, tetrazolylidenes, thiazolylidenes, 1,2,3-triazolylidenes etc. Based on heteroatom availability on the vicinity of carbene center, NHCs have been classified as normal and abnormal carbenes [22]. If carbene center is flanked by hetero atoms, at least one of which is typically a nitrogen atom, it is termed as normal carbene. If carbene center is flanked by a nitrogen atom and a non-hetero atom, typically carbon atom, it is termed as abnormal carbene. Abnormal carbenes were proved to be stronger sigma donors compared to normal carbenes [23,24]. Albrecht et al., in 2008 introduced a new class of abnormal NHC namely 1,2,3-triazolylidene as efficient ligand for transition metals [25]. Since then it has attracted numerous researchers due to its simple synthetic procedure and strong sigma donating ability. In the recent past number of publications on the synthesis and catalytic study of 1,2,3-triazolylidene-metal complexes has increased [26–40]. The structure and stereochemistry of the vast majority of the complexes reported so far correspond to either the *trans* mononuclear or bridged binuclear complex. Herein we report the synthesis and structural characterization of *cis* isomer of 1,2,3-triazol-5-ylidene based palladium complexes. 4-(Hydroxymethyl)-3-methyl-1-phenyl-1*H*-1,2,3-triazol-5-ylidene was chosen as a ligand in order to explore the possibility of chelating the oxygen atom of the pendent hydroxyl methyl group to palladium. We report the isolation and structural characterization of *cis* palladium complex formed as minor product in the synthesis of palladium complex **6**.

2. Results and discussion

2.1. Synthesis of triazolium iodide **2**

Triazolium salt **2** an effective precursor for preparing palladium complex was obtained from phenyl azide and propargyl alcohol.

* Corresponding author. Tel.: +91 44 2257 4210; fax: +91 44 2257 0545.
E-mail address: sanka@iitm.ac.in (S. Sankararaman).

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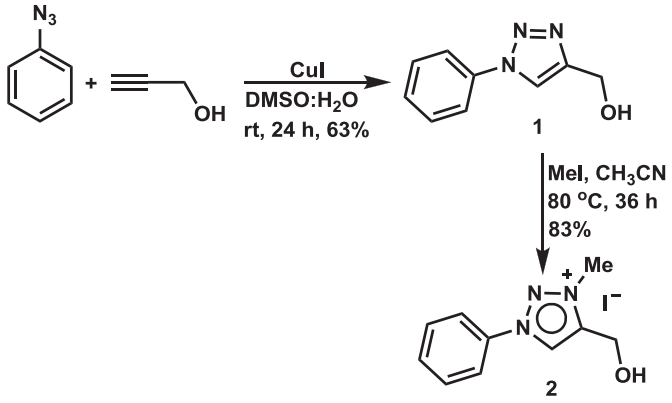


Scheme 1. Synthesis of triazolium salt **2** *via* click reaction followed by N-methylation.

Copper(I) catalyzed '*click*' reaction between phenyl azide and propargyl alcohol gave triazole **1** in 63% yield (Scheme 1). The crude triazole **1** was reacted with methyl iodide at 80 °C in a teflon lined steel autoclave to give triazolium salt **2** in 83% yield (Scheme 1). In ^{1}H NMR spectra triazole (**1**) and triazolium (**2**) protons appeared at 8.01 and 9.35 ppm, respectively.

2.2. Synthesis of palladium complex *3*

Palladium complex **3** was obtained from triazolium iodide **2** *via* silver carbene transmetalation method (Scheme 2). To a dichloromethane solution of triazolium iodide (**2**) freshly prepared Ag_2O was added and stirred at room temperature for 24 h in absence of light (complete conversion of triazolium salt **2** to silver carbene complex was confirmed by disappearance of triazolium proton at 9.35 ppm in ^{1}H NMR spectrum). The silver carbene thus generated *in situ* was reacted with $PdCl_2(CH_3CN)_2$ and stirred additionally for 12 h at room temperature. After completion, solvent was removed under reduced pressure to give crude product as pale yellow solid. Analytically pure sample was obtained by washing the crude product with acetonitrile to give off-white solid in 41% yield. The palladium complex was characterized by spectroscopic and single crystal XRD data.

The off-white solid is air and moisture stable for prolonged period. It is poorly soluble in chloroform and dichloromethane. However, it is considerably soluble in 1,1,2,2-tetrachloroethane.

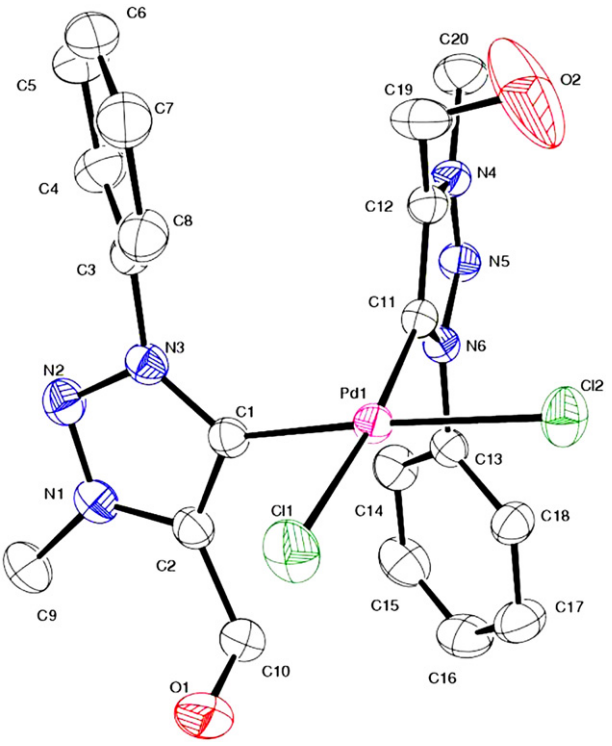
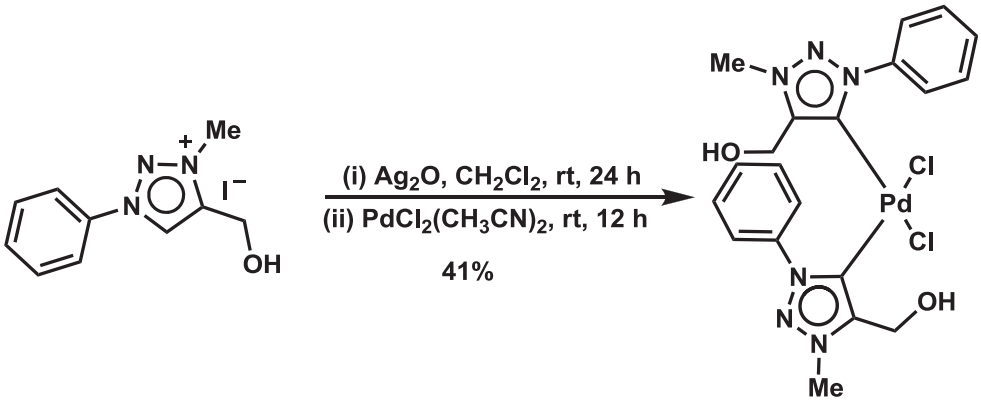


Fig. 1. ORTEP diagram of compound **3** with thermal ellipsoid drawn at 30% probability. Selected bond lengths (Å) and bond angles (°): Pd1–C1 = 1.982(3), Pd1–C11 = 1.965(4), Pd1–Cl1 = 2.371(11), N3–C1 = 1.340(5), C1–C2 = 1.382(5), N3–C1–C2 = 103.2(3), N6–C11–C12 = 103.0(3), N3–C1–Pd1 = 129.8(3), C2–C1–Pd1 = 126.9(3). Hydrogen atoms are excluded for clarity.

Hence, NMR spectra was recorded in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$). The ^{1}H NMR spectrum shows two separate AB quartet for two methylene protons (CH_2OH) at 4.82 and 3.76 ppm (assigned based on ^{1}H–^{1}H and ^{1}H–^{13}C COSY spectra, SI Figs. 5 and 6). This clearly indicated that in solution rotation about *C*–CH_2OH bond is hindered. Resonance signal due to hydroxyl proton merged with one of the methylene signal and appeared at 3.77 ppm. A singlet at 3.89 ppm corresponded to *N*-methyl protons.

Structure of the palladium complex **3** was established by single crystal XRD (Fig. 1) (Table 1). Single crystals were obtained by slow



2 3

Scheme 2. Synthesis of palladium complex **3** *via* silver carbene transmetalation method.

evaporation of chloroform–acetonitrile (1:1) solution of **3** at room temperature (35 °C). In the synthesis of palladium complex **6** (Scheme 3), *trans* isomer (*trans*-**6**) was formed as major product, whereas in the synthesis of complex **3** (Scheme 2) *cis* isomer was formed as major product. This might be due to interaction of hydroxy group with palladium center during the complex formation.

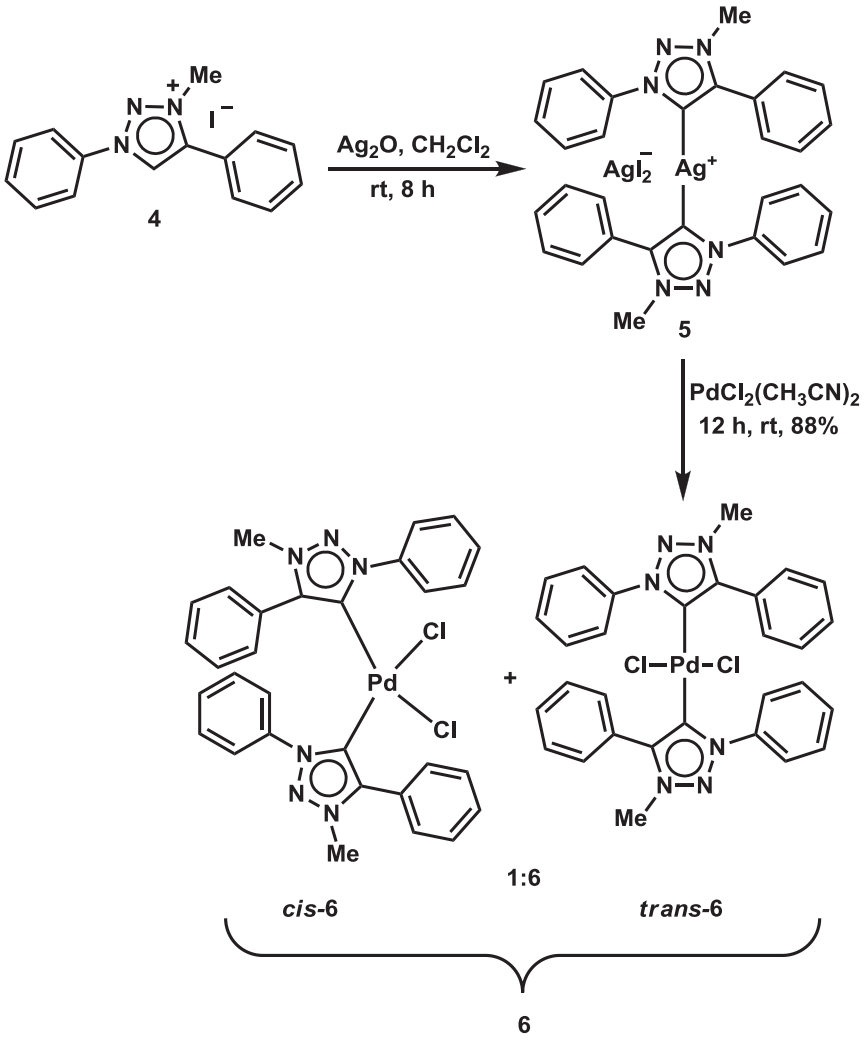
Complex **3** adopts a square planar geometry around palladium center with *cis* orientation of two 1,2,3-triazol-5-ylidene ligands and chloride ions, respectively. The *N*-methyl groups are oriented *anti* to each other with respect to C_2-axis passing between the triazolylidene ligands, bisecting the Cl1–Pd–Cl2 angle. The Pd1–C11 distance is 1.965 Å and C12–C11–N6 bond angle is 103.0(3)°, these bond length and angle are consistent with other 1,2,3-triazol-5-ylidene-palladium complexes [31]. Pd–C12 (palladium-chlorine) distance is 2.370 Å slightly longer than other *cis* imidazolylidene–palladium complexes (2.341––2.358 Å) [39]. This reflects a strong *trans* effect of 1,2,3-triazolylidene ligand. In the crystal structure four types of weak hydrogen bonds were observed between a methylene hydrogen and chloride atom (C19–H19A···Cl2, 2.805 Å), hydroxyl hydrogen and chloride atom (O1–H1···Cl1, 2.731 Å), methyl hydrogen and chloride atom (C9–H9C···Cl1, 2.796 Å) and *N*-methyl hydrogen and oxygen (C9–H9A···O2, 2.597 Å).

2.3. Synthesis of palladium complex *6*

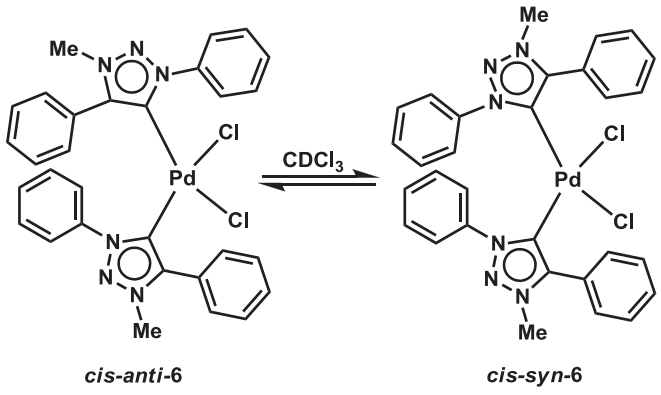
We have reported earlier [32] the synthesis and structural characterization of *trans* isomer, *trans*-**6** (Scheme 3). However, we did not realize the presence of *cis* isomer, *cis*-**6** until the crude product was recrystallized from acetonitrile. Herein we report the isolation and structural characterization of *cis* isomer, *cis*-**6**.

Addition of freshly prepared silver oxide to a dichloromethane solution of triazolium iodide **4** and stirring for 8 h at room temperature resulted in silver carbene complex **5**. The silver carbene complex **5** was isolated and characterized by spectroscopic data [32]. Palladium complex (**6**) was prepared by reacting the *in situ* generated silver carbene complex with $Pd(CH_3CN)_2Cl_2$. Removal of solvent gave crude product as pale yellow solid. In the ^{1}H NMR spectrum of crude product the signals were broad and splitting patterns were not clear. Recrystallization of crude product in chloroform–acetone (1:1) mixture resulted in single crystals along with precipitate. It was characterized by spectroscopic and single crystal XRD data [32], and it was identified as *trans* isomer, *trans*-**6**. We have established that *trans*-**6** exists as a mixture of *syn–anti* conformers in solution [32].

Recrystallization of crude product was also attempted in acetonitrile solvent. Crude product was partially soluble in acetonitrile. The acetonitrile soluble portion was separated by filtration



Scheme 3. Synthesis of palladium complex **6** *via* silver carbene transmetalation method.



Scheme 4. Interconversion of *syn–anti* conformers of *cis*-**6** in $CDCl_3$.

and set for recrystallization. Slow evaporation of acetonitrile solution resulted in single crystals suitable for X-ray analysis and spectroscopic studies. The ^{1}H NMR spectrum is different from *trans*-**6** complex but, as in the case of *trans*-**6**, the ^{1}H NMR spectrum showed two sets of signals in the aromatic and *N*-methyl regions. *N*-Methyl protons appeared as pair of singlet at δ 3.84 and 3.79 ppm, in approximately 1:2 ratio respectively. We presumed that this may also exist as a pair of conformer presumably *syn–anti* conformer in solution (Scheme 4). Like *trans*-**6**, when ^{1}H NMR spectrum was recorded at 58 °C two methyl signals merged and gave a singlet at 3.80 ppm, matched with statistical average of 3.84 and 3.79 ppm. A systematic study of dynamics using VT-NMR in the temperature range of 25–58 °C revealed the coalescence temperature to be 58 °C and free energy of activation for interconversion of presumed *syn–anti* conformers of *cis*-**6** at the coalescence temperature is estimated [41] to be 69.88 ± 0.1 kJ mol^{-1}, nearly the same as that of *trans*-**6** [32]. It must be emphasized that once isolated the *cis*-**6** and *trans*-**6** complexes were very stable and did not interconvert in solution.

Structure of the complex was unambiguously established by single-crystal XRD data (Fig. 2) (Table 1). It was identified as *cis* isomer, *cis*-**6**. A square planar geometry was observed around palladium center with two triazolylidene ligands and two chlorines placed in *cis* geometry, respectively. The Pd–C1 bond length is 1.983 Å, which is considerable shorter (2.035 Å) than the corresponding *trans* complex (*trans*-**6**) and slightly shorter than the other 1,2,3-triazolylidene-palladium complexes [31]. The *N*–$C_{carbene}$–C (N1–C7–C8) bond angle of 102.7° is consistent with other 1,2,3-triazolylidene–palladium complexes [31]. Pd1–*Cl*1 distance is 2.366 Å which is slightly longer than the *trans*-**6** complex (2.335 Å) which indicates a strong *trans* effect of 1,2,3-triazolylidene ligand.

The *cis–trans* isomer mixture of complex **6** can also be separated by two other methods. The *cis* isomer is soluble in acetonitrile while the *trans* isomer is insoluble. (1) Crude product is partially soluble in acetonitrile. Acetonitrile solution was separated by filtration. Evaporation of acetonitrile solution gave pale yellow solid. The pale yellow solid was dissolved in dichloromethane. Pure *cis* isomer precipitated as white solid upon addition of acetone to dichloromethane solution.

(2) The *cis–trans* mixture can also be separated by column chromatography. In TLC, *cis* isomer appeared at ~0.1 (R_f) and trans isomer at ~0.8 R_f when EtOAc/DCM (20:80) was used as eluent. The ^{1}H NMR spectrum of column separated *cis* isomer shows some impurity peaks hence, it was purified further. Addition of acetone to dichloromethane solution of column separated *cis* product, analytically pure sample was precipitated as white solid.

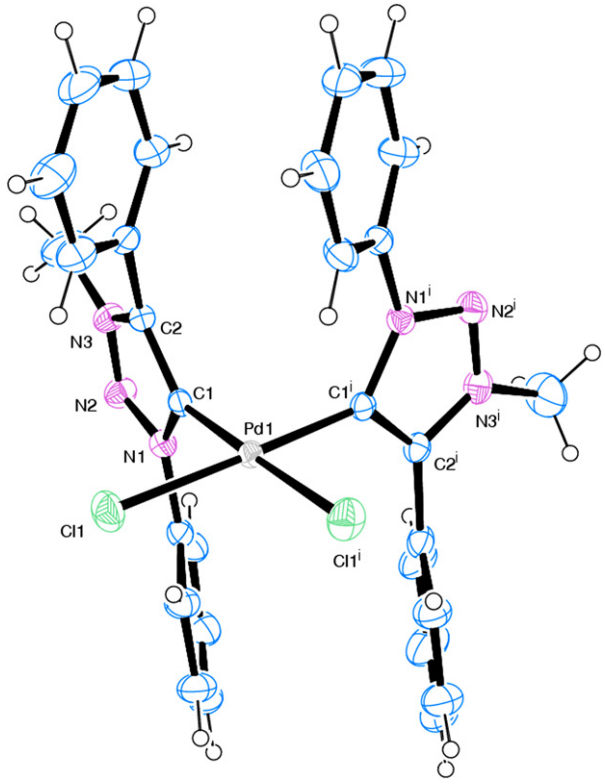


Fig. 2. ORTEP diagram of palladium complex *cis–anti*-**6** with thermal ellipsoids at 30% probability level. Selected bond distance (Å) and angles (deg): Pd1–C1 = 1.983(2), C–N1 = 1.375(3), C1–C2 = 1.384(3), Pd1–Cl1 = 2.366(8), N1–C1–C2 = 102.7(2), N1–C1–Pd1 = 127.23(17), C2–C1–Pd1 = 130.00(19), C1–Pd1–Cl1 = 90.97(7).

Table 1
Crystallographic data of complex **3** and *cis*-**6**.

Parameters	**3**	*cis*-**6**
Formula	$C_{20}H_{22}Cl_2N_6O_2Pd$	$C_{30}H_{26}Cl_2N_6Pd$
Formula weight	555.74	647.87
Radiation	Mo Kα	Mo Kα
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	Pccn
a (Å)	12.9642(3)	16.945(2)
b (Å)	16.3309(4)	11.8540(14)
c (Å)	21.1354(5)	14.030(2)
α°	90	90
β°	90	90
γ°	90	90
V (Å^3)	4474.72(18)	2818.1(7)
T (K)	298 (2)	298(2)
Z	8	4
Reflections/unique/R_{int}	6863/5541/0.0251	11236/3513/0.0307
μ mm^{-1}	1.098	0.879
F(000)	2240	1312
θ range	2.22–28.15	2.10–28.30
Goodness-of-fit on F^2	1.053	1.016
Final *R* indices	$R_1 = 0.0393$	$R_1 = 0.0306$
	$wR_2 = 0.0985$	$wR_2 = 0.0679$
R indices (all data)	$R_1 = 0.0620$	$R_1 = 0.0597$
	$wR_2 = 0.1108$	$wR_2 = 0.0785$

3. Conclusion

A hydroxy tethered 1,2,3-triazolylidene namely 4-(hydroxymethyl)-3-methyl-1-phenyl-1*H*-1,2,3-triazolylidene has been used as ligand for preparing a *cis* palladium complex (**3**). It was prepared *via* transmetalation of the corresponding silver carbene

with $PdCl_2(CH_3CN)_2$ and characterized by spectroscopic and single crystal XRD data. Single crystal analysis revealed complex **3** as a *cis* isomer. Due to hindered rotation about C–CH_2–OH axis methylene protons appear as two separate AB quartets in $C_2D_2Cl_4$. Palladium complex **6** prepared from 1,4-diphenyl-3-methyl-1,2,3-triazolium iodide and palladium *via* silver carbene transmetalation route. Synthesis of palladium complex **6** led to a mixture of *cis*–*trans* isomers. The *trans* isomer was formed as major product. We reported earlier the isolation, spectroscopic and structural characterization of *trans* isomer. However, the presence of minor isomer, *cis* (*cis*-**6**) was not recognized until the crude reaction mixture was recrystallized from acetonitrile. The *cis* (*cis*-**6**) isomer was isolated and spectroscopically and structurally characterized. Like, trans isomer (*trans*-**6**) *cis* (*cis*-**6**) also exists as *syn-anti* conformers in solution. The free energy of activation for the interconversion of the *syn* and *anti* isomers is estimated to be 69.8 ± 0.1 kJ mol-1 from the VT ^{1}H NMR data.

4. Experimental section

4.1. Synthesis of triazole *1*

To a mixture of DMSO:H_2O (9:1) (40 mL) solution phenyl azide (4.09 g, 34.33 mmol, 1.1 equiv.) and copper iodide (1.19 g, 6.24 mmol, 0.2 equiv.) were added and stirred for 10 min. To this propargyl alcohol (1.75 g, 31.21 mmol, 1 equiv.) was added and stirred additionally for 24 h. Upon adding the reaction mixture to ice cold water pale green solid was precipitated. Solvent was filtered off and precipitate was washed with water (5 × 100 mL), acetone (10 mL) and dried under vacuo to give **1** as a pale green solid in (3.4 g) 63% yield. Mp: 102 °C (decomposed); IR (KBr): 3381 (ν_{OH}), 2924, 1594, 1011 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (s, 1H), 7.69–7.66 (m, 2H), 7.49–7.39 (m, 3H), 4.87 (–CH_2–OH) (d, 2H, J = 4.4 Hz), 3.91 (broad, s, 1H) (–O*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 137.0, 129.7, 128.9, 120.5, 120.3, 56.3 (–CH_2–OH).

4.2. Synthesis of triazolium iodide *2*

Methyl iodide (7.34 g, 3.24 mL, 51.72 mmol, 6 equiv.) was added to acetonitrile (10 mL) solution of triazole **1** (1.5 g, 8.62 mmol, 1 equiv.) and heated in a teflon lined sealed steel vessel at 80 °C for 36 h. After completion of reaction, solvent was removed under vacuo and washed with ethyl acetate (5 × 10 mL) to give pale yellow crystalline solid in (2.25 g) 83% yield. Mp: 140–142 °C; IR (KBr): 3316 (ν_{OH}), 1597, 1077 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.35 (s, 1H), 7.92–7.90 (m, 2H), 7.65–7.63 (m, 3H), 5.15 (d, 2H, J = 6 Hz), 5.00 (t, 1H, J = 6 Hz), 4.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.0, 134.7, 132.2, 130.7, 128.4, 121.7, 53.0 (–CH_2–OH), 40.0 (–CH_3–N); HRMS (ESI-MS) calcd for $C_{10}H_{13}N_3O$ $[M + H]^+$ 191.1059, found 191.1067.

4.3. Synthesis of palladium complex *3*

Freshly prepared Ag_2O (0.22 g, 0.94 mmol, 0.6 equiv.) was added to CH_2Cl_2 (100 mL) solution of triazolium salt **2** (0.5 g, 1.57 mmol, 1 equiv.) under nitrogen atmosphere and stirred in absence of light for 24 h (after 8 h ^{1}H NMR for reaction mixture shows the presence of triazolium proton peak at 9.33 ppm, hence the reaction mixture was stirred for 24 h). To this $PdCl_2(CH_3CN)_2$ (0.24 g, 0.94 mmol, 0.6 equiv.) was added and the reaction mixture was continued stirring for 12 h. The reaction mixture was filtered through celite bed to remove the insolubles. Solvent was removed under reduced pressure to give crude compound **3** as pale yellow solid. Which upon washing with acetonitrile (2 × 15 mL) followed by ether (2 × 15 mL) resulted in pure compound (**3**) as off-white solid in (0.18 g) 41% yield. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of CH_3CN:$CHCl_3$ (1:1) solution of **3** at room temperature. Mp: 134–136 °C; IR (KBr): 3418 (ν_{OH}), 2917, 1594, 1167 cm^{-1}; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ: 7.65 (d, 2H, J = 7 Hz), 7.56 (t, 1H, J = 7.5 Hz), 7.47 (t, 2H, J = 8 Hz), 4.83 (dd, 1H, J = 11, 9 Hz), 3.89 (s, 3H), 3.80–3.74 (m, 2H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ: 150.1, 144.4, 138.3, 129.9, 128.9, 124.4, 53.5, 36.2; HRMS (ESI-MS): calcd for $C_{22}H_{26}N_7O_2ClPd$ [M − Cl + CH_3CN, H] 561.0871 found 561.0873, calcd for $C_{20}H_{23}N_6O_2ClPd$ [M − Cl + H] 520.0606, found 520.0588; Anal. Calcd. for $C_{20}H_{22}N_6O_2Cl_2Pd$ (555): C (43.24), H (3.96), N (15.13); found C (43.04), H (3.42), N (14.82).

4.4. Synthesis of palladium complex *6*

To a solution of **4** (250 mg, 0.69 mmol) in CH_2Cl_2 (20 mL) freshly prepared Ag_2O (96 mg, 0.41 mmol) was added and stirred at room temperature for 8 h in the dark. To this $Pd(CH_3CN)_2Cl_2$ (106 mg, 0.41 mmol) was added and stirred additionally for 8 h. It is then filter through celite bed to remove the insolubles. The filtrate was concentrated to ~2 mL and the crude product was precipitated as a yellow solid in (196 mg) 88% upon addition of excess of ether. The ^{1}H NMR spectrum of crude reaction mixture indicates that the *cis* and *trans* isomers were formed in approximately 1:6 ratio respectively.

The mixture containing *cis* and *trans* isomers can be separated in two ways

(i) The crude product was suspended in acetonitrile (60 mL) and warmed at 80 °C for 15 min. *cis* isomer dissolved in acetonitrile and the trans isomer remain undissolved. Filtration followed by slow evaporation of acetonitrile solution leads to single crystals. Alternatively, separation of acetonitrile solution by filtration and evaporation under reduced pressure gave crude *cis* isomer as pale yellow solid. Pure *cis* isomer was obtained by dissolving the crude *cis*-product in dichloromethane and precipitation by slow addition of acetone. The solution was kept undisturbed for an hour for complete precipitation. It is then filtered and dried under *vacuo* to give pure *cis*-**6** isomer as white solid in (25 mg) 11% yield.

(ii) The *cis*–*trans* mixture can also be separated by column chromatography. In TLC, *cis* isomer appeared at 0.1 (R_f) and trans isomer at 0.8 R_f when EtOAc/DCM (20:80) was used as an eluent. Column chromatography was performed with silica gel (120–200 mesh). The *trans* isomer was separated using EtOAc/DCM (5:95) as an eluent and *cis* isomer using DCM/MeOH (90:10) as an eluent. The ^{1}H NMR spectrum of column separated *cis* isomer shows some impurity peaks hence, it was purified further. Addition of acetone to dichloromethane solution of column separated *cis* product, analytically pure sample was precipitated as white solid.

Mp: 238–240 °C; IR (KBr): 2923, 1596, 1491 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 8.39 (d, 2H, J = 10.0 Hz), 8.22 (d, 2H, J = 9.5 Hz), 7.83 (d, 2H, J = 9 Hz), 7.71 (d, 2H, J = 9.5 Hz), 7.31–7.08 (m, 12H), 3.84 (s, 3H), 3.79 (s, 3H); ^{1}H NMR (400 MHz, $CDCl_3$, 58 °C) δ: 8.40–8.25 (broad m, 2H), 7.82–7.73 (broad m, 2H), 7.25–7.12 (m, 6H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 147.4, 144.3, 144.0, 138.8, 138.3, 130.5, 130.3, 130.2, 129.9, 129.8, 129.5, 129.1, 128.9, 128.8, 128.7, 126.3, 125.9, 124.6, 124.0, 37.9, 37.7; ESI-MS m/z 611 $[M - Cl]^+$ (showed the expected isotope pattern for mononuclear complex); HRMS (ESI-MS) calcd for $C_{30}H_{27}N_6ClPd$ $[M - Cl + H]^+$ 612.1020, found 612.1014.

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Appendix A. Supplementary material

CCDC 915854 and 915853 contain the supplementary crystallographic data for complexes **3** and **6** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.03.008.

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