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Synthesis and structures of π-allylpalladium(II) complexes containing bis(1,2,4-triazol-5-ylidene-1-yl)borate ligands. An unusual tetrahedral palladium complex

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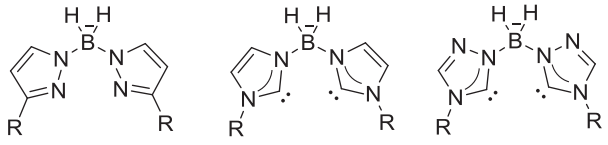
ABSTRACT

Four air stable, neutral π-allylpalladium(II) complexes containing bis(1,2,4-triazol-5-ylidene-1-yl)borate ligands [$H_2B(RBTz)_2Pd(\pi\text{-allyl})$] (R = ^{n}Bu, **2a**; ^{t}Bu, **2b**; 2,6-diisopropylphenyl, **2c**; cyclohexyl, **2d**) have been prepared and characterized. The molecular structures of **2c** and **2d** have been confirmed by single-crystal X-ray diffraction. To our surprise, the coordination geometry about the palladium atom in **2d** is distorted tetrahedron, in which the allyl group is nearly perpendicular to the plane defined by the Pd and the carbene C atoms. To our knowledge, such configuration has not been reported for a four-coordinated palladium allyl complex.

1. Introduction

N-Heterocyclic carbenes (NHC) have been actively studied, since Arduengo and coworkers isolated and characterized the first stable NHC in 1991 [1]. It has been well documented that metal-NHC complexes have broad applications in homogeneous catalysis [2–6]. Among transition metal complexes containing N-heterocyclic carbene ligands, Pd-NHC complexes have attracted particular attention mainly due to their excellent catalytic performances in the C–C cross-coupling reactions [7–15]. Several types of well defined Pd(II)–NHC complexes such as π-allylpalladium complexes [(NHC)Pd(π-allyl)X] [16–20], solvent-coordinated π-allylpalladium complexes [(NHC)Pd(solvent)(π-allyl)] [21–24], and π-allylpalladium complexes with donor-functionalized NHC have been reported [20,25–31]. Bis(pyrazolyl)borate (Bp) ligand (**A**) has been widely used in coordination and organometallic chemistry [32–45]. Its NHC analogues, which exhibit the framework of the Bp and the novel strong electronic donicity of the NHC, have attracted some attention. So far two types of such bidentate NHC ligands such as bis(imidazol-2-ylidene-1-yl)borate (BIm) (**B**) and bis(1,2,4-triazol-5-ylidene-1-yl) borate [$H_2B(RBTz)_2$, **C**] are known. Several metal complexes with bis(imidazol-2-ylidene-1-yl)borate ligands, including those of Li(I) [46,47], Pd(II) [46], Pt(II) [46], and Au(I) [46], Ca(II) [48], Sr(II) [48], Ni(II) [49], Rh(I) and Ir(I) [50], have been prepared. The studies on bis(1,2,4-triazol-5-ylidene-1-yl)borate are relatively limited. Santini et al. reported the synthesis of dinuclear silver(I) and gold(I) complexes with bis(1,2,4-triazol-5-ylidene-1-yl)borate [51]. No palladium complex with bis(1,2,4-triazol-5-ylidene-1-yl)borate has been reported. Herein we report the synthesis and characterization of four neutral π-allylpalladium(II) complexes (**2a-2d**) containing bis(1,2,4-triazol-5-ylidene-1-yl)borate ligands.



2. Results and discussion

2.1. Synthesis and characterization

4-(n-Butyl)-1,2,4-triazole, 4-(*tert*-butyl)-1,2,4-triazole, 4-cyclohexyl-1,2,4-triazole, and 4-(2,6-diisopropylphenyl)-1,2,4-triazole were synthesized by the literature procedures [52]. The

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bidentate NHC ligand precursors **1a**-**1d** were synthesized with nearly quantitative yields by the reaction of alkyl or aryl-1,2,4-triazole with a boride solution, which was obtained from the treatment of 1.0 eq of $Me_3N{:}BH_3$ in toluene with 0.5 eq of I_2 (Scheme 1).

Transmetalation from Ag-NHC complexes has been shown to be an efficient method for the preparation of NHC complexes of transition metals [53,54]. Here, a two-step process was used to prepare the π-allylpalladium(II) complexes. The first step involves deprotonation of the imidazolium salts with Ag_2O to form the Ag-NHC species. Although these complexes could be isolated [51], we used the Ag-NHC complexes *in situ*. The $[H_2B(RTz)_2Pd(\pi\text{-allyl})]$ complexes **2a**-**2d** were prepared by the reactions of the Ag-NHC complexes with $[Pd(\pi\text{-allyl})Cl]_2$ at room temperature in good yields (Scheme 1).

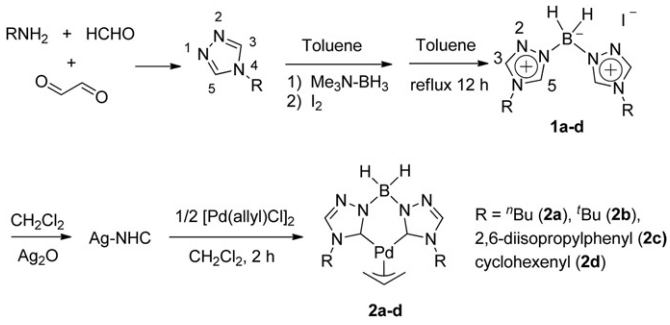
The new complexes **2a-2d** were isolated as white and air stable solids. They are insoluble in nonpolar solvents such as diethyl ether, hexane, or toluene, but soluble in polar organic solvents such as CH_2Cl_2, DMF, CH_3CN, DMSO, and acetone.

The new complexes were characterized by elemental analysis and ^1H, ^{13}C and ^{11}B NMR spectroscopies. ^1H and ^{13}C NMR spectra of **2a-2d** are given in supplementary materials. Compared with the ligand precursors, the ^1H resonances of the 3H-triazolium protons at 9–10 ppm have disappeared in **2a-2d**, indicating the formation of the carbene carbon atoms that coordinate to the palladium atoms. The formation of the metal complexes is also evident from the distinctive Pd-$^{13}C_{carbene}$ peak, appearing in the range 168–177 ppm for **2a-2d**. These signals are in the typical range for Pd-triazolylidene complexes [51,55–57].

Three ^1H NMR signals with a ratio of 2:2:1 and two ^{13}C NMR signals were observed for the allylic groups in **2a** (insert in Fig. 1), square planar **2c** and tetrahedral **2d**. This is consistent with symmetric allyl ligands ($CH_2CHCH_2^-$), leading to two equivalent CH_2 groups in the allyl ligands. As in the reported allyl ligands in, e.g., asymmetric allyl Pd NHC complexes by Li and coworkers [27], the two H atoms in the CH_2 groups are in the *syn* and *anti* configurations with respect to the H atom in the CH group in the allyl ligands (Table 1). The assignment of the H_{syn} and H_{anti} atoms in **2a**, **2c**, and **2d** was based on comparison with those in other reported allyl Pd NHC complexes [27]. The peak of the *syn* H atoms is downfield from that of the *anti* atoms. The $J_{H\text{-}H}$ couplings between the C*H* and H_{syn} and H_{anti} atoms are 6.5–7.5 and 13.0 Hz, respectively. Similar couplings were also observed in chloroethene ($ClHC=CH_2$, Scheme 2), where J_{ac} and J_{bc} = 7.0 and 14.6 Hz, respectively (Fig. 1) [58].

As shown in Table 1, the chemical shifts of ^1H NMR peaks of the alkyl ligand in tetrahedral **2d** is downfield shifted from those of square planar **2c**. The separation of the *syn* and *anti* peaks in **2d** (1.21 ppm) is larger than that (0.60 ppm) in **2c**. The ^{13}C NMR chemical shifts in both complexes are similar (Table 1).

The α-H atoms in the ^{n}Bu (N–CH2–CH2–CH_2–CH_3) groups in **2a** are diastereotopic, as shown in the Newman projection in Fig. 2.



Scheme 1. Synthesis of precursors **1a**-**1d** and NHC-Pd(II) complexes **2a-d**.

In addition, their chemical shift difference is very small. Thus their mutual coupling in an AB pattern as well as the coupling by the two β-H atoms in N-CH_AH_B–CH_2–CH_2–CH_3 lead to a complex ^1H NMR spectrum for the diastereotopic CH_AH_B atoms, as shown in the insert in Fig. 2. The effect of the pro-chiral NHC ring on the two β-H atoms is much smaller. In addition, the chemical environment between α-H_A and H_B atoms is small so that, to the β-H atoms, α-H_A and H_B atoms are close to being identical. The ^1H peak of β-H atoms in **2a** is thus a quintet (Supplementary material).

The ^1H and ^{13}C NMR spectra of the ^{t}Bu analog **2b** show that there are two isomers (Fig. 3). Two sets of peaks, one for each isomer, were observed at room temperature. The allyl ligand in both isomers show features similar to those of **2a**, **2c**, and **2d** discussed earlier (Fig. 1 and Table 1). It is not clear what these isomers are. Attempts to obtain the X-ray quality crystals of **2b** were unsuccessful. Without its crystal structure(s), we speculate that these two isomers are square planar and tetrahedral, and their interchange (or the rotation of allyl ligand in solution) is probably restricted by the bulky ^{t}Bu groups in **2b**.

The ^1H and ^{13}C NMR spectra of 2,6-diisopropylphenyl analog **2c** give one resonance each for the 3-*H*-triazole (8.06 ppm), triazole (143.20 ppm), and the $C_{carbene}$ atoms (174.27 ppm), indicating that there is a reflection plane (mirror) through the Pd and B atoms (Fig. 4) and perpendicular to the plane defined by the Pd, C1 and C3 atoms (Fig. 5), as discussed in detail later in the crystal structure of **2c**. The NMR peaks of the allyl group (Supplementary material and Table 1) are also consistent with the presence of the mirror symmetry. The peaks of the isopropyl groups in **2c** (Fig. 4) show there are two –CH- and four methyl groups. There is an accidental degeneracy of two methyl peaks at 2.084 ppm in the ^1H NMR spectrum. A structure consistent with the NMR observations is given in Fig. 4. This is a crowded molecule, as its structure in Fig. 5 demonstrates later, and the rotation of the isopropyl groups is limited, resulting in four methyl resonances.

2.2. Molecular structures of *2c* and *2d*

Crystals of **2c**·**1/2H$_2$O** and **2d**·**1/2CH$_2$Cl$_2$** were obtained by slow evaporation of their dichloromethane solutions. The structures were determined by single-crystal X-ray diffraction. Molecular structures of **2c** and **2d** are shown in Figs. 5 and 6, respectively. Crystallographic data for **2c**·**1/2H$_2$O** and **2d**·**1/2CH$_2$Cl$_2$** are presented in Table 2. Selected bond distances and angles are given in Table 2. There are two crystallographically independent molecules in the crystal structure of **2c**·**1/2H$_2$O**. Bond distances and angles of the two molecules are similar, and those of one molecule are listed in Table 3.

The coordination geometry around the Pd atom in **2c** is distorted square planar with two carbene carbons and two peripheral allyl carbon atoms. Here the coordinated allyl ligand is considered bidentate. The two substituent phenyl rings are almost perpendicular to the corresponding triazolyl rings with the dihedral angle of 75.8(7)° and 76.6(4)°, respectively. The two triazolyl rings have a dihedral angle of 145.8(5)°. The dihedral angle of the plane of C1-Pd-C3 and the plane of C17-Pd-C19 is 4.6(5)°, indicating that the π-allyl group is almost parallel to the plane of C1-Pd-C3.

The coordination geometry about the Pd atom in **2d** is distorted tetrahedron with two carbene carbons and two terminal allyl carbons. In **2d**, the two triazolyl rings have a dihedral angle of 131.4(4)°. The dihedral angle of the plane of C1-Pd-C3 and the plane of C17-Pd-C19 is 70.0(1)°, indicating that the π-allyl group is almost perpendicular to the plane of C1-Pd-C3, in sharp contrast to the nearly planar geometry around the Pd atom in **2c**. To our knowledge, such distorted tetrahedral configuration in **2d** has not been reported for a four-coordinated allyl palladium complex. The difference

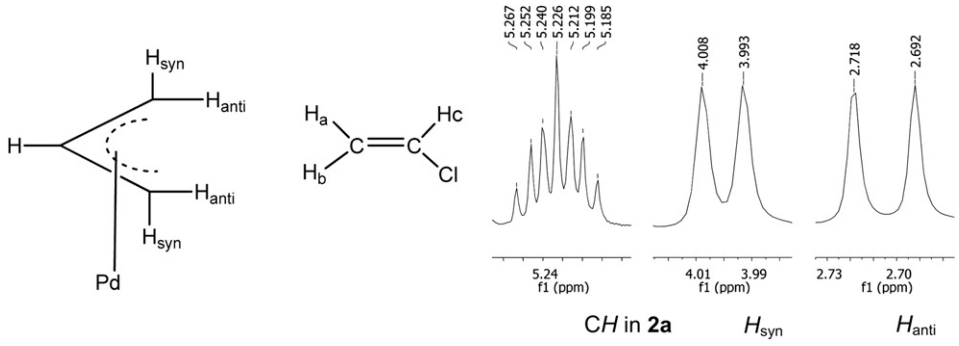


Fig. 1. H_{syn} and H_{anti} atoms in the symmetric allyl ligands in **2a-d**, in comparison to CH_2=CHCl. Insert: ^1H NMR spectrum of the allyl ligand in **2a**.

between the coordination modes of the π-allyl ligands in **2c** and **2d** may be attributed to the larger steric effect by the cyclohexyl groups in **2d**. Chen et al. have examined the steric effects of the substutuents on the structures of the Ni and Pd NHC complexes, in which bulky substitutents induced distortion (steric pressure) [59,60].

The Pd-$C_{carbene}$ bond lengths of 2.064(6) Å and 2.050(6) Å in **2c** and 2.080(7) Å and 2.137(7) Å in **2d** are in the range of the reported values [25–31]. Due to the chelating effect, the bite angles of C1-Pd1-C3 are 89.1(3)° in **2c** and 90.5(2)° in **2d**. The bond distances of η^3 coordination of the allyl group and the palladium center in **2c** and **2d** are comparable to those reported [19,25–31].

3. Experimental

3.1. Instruments and reagents

All the reagents were purchased from Aldrich or Acros and used without further purification. All solvents were distilled prior to use. The starting materials 4-(n-butyl)-4H-1,2,4-triazole, 4-(tert-butyl)-4H-1,2,4-triazole ,4-(2,6-diisopropylphenyl)-4H-1,2,4-triazole, and 4-cyclohexyl-4H-1,2,4-triazole were prepared by the literature procedure [52]. Elemental analyses were performed in an Elementar Vario ELIII elemental analyzer. NMR measurements were obtained in DMSO-d_6 and $CDCl_3$ on a Bruker AM-500 spectrometer. Chemical shifts for ^1H, and ^{13}C NMR are given in parts per million relative to Me_4Si while chemical shifts for ^{11}B NMR is relative to external Et_2O-BF_3 (δ $^{11}B = 0$). ESI mass spectra were recorded on an APEX II FTICR Mass Spectrometer (Bruker-Franzen).

3.2. Preparation of *1a-1d*

The general procedure for synthesis of **1a**, **1b**, **1c** and **1d** is given here. To a solution of $Me_3N{:}BH_3$ (1.2 g, 16.45 mmol) in toluene (60 mL) was slowly added I_2 (2.08 g, 8.04 mmol). The reaction mixture was stirred at room temperature for 1 h. Alkyl or aryl 1,2,4-triazole (32.9 mmol) was added to the yellow solution and refluxed for 24 h. After filtration, the solvent was decanted and the residue was washed with hexane, Et_2O and toluene (20 mL × 2) each. The white oily solid was heated to 80 °C under vacuum for several hours. The pure product was obtained from recrystallization in hot ethanol.

1a (5.505 g, 85.8% yield). ^1H NMR (500 MHz, *J* in Hz, $CDCl_3$) δ 9.84 (s, 2H, 5-*H*-triazole), 8.61 (s, 2H, 3-*H*-triazole), 4.37 (t, $J = 7.5$, 4H, NCH_2CH_2), 3.55 (b, B-*H*), 1.93 (quintet, $J = 7.5$, 4H, NCH_2CH_2), 1.39 (sextuple, $J = 7.5$, 4H, CH_2CH_3), 0.95 (t, $J = 7.5$ Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.98 (5-*C*-triazole), 144.05 (3-*C*-triazole), 47.61 (^{n}Bu), 31.94 (^{n}Bu), 19.48 (^{n}Bu), 13.41 (^{n}Bu). ^{11}B NMR (160 MHz, $CDCl_3$) δ −4.44 (s, 1B). Elemental analysis (%) calcd. for $C_{12}H_{24}BIN_6$: C, 36.95; H, 6.20; N, 21.54; found: C, 36.91, H, 6.32, N, 21.39. MS (ESI): calcd. for $C_{12}H_{24}BIN_6$ *m*/*z* 263.22 ($[M - I]^+$), observed 263.17.

1b (5.781 g, 90.1% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 2H, 5-*H*-triazole), 8.31 (s, 2H, 3-*H*-triazole), 4.1–3.3 (b, B-*H*), 1.78 (s, 18H, CMe_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.78 (5-*C*-triazole), 144.65 (3-*C*-triazole), 61.40 (CMe_3), 30.15 (CMe_3). ^{11}B NMR (160 MHz, $CDCl_3$) δ −4.40 (s, 1B). Elemental analysis (%) calcd. for $C_{12}H_{24}BIN_6$: C, 36.95; H, 6.20; N, 21.54; found: C, 36.75, H, 6.12, N, 21.34. MS (ESI): calcd. for $C_{12}H_{24}BIN_6$ *m*/*z* 263.22 ($[M - I]^+$), observed 263.25.

1c (7.235 g, 73.5% yield). ^1H NMR (500 MHz, *J* in Hz, DMSO-d_6) δ 10.46 (s, 2H, 5-*H*-triazole), 9.58 (s, 2H, 3-*H*-triazole), 7.66 (t, $J = 8.0$, 2H, C_6H_3), 7.48 (d, $J = 8.0$, 4H, C_6H_3), 4.0–3.2 (b, B-*H*), 2.21 (m, $J = 6.5$, 4H, $CHMe_2$), 1.11 (dd, $^3J = 19$, $^5J = 7.0$ Hz, 24H, $CHMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.79 (C_6H_3), 147.42 (C_6H_3), 145.58 (5-*C*-triazole), 144.95 (3-*C*-triazole), 132.40 (C_6H_3), 127.82 (C_6H_3), 125.07 (C_6H_3), 124.43 (C_6H_3), 28.67 ($CHMe_2$), 24.19 ($CHMe_2$), 23.87

Table 1
NMR chemical shifts of the allyl ligands in **2c** and **2d** (*J* in Hz).

Complexes	^1H NMR		
	CH	H_{syn}	H_{anti}
2a	5.23 (m)	4.00 (d), $J_{H\text{-}Hsyn} = 7.5$	2.71 (d), $J_{H\text{-}Hanti} = 13.0$
2b-1	5.28 (m)	3.76 (d), $J_{H\text{-}Hsyn} = 7.5$	2.79 (d), $J_{H\text{-}Hanti} = 13.0$
2b-2	5.27 (m)	3.92 (d), $J_{H\text{-}Hsyn} = 7.5$	2.59 (d), $J_{H\text{-}Hanti} = 13.0$
2c	4.44 (m)	2.33 (d), $J_{H\text{-}Hsyn} = 7.5$	1.73 (d), $J_{H\text{-}Hanti} = 13.0$
2d	5.18 (m)	3.84 (d), $J_{H\text{-}Hsyn} = 6.5$	2.63 (d), $J_{H\text{-}Hanti} = 13.0$
{^1H}-^{13}C NMR			
		CH	CH_2
2a		118.3	56.2
2b-1		114.9	58.9
2b-2		118.1	59.6
2c		117.0	57.9
2d		118.3	57.8

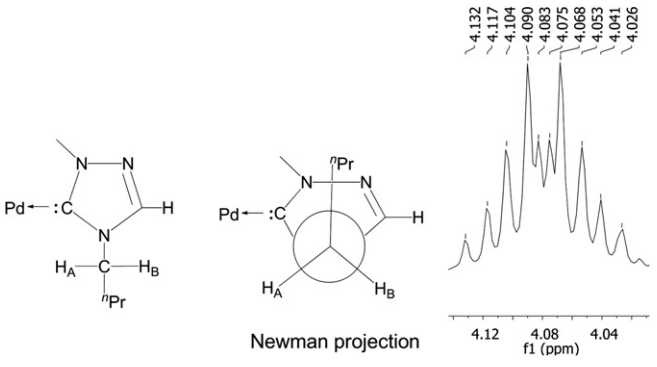


Fig. 2. Diastereotopic α-H atoms in the ^{n}Bu groups in **2a**.

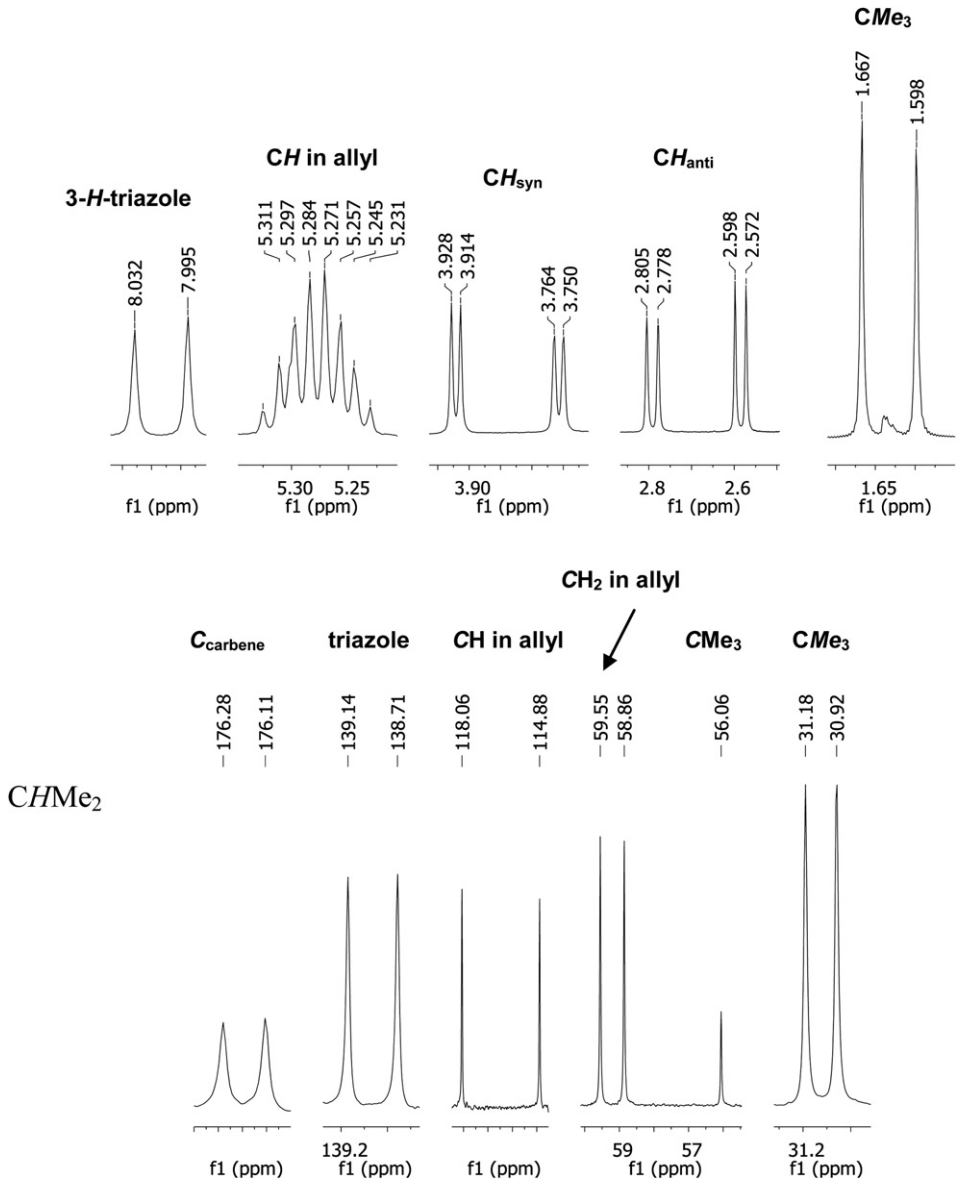


Fig. 3. ^{1}H and ^{13}C NMR spectra of **2b**, showing two isomers. The B-H peak is not shown.

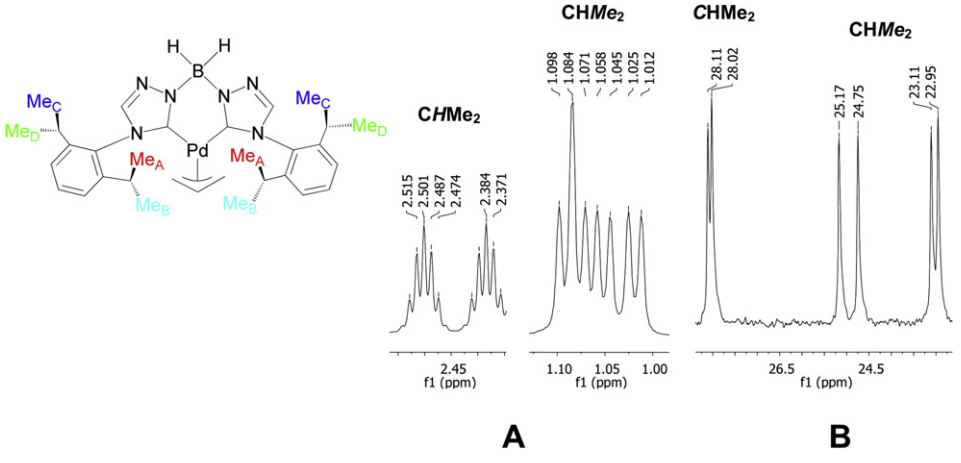


Fig. 4. A possible structure of **2c** showing four inequivalent methyl groups. Inserts: ^{1}H (A) and ^{13}C (B) NMR peaks the $-CHMe_2$ groups in **2c**.

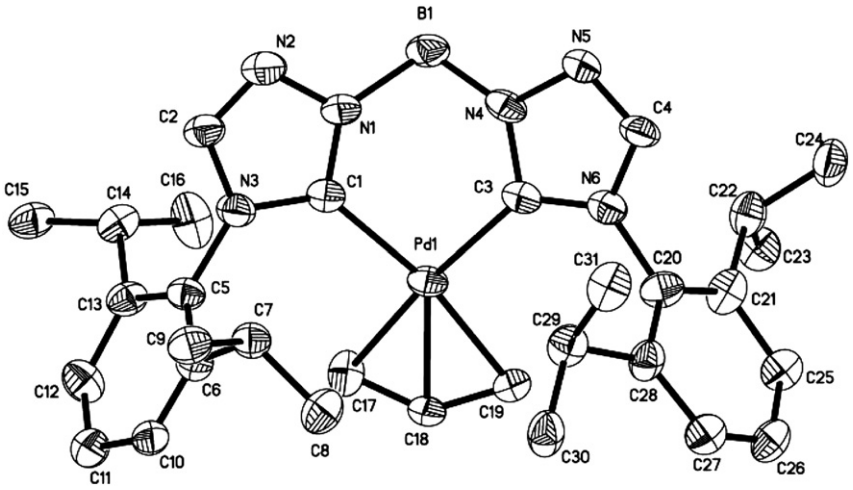


Fig. 5. Molecular structure and atom numbering scheme for **2c** (with 30% probability ellipsoids). Hydrogen atoms and solvent molecule are omitted for clarity.

(CH*Me*$_2$). ^{11}B NMR (160 MHz, $CDCl_3$) δ −4.95 (s, 1B). **1c** was too moisture-sensitive to conduct its elemental analysis. MS (ESI): calcd. for $C_{28}H_{40}BIN_6$ *m*/*z* 471.34 ([M − I]$^+$), observed 471.42.

1d (6.444 g, yield 92.8%). ^{1}H NMR (500 MHz, *J* in Hz, $CDCl_3$) δ 9.90 (s, 2H, 5-*H*-triazole), 8.62 (s, 2H, 3-*H*-triazole), 4.46 (t, 2H, C*H* in Cy), 3.9–3.1 (b, B-*H*), 2.26–1.27 (10H, CH_2 in Cy). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.40 (5-*C*-triazole), 142.39 (3-*C*-triazole), 57.36 (*C*H in Cy), 33.30 (*C*H_2 in Cy), 32.77 (*C*H_2 in Cy), 26.02 (*C*H_2 in Cy), 24.92 (*C*H_2 in Cy), 24.66 (*C*H_2 in Cy). ^{11}B NMR (160 MHz, $CDCl_3$) δ −4.45 (s, 1B). Elemental analysis (%) calcd. for $C_{16}H_{28}BIN_6$: C, 43.46; H, 6.38; N, 19.01; found: C, 43.26, H, 6.31, N, 19.07. MS (ESI): calcd. for $C_{16}H_{28}BIN_6$ *m*/*z* 315.25 ([M − I]$^+$), observed 315.33.

3.3. Preparation of *2a-2d*

A mixture of **1a-1d** (1 mmol) and Ag_2O (1.1 mmol) was stirred in CH_2Cl_2 (20 mL) at room temperature for 12 h. Then [Pd(π-allyl)Cl]$_2$ (0.5 mmol) was added and stirred for 2 h. The mixture was filtrated. The colorless filtrate was concentrated under vacuum and the residue was purified by chromatography on silica gel. Elution with CH_2Cl_2/CH_3OH (20:1) afforded the separation of a colorless portion. Removing the solvent gave the desired products as white solids. Recrystallization from acetone or CH_2Cl_2 gave the pure products suitable for elemental analysis and crystals for X-ray diffraction (for **2c** and **2d**).

2a (0.360 g, yield 88.1%). ^{1}H NMR (500 MHz, *J* in Hz, $CDCl_3$) 7.96 (s, 2H, 3-*H*-triazole), 5.23 (m, *J* = 7.5, 1H, C*H* in allyl), 4.08 (m, *J* = 7.5, 4H, NCH_2CH_2CH_2CH_3), 4.00 (d, *J* = 7.5, 2H, CH_{syn} in allyl), 3.7 (b, B-*H*), 2.71 (d, *J* = 13, 2H, CH_{anti} in allyl), 1.74 (quintet, *J* = ca. 7.5, 4H, NCH_2CH_2CH_2CH_3), 1.31 (sextuple, *J* = 7.5, 4H, NCH_2CH_2CH_2CH_3), 0.91 (t, *J* = 7.5, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1 ($C_{carbene}$), 140.8 (triazole), 118.3 (*C*H in allyl), 56.2 (*C*H_2 in allyl), 47.3 (^{n}Bu), 33.2 (^{n}Bu), 19.4 (^{n}Bu), 13.3 (^{n}Bu). ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.20 (broad). Elemental analysis (%) calcd. for $C_{15}H_{27}BN_6Pd$: C, 44.09; H, 6.66; N, 20.57; found: C, 44.07, H, 6.74, N, 20.78.

2b-1 and **2b-2** (0.382 g, yield 93.5%). **2b-1**: ^{1}H NMR (500 MHz, *J* in Hz, $CDCl_3$) 8.03 (s, 1H, 3-*H*-triazole), 5.28 (m, *J* = 7.5, 1H, C*H* in allyl), 3.76 (d, *J* = 7.5, 2H, CH_{syn} in allyl), 2.79 (d, *J* = 7.5, 2H, CH_{anti} in allyl), 1.60 (s, 9H, C*Me*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3 ($C_{carbene}$), 139.1 (triazole), 114.9 (*C*H in allyl), 58.9 (*C*H_2 allyl), 56.1 (*C*Me$_3$), 30.9 (C*Me*$_3$). **2b-2** ^{1}H NMR (500 MHz, *J* in Hz, $CDCl_3$) 8.00 (s, 1H, 3-*H*-triazole), 5.27 (m, *J* = 7.5, 1H, C*H* in allyl), 3.92 (d, *J* = 7.5, 2H, CH_{syn} in allyl), 4.0–3.2 (b, B-*H*), 2.59 (d, *J* = 7.5, 2H, CH_{anti} in allyl), 1.67 (s, 9H, C*Me*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) 176.1 ($C_{carbene}$), 138.7 (triazole), 118.1 (*C*H in allyl), 59.6 (*C*H_2 in allyl), 56.1 (*C*Me$_3$), 31.2 (C*Me*$_3$). ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.24 (broad for both **2b-1** and **2b-2**). Elemental analysis (%) calcd. for $C_{15}H_{27}BN_6Pd$: C, 44.09; H, 6.66; N, 20.57; found: C, 44.01, H, 6.86, N, 20.67.

2c (0.533 g, yield 86.5%). ^{1}H NMR (500 MHz, *J* in Hz, $CDCl_3$) 8.06 (s, 2H, 3-*H*-triazole), 7.49 (t, *J* = 8.0, 2H, C_6H_3), 7.26 (d, *J* = 8.0, 4H,

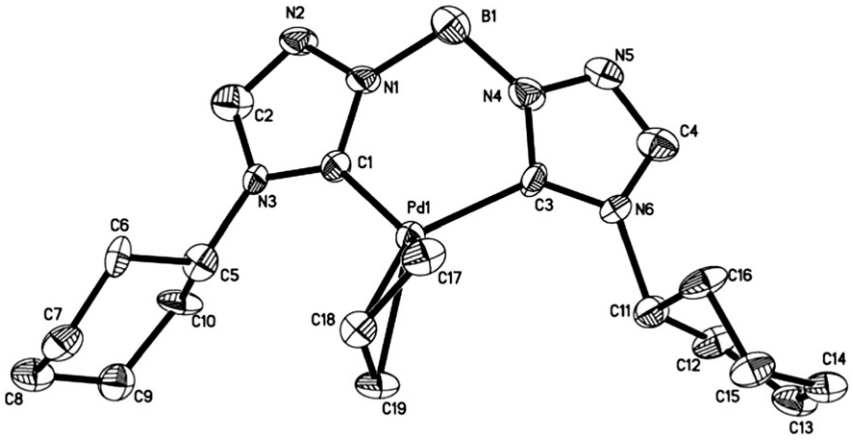


Fig. 6. Molecular structure and atom numbering scheme for **2d** (with 30% probability ellipsoids). Hydrogen atoms and solvent molecule are omitted for clarity.

Table 2
Crystallographic data for **2c·1/2H$_2$O** and **2d·1/2CH$_2$Cl$_2$**.

	2c·1/2H$_2$O	**2d·1/2CH$_2$Cl$_2$**
Empirical formula	$C_{62}H_{88}B_2N_{12}OPd_2$	$C_{39}H_{66}B_2Cl_2N_{12}Pd_2$
Formula weight	1251.86	1008.36
T (K)	291(2)	291(2)
Crystal size (mm^3)	0.28 × 0.22 × 0.20	0.28 × 0.24 × 0.22
Crystal system	monoclinic	monoclinic
Space group	$P2(1)/c$	$C2$
a (Å)	22.612(6)	24.831(5)
b (Å)	17.292(5)	9.0502(17)
c (Å)	18.352(5)	11.503(2)
α (°)	90.00	90.00
β (°)	111.221(4)	104.416(3)
γ (°)	90.00	90.00
Volume (Å^3)	6689(3)	2503.7(8)
Z	4	2
D_{calc} (g/cm^3)	1.243	1.338
Absorption coefficient (mm^{-1})	0.584	0.864
F(000)	2616	1040
θ Range for data collection (°)	1.52–26.00	1.69–25.99
Index ranges	$-27 \le h \le 15$	$-30 \le h \le 30$
	$-21 \le k \le 21$	$-11 \le k \le 10$
	$-21 \le l \le 22$	$-14 \le l \le 11$
Reflections collected/unique	35571/13040	6939/4253
R(int)	0.0562	0.0346
Completeness to $\theta = 26.00$ (%)	99.2	99.4
Max. and min. transmission	0.892 and 0.861	0.8327 and 0.7940
Data/restraints/parameters	13040/0/737	4253/1/271
GOF	1.043	1.076
Final R indices [$I > 2\sigma(I)$][a]	$R1 = 0.0486$	$R1 = 0.0499$
	w$R2 = 0.0870$	w$R2 = 0.1329$
R indices (all data)	$R1 = 0.0975$	$R1 = 0.0571$
	w$R2 = 0.0947$	w$R2 = 0.1366$
Largest differences in peak and hole (e Å^{-3})	1.297 and −0.583	0.625 and −0.609

[a] $R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; GOF $= [\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$.

C_6H_3), 4.44 (m, J = 7.0, 1H, CH in allyl), 4.4–3.8 (b, B-H), 2.50 [quintet, J = 7.0, 2H, CHMe$_2$], 2.38 (quintet, J = 7.0, 2H, CHMe$_2$), 2.33 (d, J = 6.5, 2H, CH_{syn} in allyl), 1.73 (d, J = 13.0, 2H, CH_{anti} in allyl), 1.09 (d, J = 7.0, 6H, CHMe_2), 1.08 (d, J = 6.5, 6H, CHMe_2), 1.05 (d, J = 6.5, 6H, CHMe_2), 1.02 (d, J = 6.5, 6H, CHMe_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3 ($C_{carbene}$), 146.4 (C_6H_3), 146.2 (C_6H_3), 143.2 (triazole), 134.2 (C_6H_3), 130.3 (C_6H_3), 123.9 (C_6H_3), 123.8 (C_6H_3), 117.0 (CH in allyl), 57.9 (CH_2 in allyl), 28.1 (CHMe$_2$), 28.0 (CHMe$_2$), 25.2 (CHMe_2), 24.8 (CHMe_2), 23.1 (CHMe_2), 23.0 (CHMe_2). ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.32 (broad). Elemental analysis (%) calcd. for $C_{31}H_{43}BN_6Pd$: C, 60.35; H, 7.03; N, 13.62; found: C, 60.25, H, 6.93, N, 13.66.

2d (0.339 g, yield 73.7%). ^{1}H NMR (500 MHz, J in Hz, $CDCl_3$) 7.94 (s, 2H, 3-H-triazole), 5.18 (m, J = 7.5, 1H, CH in allyl), 4.19 (m, 2H, CH in Cy), 3.84 (d, J = 6.5, 2H, CH_{syn} in allyl), 4.0–3.3 (b, B-H), 2.63 (d, J = 13.0, 2H, CH_{anti} in allyl), 2.00–1.12 (10H, CH_2 in Cy). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5 ($C_{carbene}$), 138.3 (triazole), 118.3 (CH in allyl), 57.8 (CH_2 in allyl), 56.3 (CH in Cy), 34.6–24.9 (CH_2 in Cy). ^{11}B NMR (160 MHz, $CDCl_3$) δ −2.28 (broad). Elemental analysis (%) calcd. for $C_{19}H_{31}BN_6Pd$: C, 49.53; H, 6.78; N, 18.24; found: C, 49.47, H, 6.71, N, 18.17.

Table 3
Selected bond distances (Å) and angles (°) in **2c** and **2d.**

2c			
Pd(1)–C(1)	2.080(7)	Pd(1)–C(19)	2.244(7)
Pd(1)-C(3)	2.137(7)	C(17)–C(18)	1.499(11)
Pd(1)–C(17)	2.108(7)	C(18)–C(19)	1.499(10)
Pd(1)–C(18)	2.245(7)	C(1)-Pd(1)–C(19)	119.0(3)
N(4)-B(1)–N(1)	106.6(7)	C(3)-Pd(1)–C(19)	128.5(3)
C(1)-Pd(1)-C(3)	89.1(3)	C(3)-Pd(1)–C(17)	110.4(3)
C(1)-Pd(1)–C(17)	143.0(4)	C(19)–C(18)–C(17)	121.0(7)
2d			
Pd(1)–C(1)	2.064(6)	Pd(1)–C(19)	2.198(6)
Pd(1)-C(3)	2.050(6)	C(17)–C(18)	1.330(9)
Pd(1)–C(17)	2.110(6)	C(18)–C(19)	1.323(9)
Pd(1)–C(18)	2.134(6)	C(1)-Pd(1)–C(19)	166.9(2)
N(4)-B(1)–N(1)	107.8(5)	C(3)-Pd(1)–C(19)	102.1(2)
C(1)-Pd(1)-C(3)	90.5(2)	C(3)-Pd(1)–C(17)	171.3(2)
C(1)-Pd(1)–C(17)	97.1(2)	C(19)–C(18)–C(17)	137.6(7)

3.4. X-ray crystallography

A suitable single crystal of **2c·1/2H$_2$O** or **2d·1/2CH$_2$Cl$_2$** was mounted on the top of glass fibers for X-ray structure analysis. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) at room temperature and corrected for absorption using SADABS program [61]. The structures were solved by direct methods and refined on F^2 against all reflections by full-matrix least-squares methods with SHELXTL program [62]. Anisotropy thermal parameters were assigned to all non-hydrogen atoms.

4. Conclusions

Four air stable , neutral π-allylpalladium(II) complexes **2a-2d** have been prepared and characterized. The molecular structures of **2c** and **2d** have been confirmed by single-crystal X-ray diffraction. To our surprise, the coordination geometry about the palladium atom in **2d** is distorted tetrahedron, in which the allyl group is nearly perpendicular to the plane defined by the Pd and the carbene C atoms. To our knowledge, such configuration has not been reported for a four-coordinated palladium allyl complex.

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Supplementary material

CCDC 818081-818082 contain the supplementary crystallographic data for **2c** and **2d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Catalytic studies are given in Supplementary material.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.09.003.

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