Inorganica Chimica Acta 376 (2011) 144–151

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Facile synthesis and characterization of μ-chloro, azido, thiocyanato bridged cyclometallated Pd(II) containing Schiff-base ligands

Yuchun Jiang [a], Yonglin Guo [a], Xia Zhu [a], Dandan Song [a], Yu Wang [a], Ximing Song [a], Francis Verpoort [b,c], Xiaohong Chang [a,*]

[a] Liaoning Provincial Key Laboratory for Green Synthesis and Preparative Chemistry of Advanced Materials, College of Chemistry, Liaoning University, Shenyang 110036, PR China
[b] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, PR China
[c] Department of Inorganic and Physical Chemistry, Laboratory of Organometallic Chemistry and Catalysis, Ghent University, Krijgslaan 281 (S-3), 9000 Ghent, Belgium

ARTICLE INFO

*Article history:*
Received 4 March 2011
Received in revised form 23 May 2011
Accepted 2 June 2011
Available online 12 June 2011

*Keywords:*
Cyclometallation
Schiff-base
Palladium

ABSTRACT

μ-Chloro bridged dinuclear cyclometallated Pd(II) complexes $[Pd\{(4\text{-}R)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Cl)]_2$ (R = H, OMe) were prepared by reaction of $Na_2PdCl_4$ with benzylideneanilines. Unexpectedly, $Na_2PdCl_4$ reacted with Schiff-bases bearing a furyl or a thienyl ring to give N-coordinated non-cyclometallated Pd(II) species $[Pd(C_4H_3XCH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_2]$ (X = O, S). Treating $[Pd\{(4\text{-}R)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Cl)]_2$ (R = H, OMe) with an excess of $NaN_3$ or $NH_4SCN$ generated μ-$N_3$ bridged or μ-SCN bridged cyclometallated Pd(II) complexes $[Pd\{(4\text{-}R)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Y)]_2$ (R = H, OMe; Y = $N_3$, NCS). The complexes were characterized by FTIR, NMR spectroscopy, elemental analysis and X-ray crystallography.



## 1. Introduction

In the last few decades, cyclometallated Pd(II) complexes containing C,N-chelating ligands have attracted more and more interest because of their application as catalysts in organic reactions and as key intermediates in organic and organometallic synthesis [1–8]. Moreover, cyclopalladation of C,N-chelating Schiff-base ligands is one of the most extensively studied areas in Pd-chemistry [9–17]. It is worth noticing that in most cases cyclopalladation of Schiff-bases is completed by the reaction of $Pd(OAc)_2$ and Schiff-base ligands to produce μ-acetato bridged cyclometallated Pd(II) complexes. However, the examples of cyclopalladation obtained by the combination of $Na_2PdCl_4$ and Schiff-base ligands are relatively rare. To the best of our knowledge, similar μ-pseudohalide (e.g. μ-$N_3$ or μ-SCN) bridged cyclometallated Pd(II) complexes characterized by molecular structure containing C,N-chelating Schiff-base ligands have not been reported. Furthermore, it is also known that coordinated azido and isothiocyanato (or thiocyanato) groups show various coordination modes (Charts 1 and 2) [18–22]. Herein, we report on the facile synthesis and the structures of di-μ-X (X = Cl, $N_3$, SCN) bridged cyclometallated Pd(II) complexes bearing Schiff-base ligands.

## 2. Results and discussion

### 2.1. Preparation of μ-chloro bridged dinuclear cyclometallated Pd(II) complexes

One of the most common compounds used for cyclopalladation of C,N-chelating Schiff-base ligands is $Pd(OAc)_2$. Recently Albert et al. reported that all attempts for cyclopalladation of imines by condensation of corresponding amino acid with 4-chlorobenzaldehyde using mixtures of $PdCl_2$/NaCl/$Na_2OAc$, in different conditions, were unsuccessful [9]. Liu and co-workers prepared the μ-chloro bridged binuclear cyclometallated Pd(II) complex $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ by stirring a mixture of $(CH_3CN)_2PdCl_2$, sodium acetate and benzylidene(2,6-diisopropylphenyl)amine in tetrahydrofuran at ambient temperature for 38 h [23]. In this study, the reactions of $Na_2PdCl_4$ with Schiff-bases, as depicted in Schemes 1 and 2, are studied.

The Schiff-base ligands 2,6-diisopropyl-*N*-(benzylidene)aniline (**$L_1$**), 2,6-diisopropyl-*N*-(4-methoxybenzylidene)aniline (**$L_2$**), 2,6-diisopropyl-*N*-(2-furylmethylidene)aniline (**$L_3$**) and 2,6-diisopropyl-*N*-(2-thienyl methylidene)aniline (**$L_4$**) were prepared by condensation of 2,6-diisopropylaniline with the corresponding aldehyde in dried alcohol as solvent to which two drops formic acid were added. Treating Schiff-base ligand **$L_1$** or **$L_2$** with $Na_2PdCl_4$ in the presence of NaOAc in methanol at room temperature, μ-chloro bridged dinuclear cyclometallated Pd(II) complex $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ (**1**) or $[Pd\{(4\text{-}OMe)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Cl)]_2$ (**2**) was generated, respectively. Both

* Corresponding author. Tel.: +86 24 62207823; fax: +86 24 62202380.
*E-mail addresses:* cxh@lnu.edu.cn, c_x_hong@sina.com (X. Chang).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.06.003

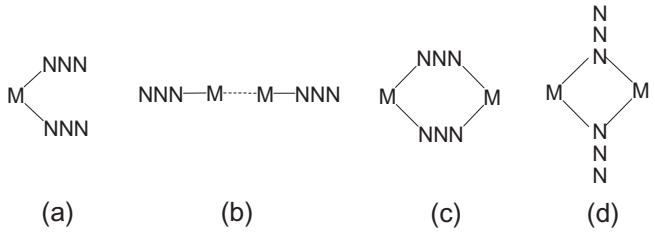



**Chart 1.** Coordination modes of the azido ligand ($N_3$).

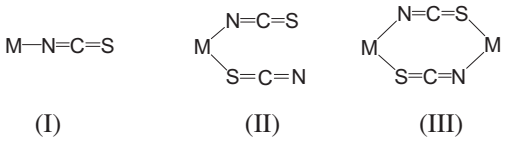
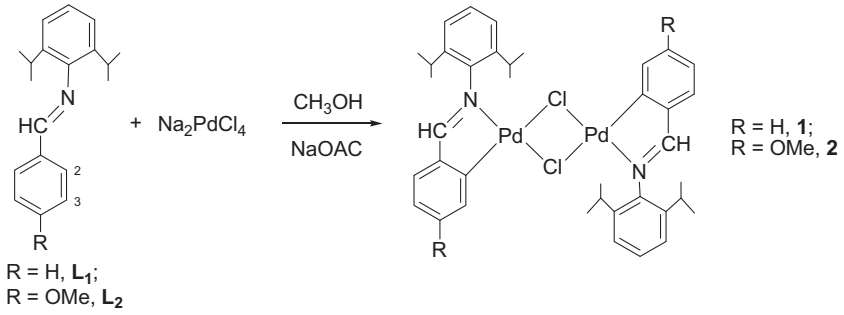


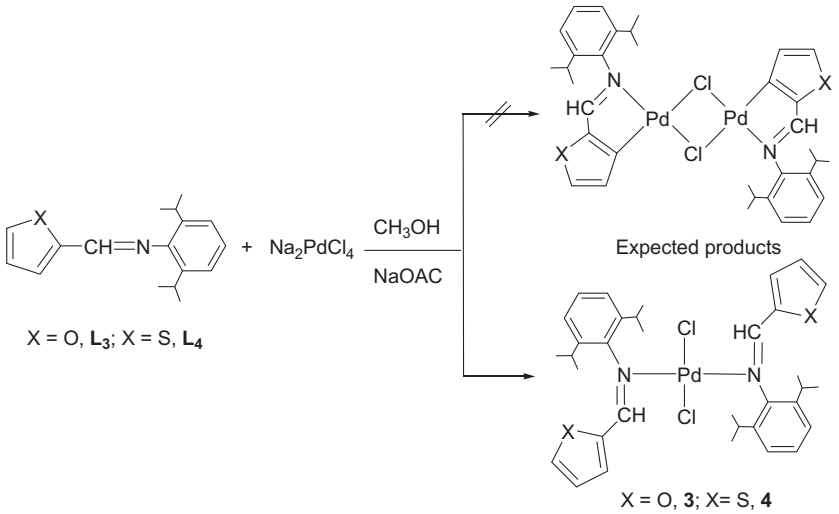

**Chart 2.** Coordination modes of the isothiocyanate ligand (NCS).

complexes were characterized by elemental analysis, spectroscopic techniques (NMR, FTIR) and the molecular structure of **2** was determined by single crystal X-ray analysis. The IR spectra of **1** and **2** show a strong stretch vibration at 1600 and 1601 $cm^{-1}$, respectively, due to the $\nu$(C=N), which was shifted to lower wavenumbers compared to that of the free ligands (1636 and 1643 $cm^{-1}$) indicating that the N of the imine group coordinate to the Palladium [24]. The $^1H$ NMR spectra of **1** and **2** displayed the resonance for C*H*=NC proton at $\delta$ 7.74 and $\delta$ 7.61 ppm, respectively, which was shifted to lower frequency due to N-coordination of the imine [25]. And, two doublets at $\delta$ 1.38 and 1.14 ppm for **1** and **2** were found for the methyl protons from the isopropyl group compared to a doublet at $\delta$ 1.17 ppm in the corresponding free ligands due to the lack of free rotation around the aryl-N bond which renders the two methyls inequivalent. Moreover, the signal of the 2-position H proton of the benzyl ring (Scheme 1) was not observed, indicating the formation of Pd–C bond due to C–H activation.

Since $\mu$-chloro bridged dinuclear cyclometallated Pd(II) complexes **1** and **2** could be readily formed by the reaction of $Na_2PdCl_4$ with *N*-benzylideneaniline, we examined the reaction of $Na_2PdCl_4$ with Schiff-base ligands bearing a five-membered heterocycles (Scheme 2). Initially the formation of novel cyclometallated Pd(II) complexes was expected, however, when Schiff-base ligand, bearing a five-membered heterocycle $\mathbf{L_3}$ or $\mathbf{L_4}$, was treated with $Na_2PdCl_4$ in the presence of NaOAc in methanol at room temperature, no dinulear cyclometallated Pd(II) complexes were obtained. This procedure generated only mononuclear non-cyclometallated Pd(II) complexes [Pd($C_4H_3OCH$=$NC_6H_3$-2,6-*i*-$Pr_2$)$_2Cl_2$] (**3**) and [Pd($C_4H_3SCH$=$NC_6H_3$-2,6-*i*-$Pr_2$)$_2Cl_2$] (**4**). The outcome of the reaction is similar to the reaction reported by Lee and Lee [26]. On the other hand, Kim and co-workers reported the reaction of $Na_2PdCl_4$ with 2-(2′-thienyl)pyridine resulting in a cyclometallated Pd(II) complex [27]. Most probably the cyclometallation depends on the rigid structure of 2-(2′-thienyl)pyridine. After the coordination of N from pyridyl with Pd, rotation of the thienyl ring around C–C axis to a suitable position can result in the activation of the $\beta$-H and




**Scheme 1.** Synthesis of $\mu$-chloro bridged dinuclear cyclometallated Pd(II) complexes.




**Scheme 2.** Synthesis of mononuclear non-cyclometallated Pd(II) complexes.

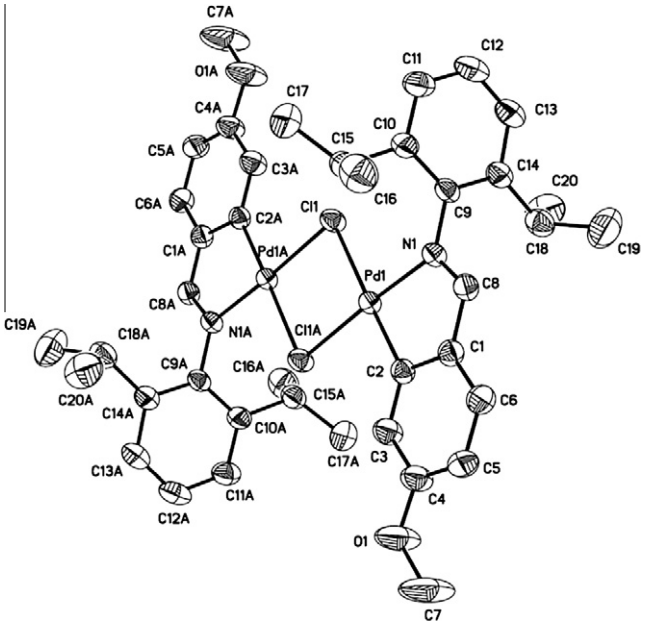



**Fig. 1.** Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Pd1–C2 1.971(4), Pd1–N1 2.036(3), Pd1–Cl1A 2.338(14), Pd1–Cl1 2.453(12), Pd1A–Cl1A 2.453(12), N1–C8 1.294(56); N1–Pd1–Cl1A 175.71(9), N1–Pd1–Cl1 97.817(86), C2–Pd1–N1 80.949(137), C2–Pd1–Cl1 178.73(10), C2–Pd1–Cl1A 94.887(11).

thus to the formation of a cyclometallated Pd(II) complex. In contrast to the 2-(2′-thienyl)pyridine, due to the flexible structure of a Schiff-base ligand bearing a furyl or a thienyl ring lead to the $\beta$-C is drawn apart from the Pd center after coordination of the N atom of the imine group with Pd. Confirmation is obtained by the molecular structures of complexes **3** and **4**. Both complexes were characterized by spectroscopic and elemental analysis and their molecular structures were determined by single crystal X-ray analysis. The IR spectra of **3** and **4** showed a strong stretch vibration assignable to the $\nu$(C=N) at 1616 and 1596 cm$^{-1}$, respectively, which were shifted to lower wavenumbers compared to that of free ligands (1633 and 1627 cm$^{-1}$). Although, this observation in IR is analogous to complexes **1** and **2**, a different observation was made in $^1$H NMR for **3** and **4**, both displayed the resonance for the C*H*=NC protons at $\delta$ 9.13 and $\delta$ 9.36 ppm, respectively, which was shifted to higher frequency, indirectly proving that the $\beta$-H from the furyl or the thienyl ring was not activated and hence no cyclometallation occurred. Moreover, the signal of the $\beta$-H proton of the furyl or the thienyl ring did not disappear, demonstrating the formation of only a Pd–N coordinated complex.

Single crystals of **2**–**4** suitable for X-ray diffraction analysis were obtained from a dichloromethane/hexane solution. Figs. 1–3 show molecular structures of **2**, **3**, and **4**, respectively. Details on crystal data, intensity collection, and refinement details are given in Table 1. As depicted in Fig. 1, the ligand $\mathbf{L_2}$ is bonded to the di-$\mu$-chloro-bridge unit through the nitrogen of imine group and an aromatic carbon atom providing a five-membered chelate ring. Each palladium center adopt a square planar coordination geometry with two cyclometallated ligands in a *trans* arrangement with respect to the Pd···Pd axis, being similar to those reported by Crispini et al. [28]. The five-membered chelate ring defined by Pd1, C2, C1, C8 and N1 is essentially planar with the atomic displacements not exceeding 0.0319 Å, to which the diisopropylphenyl ring is nearly perpendicular with a dihedral angle 79.6(1)°.

The two molecules shown in Figs. 2 and 3 possess similar structural features. The Pd atom in complexes **3** and **4** reveals a square planar coordination containing two trans-N-coordinated Schiff-base ligands and two coordinated chloride atoms. The torsion angle defined by Pd1, N1, C13 and C14 for **3** and by Pd1, N1, C1 and C2 for **4** is 171.8(2)° and 170.6(2)°, respectively. Confirming that the $\beta$-C is drawn apart from the Pd center due to the hindered rotation of bulky isopropyl group and thus no C–H activation occurred. Moreover, the distance of Pd with a proton of a methyl of isopropyl units is ca. 2.78 Å in compound **3** and ca. 3.07 Å in compound **4**, indicating that the non-bonding interaction results in the location of a proton of a methyl in the 5th coordination site of Pd. The furyl and the thienyl groups cannot interact with Pd probably because one methyl group of the isopropyl units is taking this position. Also, this interaction of non-bonding renders a

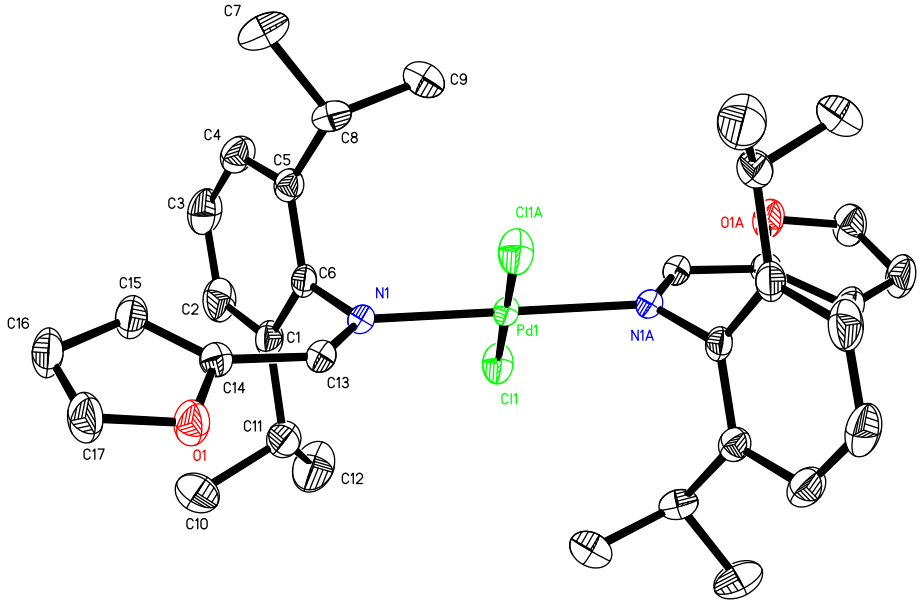



**Fig. 2.** Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Pd1–N1 2.0500(18), Pd1–Cl1 2.2928(7), Pd1–N1A 2.0500(17), Pd1–Cl1A 2.2928(7), C13–N1 1.289(3); N1–Pd1–N1A 180.000(1), N1–Pd1–Cl1A 88.93(6), N1A1–Pd1–Cl1A 191.07(6), N1–Pd1–Cl1 91.07(6), N1A–Pd1–Cl1 88.93(6), Cl1A–Pd1–Cl1 180.00(3), C13–N1–Pd1 117.98(16), C6–N1–Pd1 121.77(15).

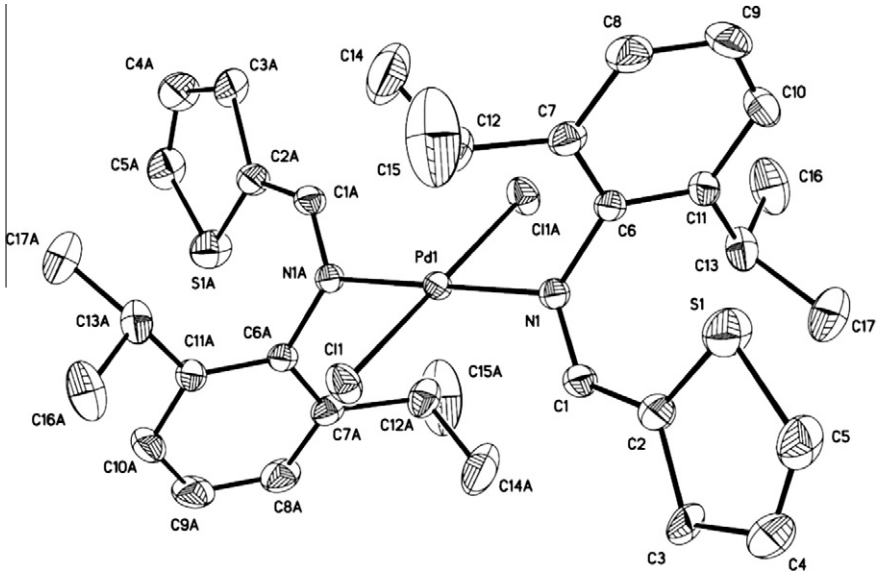



**Fig. 3.** Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Pd1–Cl1 2.2962(10), Pd1–N1 2.042(2), Pd1–N1A 2.042(2), Pd1–Cl1A 2.2962(10), C6–N1 1.451(3); C1–N1–Pd1 118.33(19), C6–N1–Pd1 123.14(17), N1–Pd1–N1A 180.0, N1–Pd1–Cl1A 90.09(7), N1–Pd1–Cl1 89.91(7), N1A–Pd1–Cl1A 89.91(7), N1A–Pd1–Cl1 90.09(7), Cl1–Pd1–Cl1A 180.0.

lowering of the chemical shift (downfield) of the CH unit interacting with Pd. The $^1$H NMR of compounds **3** and **4** displayed the different chemical shifts of both methyl protons (1.54 versus 0.81 ppm for **3** and 1.58 versus 0.83 ppm for **4**). This non-bonding interaction of CH with Pd(II) has been studied, which is different from the well-known agostic CH...Pd interaction that usually leads to up-field chemical shifts [29,30]. Both, the furyl ring and the thienyl ring are nearly orthogonal with respect to the diisopropylphenyl ring with a dihedral angle of 83.7(1)° and 75.7(1)°, respectively.

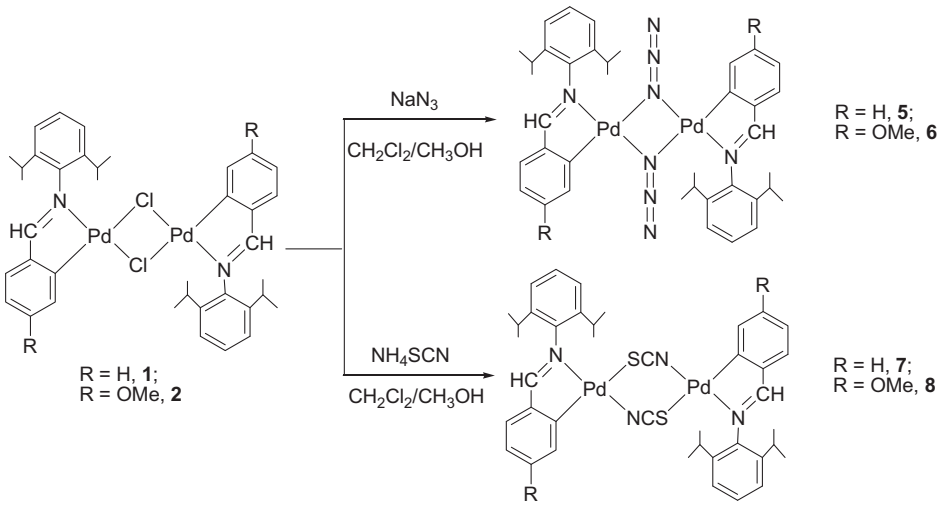
### *2.2. Preparation of μ-$N_3$ and μ-SCN bridged dinuclear cyclometallated Pd(II) complexes*

Since various coordination modes in pseudohalide ligands such as $N_3$ and SCN also belongs to our interest preparation of di-μ-$N_3$ bridged and di-μ-SCN bridged cyclometallated Pd(II) complexes $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}N_3)]_2$ (**5**), $[Pd\{(4\text{-}MeO)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}N_3)]_2$ (**6**), $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}SCN)]_2$ (**7**) and $[Pd\{(4\text{-}MeO)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}SCN)]_2$ (**8**)

**Table 1**
X-ray data collection and structure refinement.

| | **2** | **3** | **4** | **5** | **7** |
|---|---|---|---|---|---|
| Formula | $C_{40}H_{48}Cl_2N_2O_2Pd_2$ | $C_{34}H_{42}Cl_2N_2O_2Pd$ | $C_{34}H_{42}Cl_2N_2PdS_2$ | $C_{38}H_{44}N_8Pd_2$ | $C_{40}H_{44}N_4Pd_2S_2$ |
| Formula weight | 872.50 | 688.00 | 720.12 | 825.61 | 857.71 |
| $T$ (K) | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| Crystal size (mm) | 0.30 × 0.26 × 0.22 | 0.37 × 0.32 × 0.27 | 0.30 × 0.26 × 0.21 | 0.31 × 0.25 × 0.21 | 0.30 × 0.26 × 0.21 |
| Crystal system | triclinic | monoclinic | ticlinic | monoclinic | ticlinic |
| Space group | $P\bar{1}$ | $C2/c$ | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 12.601(3) | 24.757(4) | 9.1304(18) | 11.179(2) | 10.812(2) |
| $b$ (Å) | 13.411(3) | 9.0386(16) | 13.845(3) | 10.436(2) | 11.100(2) |
| $c$ (Å) | 13.767(3) | 15.166(4) | 14.119(3) | 16.564(3) | 18.401(4) |
| $\alpha$ (°) | 92.47(3) | 90 | 90.00 | 90.00 | 84.33(3) |
| $\beta$ (°) | 116.88(3) | 97.359(18) | 92.79(3) | 104.35(3) | 87.96(3) |
| $\gamma$ (°) | 105.20(3) | 90 | 90.00 | 90.00 | 61.56(3) |
| $V$ (Å$^3$) | 1966.9(8) | 3365.7(12) | 1782.7(6) | 1872.1(6) | 1932.2(7) |
| $Z$ | 2 | 4 | 2 | 2 | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.470 | 1.358 | 1.342 | 1.465 | 1.474 |
| $\mu$ (mm$^{-1}$) | 1.085 | 0.741 | 0.812 | 0.988 | 1.071 |
| $F$(0 0 0) | 884 | 1424 | 744 | 840 | 872 |
| $T_{min}$ | 0.7367 | 0.7716 | 0.7928 | 0.755 | 0.7394 |
| $T_{max}$ | 0.7963 | 0.8261 | 0.8480 | 0.827 | 0.8261 |
| Number of reflections measured | 15 794 | 4028 | 13 961 | 14 565 | 15 443 |
| Number of unique reflections | 7052 | 3313 | 3201 | 3373 | 6916 |
| Number of parameters refined | 443 | 188 | 191 | 221 | 436 |
| Maximum in $\Delta\rho$ (e Å$^{-3}$) | 0.644 | 0.240 | 0.608 | 0.912 | 1.522 |
| Minimum in $\Delta\rho$ (e Å$^{-3}$) | −0.379 | −0.329 | −0.438 | −1.004 | −1.453 |
| Goodness-of-fit (GOF) on $F^2$ | 1.083 | 1.021 | 1.082 | 1.155 | 1.193 |
| $R$ ($I > 2\sigma(I)$) | 0.0307 | 0.0281 | 0.0308 | 0.0373 | 0.0576 |
| $wR_2$[a] ($I > 2\sigma(I)$) | 0.0737 | 0.0688 | 0.0795 | 0.0867 | 0.1491 |
| $R$ (all data) | 0.0482 | 0.0389 | 0.0386 | 0.0736 | 0.1086 |
| $wR_2$[a] (all data) | 0.0843 | 0.0743 | 0.0867 | 0.1405 | 0.2366 |

[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.




**Scheme 3.** Synthesis of di-$\mu$-$N_3$ bridged and di-$\mu$-SCN bridged cyclometallated Pd(II) complexes.

by means of metathesis using complex **1** or **2** was performed, see Scheme 3.

Recently, Kim and co-workers reported on $\mu$-$N_3$ bridged cyclometallated Pd(II) complexes containing C,N-chelating ligands, e.g. 2-(2′-thienyl)pyridine, azobenzene, 3,3′-dimethyl azobenzene, *N,N′*-dimethylbenzylamine, 2-phenylpyridine [27]. However, it was found difficult to purify and structurally characterize those complexes due to their poor solubility in organic solvents. Complexes **5**, **6**, **7** and **8** were characterized by spectroscopic and elemental analysis and the molecular structure of **5** and **7** were determined by single crystal X-ray analysis. The formation of complexes **5** and **6** were readily confirmed by a characteristic stretch vibration band at 2062 $cm^{-1}$ assigned to the bridged $N_3$ group. The formation of complexes **7** and **8** was readily confirmed by two characteristic stretch vibrations, at 2142 and 2150 $cm^{-1}$ assigned to the bridged SCN group.

Single crystals of **5** and **7** suitable for X-ray diffraction analysis were obtained from a dichloromethane/hexane solution. Figs. 4 and 5 show the molecular structure of **5** and **7**, respectively. Details on crystal data, intensity collection, and refinement details are given in Table 1. As shown in Fig. 4, in complex **5** each of two azido groups bridges with two Pd atoms through the same nitrogen creating a four-membered ring. Each palladium center adopts square planar coordination geometry with two cyclometallated ligands in a *trans* arrangement with respect to the Pd···Pd axis, which is similar to those of complex **2**. The Pd···Pd distance (3.268 Å) excludes the possibility of a metal–metal bond. The five-membered chelate ring defined by Pd1, N1, C13, C14 and C15 is essentially planar with atomic displacements not exceeding 0.0357 Å, to which the diisopropylphenyl ring is nearly perpendicular with a dihedral angle 84.4(1)°. The azido group is essentially linear with the bond angle of 179.0(10)°. The Pd1–C15 bond (1.983(6) Å) is slightly longer

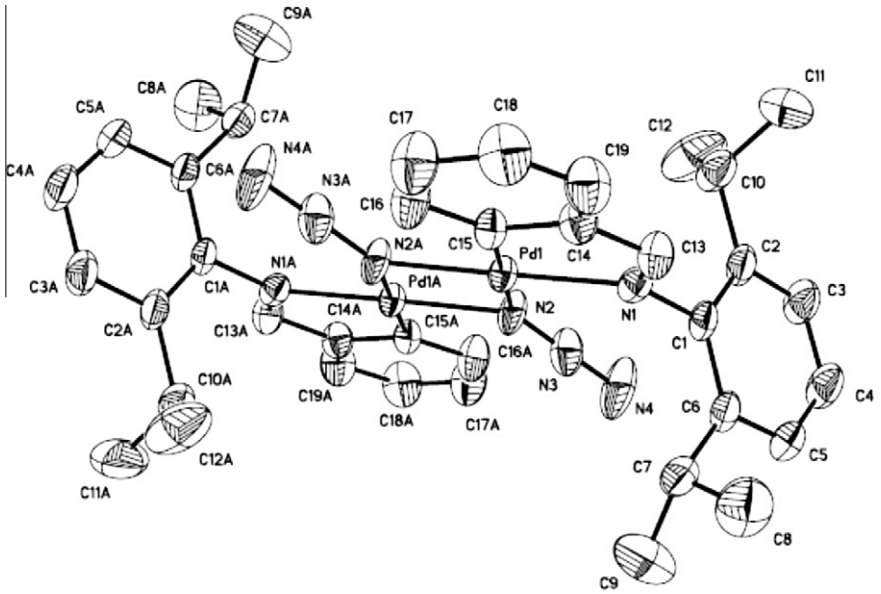



**Fig. 4.** Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Pd1–N1 2.037(5), Pd1–N2A 2.048(5), Pd1–N2 2.166(5), Pd1–C15 1.983(6), N2–N3 1.202(7), N3–N4 1.164(8); N3–N2–Pd1 127.3(5), Pd1–N2–Pd1A, 101.7(2), N4–N3–N2 179.0(10), C15–Pd1–N1 80.9(2), C15–Pd1–N2A 100.2(2), N1–Pd1–N2A 178.3(2), C15–Pd1–N2 177.3(2), N1–Pd1–N2 100.5(2), N2–Pd1–N2A 78.3(2).

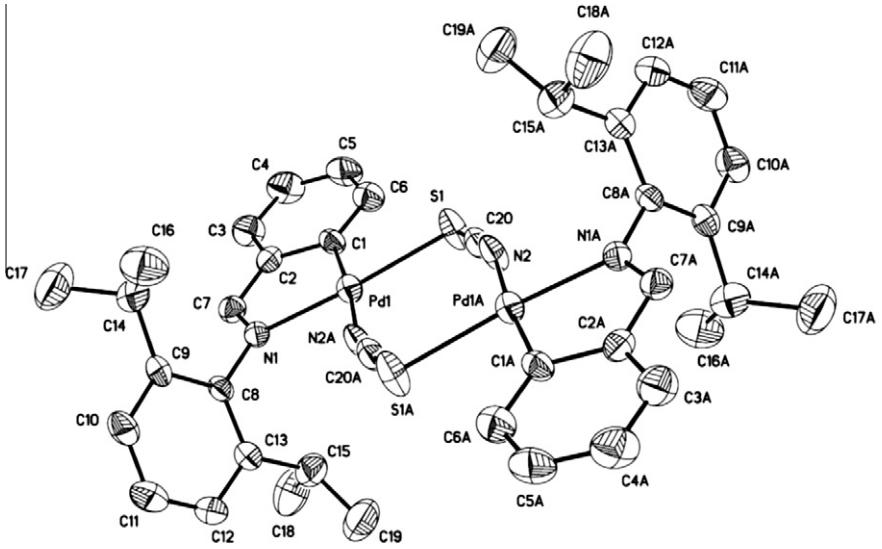



**Fig. 5.** Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Pd1–N1 2.066(7), Pd1–N2A 2.081(9), Pd1–S1 2.320(3), Pd1–C1 1.982(10), N2A–C20A 1.159(13), C20A–S1A 1.660(11); C1–Pd1–N1 82.2(3), N1–Pd1–N2A 93.5(3), C1–Pd1–S1 89.7(3), N1–Pd1–S1 171.8(2), C1–Pd1–N2 174.2(3), N2A–Pd1–S1 94.7(2), N2–C20–S1 178.7(10).

than in **2** (1.971(4) Å) and shorter than the calculated value of 2.05 Å based on the sum of the covalent radii of carbon and palladium. The Pd1–N2 bond (2.166(5) Å) and Pd1–N2A bond (2.048(5) Å) are longer than those found for the related complex $[Pd_2(N_3)_6]^{2-}$ ((2.016(11) Å) and (1.993(11) Å)) [31].

Fig. 5 reveals that both SCN groups bridges two Pd atoms through both S and N atoms forming an eight-membered ring in **7**. The molecular of **7** shows a slightly distorted square-planar coordination around the Pd center. The eight-membered heteroatom ring is non-planar. The distance from Pd to the plane defined by S1, C20, N2, N2A, C20A, S1A measures 0.3064 Å. The thiocyanato group is basically linear with the bond angle of 178.7(10)°. The Pd···Pd separation is 5.587(2) Å due to the bridging SCN group to excluding any Pd···Pd interaction. The length of Pd–C bond is similar to the length found in **5** and Pd–N1 bond is longer than measured in **5**.

In summary, $\mu$-chloro bridged dinuclear cyclometallated Pd(II) complexes were prepared by reaction of $Na_2PdCl_4$ with benzylideneaniline. However, the reaction of $Na_2PdCl_4$ with Schiff-base ligands bearing a five-membered heteroatom ring only resulted in mononuclear non-cyclometallated Pd(II) species.

Di-$\mu$-$N_3$ bridged and di-$\mu$-SCN bridged cyclometallated Pd(II) complexes were synthesized by means of metathesis of the corresponding $\mu$-chloro bridged cyclometallated Pd(II) complex with an excess of $NaN_3$ or $NH_4SCN$. The molecular structures of $\mu$-$N_3$ bridged and $\mu$-SCN bridged cyclometallated Pd(II) complexes confirmed that the azido group bridged two palladium atoms through the same nitrogen atom and the thiocyanato group bridged two palladium atoms through both S and N atoms. Further studies are in progress to explore applicability of these cyclometallated Pd(II) complexes as building blocks toward supramolecular construction.

## 3. Experimental

### 3.1. General, materials and measurements

All manipulations of air-sensitive compounds were performed under inert atmosphere using standard Schlenk techniques. All solvents were purified and degassed before use. Other reagents were used as supplied. $^1$H NMR spectra were obtained using a Mercury-300 spectrophotometer in $CDCl_3$ and TMS was applied as an internal standard. IR spectra were recorded on a Niclolet AVATAR 330 FT-IR spectrometer. Elemental analyses were performed on a Thermo Flash EA1112 Analyzer.

### 3.2. Preparations

*2,6-Diisopropyl-N-(benzylidene)aniline (**L$_1$**).* To a stirred solution of benzaldehyde (1.1 mL, 10.6 mmol) in dried ethanol (15 mL), 2,6-diisopropylaniline (2.0 mL, 10.6 mmol) and formic acid (two drops) were added. The reaction mixture was stirred for 24 h at room temperature. Subsequently, the resulting solution was concentrated to dryness resulting in an oily substance, which was dissolved in hexane and cooled to −20 °C overnight to afford pale green crystals of **L$_1$** (2.1 g, 78%). IR (KBr, cm$^{-1}$): 1636 ($\nu_{C=N}$); m.p. : 58–60 °C; $^1$H NMR (300 MHz in $CDCl_3$, $\delta$): 8.19 (s, 1H, –C*H*=N), 7.93–7.89 (m, 2H, Ar), 7.52–7.49 (m, 3H, Ar), 7.17–7.10 (m, 3H, Ar), 2.98 (hepta, 2H, –C*H*), 1.17 (d, 12H, –C$H_3$). *Anal.* Calc. for $C_{19}H_{23}N$: C, 85.99; H, 8.74; N, 5.28. Found: C, 86.01; H, 8.81; N, 5.19%.

2,6-Diisopropyl-*N*-(4-methoxybenzylidene)aniline (**L$_2$**, 77%), 2,6-diisopropyl-*N*-(2-furylmethylidene)aniline (**L$_3$**, 76%) and 2,6-diisopropyl-*N*-(2-thienyl methylidene)aniline (**L$_4$**, 71%) were prepared in a similar manner.

***L$_2$*:** White crystals: IR (KBr, cm$^{-1}$): 1643 ($\nu_{C=N}$); m.p.: 109–110 °C; $^1$H NMR (300 MHz in $CDCl_3$, $\delta$): 8.12 (s, 1H, –C*H*=N), 7.86 (d, 2H, Ar), 7.17–7.10 (m, 3H, Ar), 7.04–7.00 (m, 2H, Ar), 3.89 (s, 3H, –OC$H_3$), 2.99 (hepta, 2H, –C*H*), 1.17 (d, 12H, –C$H_3$). *Anal.* Calc. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.35; H, 8.53; N, 4.64%.

***L$_3$*:** Pale yellow crystals: IR (KBr, cm$^{-1}$): 1633 ($\nu_{C=N}$); m.p.: 55–56 °C; $^1$H NMR (300 MHz in $CDCl_3$, $\delta$): 7.98 (s, 1H, –C*H*=N), 7.64 (s, 1H, furyl), 7.17–7.10 (m, 3H, Ar), 6.95 (d, 1H, furyl), 6.59–6.57 (m, 1H, furyl), 3.00 (hepta, 2H, –C*H*), 1.17 (d, 12H, –C$H_3$). *Anal.* Calc. for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.10; H, 8.23; N, 5.56%.

***L$_4$*:** Pale yellow crystals: IR (KBr, cm$^{-1}$): 1627 ($\nu_{C=N}$); m.p.: 48–49 °C; $^1$H NMR (300 MHz in $CDCl_3$, $\delta$): 8.27 (s, 1H, –C*H*=N), 7.53 (d, 1H, thienyl), 7.43 (d, 1H, thienyl), 7.17–7.06 (m, 4H, Ar, thienyl), 3.00 (hepta, 2H, –C*H*), 1.17 (d, 12H, –C$H_3$). *Anal.* Calc. for $C_{17}H_{21}NS$: C, 75.23; H, 7.80; N, 5.16. Found: C, 75.05; H, 8.07; N, 5.02%.

$[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ (**1**), $[Pd\{(4\text{-}OMe)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Cl)]_2$ (**2**), $[Pd(C_4H_3OCH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_2]$ (**3**) and $[Pd(C_4H_3SCH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_2]$ (**4**). To a 20 mL methanol solution of $Na_2PdCl_4$ (0.500 g, 1.70 mmol) was added 2,6-diisopropyl-*N*-(benzylidene)aniline (0.901 g, 3.40 mmol) and sodium acetate (0.279 g, 3.40 mmol). After stirring for 6 h at room temperature, the dark green solids were filtered off and washed with distilled water and ether. The crude product was dissolved in $CH_2Cl_2$ and filtered, removing the insoluble materials. Evaporating the solvent a yellow solid was obtained that was recrystallized from $CH_2Cl_2$/hexane to give yellow crystals of $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ (**1**, 0.573 g, 83%). IR (KBr, $cm^{-1}$): 1601 ($\nu_{C=N}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 7.74 (s, 2H, –C*H*=N), 7.33–7.27 (m, 4H, Ar), 7.23–7.14 (m, 6H, Ar), 7.08–7.03 (m, 4H, Ar), 3.51 (hepta, 4H, –C*H*), 1.38 (d, $J$ = 6.6 Hz, 12H, –C$H_3$), 1.14 (d, $J$ = 6.9 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{38}H_{44}Cl_2N_2Pd_2$: C, 56.17; H, 5.46; N, 3.45. Found: C, 56.19; H, 5.48; N, 3.27%.

Complexes **2**, **3** and **4** were prepared in a similar manner as complex **1**.

*$[Pd\{(4\text{-}OMe)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Cl)]_2$ (**2**, 55%):* IR (KBr, $cm^{-1}$): 1600 ($\nu_{C=N}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 7.61 (s, 2H, –C*H*=N), 7.26–7.14 (m, 8H, Ar), 6.71 (d, 2H, Ar), 6.58 (d, $J$ = 8.4 Hz, 2H, Ar), 3.73 (s, 6H, –OC$H_3$), 3.52 (hepta, 4H, –C*H*), 1.38 (d, $J$ = 6.9Hz, 12H, –C$H_3$), 1.14 (d, $J$ = 6.6 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{40}H_{48}Cl_2N_2O_2Pd_2$: C, 55.06; H, 5.54; N, 3.21. Found: C, 54.61; H, 5.35; N, 3.13%.

*$[Pd(C_4H_3OCH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_2]$ (**3**, 79%):* IR (KBr, $cm^{-1}$): 1616 ($\nu_{C=N}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 9.13 (s, 2H, –H*C*=N), 7.44 (s, 2H, furyl), 7.33 (m, 2H, Ar), 7.20 (d, $J$ = 7.8 Hz, 4H, Ar), 6.25 (m, 2H, furyl), 5.26 (br, 2H, furyl), 3.44 (hepta, 4H, –C*H*), 1.54 (d, $J$ = 6.6 Hz, 12H, –C$H_3$), 0.81 (d, $J$ = 6.9Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{34}H_{42}Cl_2N_2O_2Pd$: C, 59.35; H, 6.15; N, 4.07. Found: C, 59.60; H, 6.14; N, 4.15%.

*$[Pd(C_4H_3SCH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_2]$ (**4**, 87%):* IR (KBr, $cm^{-1}$): 1596 ($\nu_{C=N}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 9.36 (s, 2H, –H*C*=N), 7.44–7.36 (m, 6H, Ar), 7.25 (d, $J$ = 3.9 Hz, 4H, thienyl), 6.96 (t, $J$ = 4.5 Hz, 2H, thienyl), 3.42 (hepta, 4H, –C*H*), 1.58 (d, $J$ = 6.9 Hz, 12H, –C$H_3$), 0.83 (d, $J$ = 7.2 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{34}H_{42}Cl_2N_2PdS_2$: C, 56.70; H, 5.88; N, 3.89; S, 8.90. Found: C, 56.43; H, 6.01; N, 3.93; S, 8.76%.

*$[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}N_3)]_2$ (**5** ) and $[Pd\{(4\text{-}MeO)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}N_3)]_2$ (**6**).* To a 10 mL $CH_2Cl_2$ solution of complex **1** (0.101 g, 0.12 mmol) was added $NaN_3$ (0.033 g, 0.51 mmol) solution dissolved in 4 mL methanol. The initial yellow solution turned to a yellow suspension. After stirring for 20 h at room temperature, the solvent was completely evaporated. The resulting residue was dissolved in $CH_2Cl_2$ and insoluble material was filtered out. The filtrate was evaporated to remove solvents completely to give yellow solids, which were recrystallized from $CH_2Cl_2$/hexane to give yellow crystals of $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}N_3)]_2$ (**5**, 0.0710 g, 72%). IR (KBr, $cm^{-1}$): 1600 ($\nu_{C=N}$), 2062 ($\nu_{N=N=N}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 7.75 (s, 2H, –C*H*=N), 7.34 (m, 4H, Ar), 7.26 (d, $J$ = 6.9 Hz, 4H, Ar), 7.15 (m, 4H, Ar), 6.99 (d, $J$ = 6.9 Hz, 2H, Ar), 3.51 (hepta, 4H, –C*H*), 1.46 (d, $J$ = 6.6 Hz, 12H, –C$H_3$), 1.18 (d, $J$ = 6.6 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{38}H_{44}N_8Pd_2$: C, 55.28; H, 5.37; N, 13.57. Found: C, 55.16; H, 5.31; N, 13.13%.

Complex **6** was prepared in a similar manner.

*$[Pd\{(4\text{-}MeO)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}N_3)]_2$ (**6**, 71%):* IR (KBr, $cm^{-1}$): 1598 ($\nu_{C=N}$), 2062 ($\nu_{N=N=N}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 7.61 (s, 2H, –C*H*=N), 7.32–7.21 (m, 8H, Ar), 6.63 (dd, $J$ = 2.4, 2.1 Hz, 4H, Ar), 6.53 (d, 2H, $J$ = 2.1 Hz, Ar), 3.75 (s, 6H, –OC$H_3$), 3.53 (hepta, 4H, –C*H*), 1.45 (d, $J$ = 6.6 Hz, 12H, –C$H_3$), 1.18 (d, $J$ = 6.9 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{40}H_{48}N_8O_2Pd_2$: C, 54.24; H, 5.46; N, 12.65. Found: C, 54.26; H, 5.53; N, 12.50%.

*$[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}SCN)]_2$ (**7**) and $[Pd\{(4\text{-}MeO)C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}SCN)]_2$ (**8**).* To a 10 mL $CH_2Cl_2$ solution of complex **1** (0.0980 g, 0.12 mmol) was added $NH_4SCN$ (0.0380 g, 0.50 mmol) solution dissolved in 2 mL methanol. The initial yellow solution turned to a yellow suspension. After stirring for 18 h at room temperature, the solvent was completely evaporated. The resulting residue was dissolved in $CH_2Cl_2$ and insoluble material was filtered out. The filtrate was evaporated to remove the solvent completely and the obtained yellow solid was recrystallized from a $CH_2Cl_2$/hexane solution to give yellow crystals of $[Pd(C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}SCN)]_2$ (**7**, 0.0875 g, 85%). IR (KBr, $cm^{-1}$): 1602 ($\nu_{C=N}$), 2142 ($\nu_{SCN}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 7.83 (s, 2H, –C*H*=N), 7.35 (m, 2H, Ar), 7.29 (d, $J$ = 8.1 Hz, 2H, Ar), 7.20 (d, $J$ = 7.5 Hz, 4H, Ar), 7.10 (m, 4H, Ar), 6.91 (m, 2H, Ar), 3.40 (hepta, 4H, –C*H*), 1.36 (d, $J$ = 6.6 Hz, 12H, –C$H_3$), 1.15 (d, $J$ = 6.9 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{40}H_{44}N_4Pd_2S_2$: C, 56.01; H, 5.17; N, 6.53; S, 7.48. Found: C, 55.92; H, 5.10; N, 6.51; S, 7.32%.

Complex **8** was prepared in similar manner.

*$[Pd\{(4\text{-}MeO)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}SCN)]_2$ (**8**, 79%):* IR (KBr, $cm^{-1}$): 1599 ($\nu_{C=N}$), 2150 ($\nu_{SCN}$); $^1H$ NMR (300 MHz in $CDCl_3$, $\delta$): 7.68 (s, 2H, –C*H*=N), 7.28 (m, 2H, Ar), 7.17 (d, $J$ = 7.8 Hz, 4H, Ar), 7.08 (m, 2H, Ar), 6.58 (dd, $J$ = 2.4 Hz, 2H, Ar), 6.41 (d, $J$ = 2.4 Hz, 2H, Ar), 3.77 (s, 6H, –OC$H_3$), 3.38 (hepta, 4H, –C*H*), 1.34 (d, $J$ = 6.9 Hz, 12H, –C$H_3$), 1.12 (d, $J$ = 6.9 Hz, 12H, –C$H_3$). *Anal.* Calc. for $C_{42}H_{48}N_4Pd_2S_2{\cdot}0.5CH_2Cl_2$: C, 54.99; H, 5.32; N, 6.04; S, 6.91. Found: C, 55.06; H, 5.44; N, 6.05; S, 6.56%.

### 3.3. X-ray structure determination

Suitable crystals for X-ray analysis of **2**, **3**, **4**, **5** and **7** were obtained by recrystallization from $CH_2Cl_2$/hexane. X-ray data of the complexes were collected on a D-MAX 2200 VPC diffractometer. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). All data were collected at room temperature using the ω-scan technique. Details of the data collection and refinement are summarized in Table 1. All calculations were carried out with the SHELXL-97 programs [32]. The structures were solved by direct methods. The non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods.

## Acknowledgments

This work was supported by the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (2008), by the Scientific Research Foundation funded by Liaoning Provincial Education Department of China [No. 2008T073] and by the Scientific Research Foundation funded by Liaoning University of China for young scholar [No. 2007LDQN04].

## Appendix A. Supplementary material

CCDC 806544 contains the supplementary crystallographic data for **2**, **3**, **4**, **5** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/deposit. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.06.003.

## References

[1] J. Dupont, M. Pfeffer, Palladacycles, Wiley-VCH, Weinheim, 2008.
[2] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527.
[3] V.K. Jain, L. Jain, Coord. Chem. Rev. 249 (2005) 3075.

[4] I.P. Beletskaya, A.V. Cheprakov, J. Orgnomet. Chem. 689 (2004) 4055.
[5] I. Omae, Coord. Chem. Rev. 248 (2004) 995. and references therein.
[6] E. Negishi, Handbook of Organopalladium Chemistry for Organic Synthesis, vol. 1, Wiley & Sons, Inc., 2002. p. 147.
[7] G. Wilkinson, R.D. Gillard, J.A. McCleverty, Comprehensive Coordination Chemistry, vol. 6, Pergamon, Oxford, 1987. p. 279.
[8] I. Omae, Organometallic Intramolecular-Coordination Compounds, J. Organomet. Chem. Library 18, Elsevier, Amsterdam, 1986.
[9] J. Albert, M. Crespo, J. Granell, J. Rodríguez, J. Zafrilla, T. Calvet, M. Font-Bardia, X. Solans, Organometallics 29 (2010) 214.
[10] R. Martín, M. Crespo, M. Font-Bardia, T. Calvet, Organometallics 28 (2009) 587.
[11] J. Martínez, M.T. Pereira, I. Buceta, G. Alberdi, A. Amoedo, J.J. Fernández, M. López-Torres, J.M. Vila, Organometallics 22 (2003) 5581.
[12] M. Gómez, J. Granell, M. Martinez, Organometallics 16 (1997) 2539.
[13] I. Aiello, D. Dattilo, M. Ghedini, A. Golemme, J. Am. Chem. Soc. 123 (2001) 5598.
[14] A.D. Ryabov, A.K. Yatsimirski, Inorg. Chem. 23 (1984) 789.
[15] L. Adrio, J.M. Antelo, J.M. Ortigueira, J.J. Fernández, A. Fernández, M.T. Pereira, J.M. Vila, J. Organomet. Chem. 694 (2009) 1273.
[16] T. Schultz, N. Schmees, A. Pfaltz, Appl. Organomet. Chem. 18 (2004) 595.
[17] D.J. Saccomando, C. Black, G.W.V. Cave, D.P. Lydon, J.P. Rourke, J. Organomet. Chem. 601 (2000) 305.
[18] Z. Dori, R.F. Ziolo, Chem. Rev. 73 (1973) 247.
[19] G. Wilkinson, R.D. Gillard, J.A. McCleverty, Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987. p. 127.
[20] J.L. Burmeister, Coord. Chem. Rev. 3 (1968) 225.
[21] A.H. Norbury, A.J.P. Sinha, Rev. Chem. Soc. 24 (1970) 69.
[22] X. Chang, K.-E. Lee, S.I. Jeon, Y.-J. Kim, H.-K. Lee, S.W. Lee, Dalton Trans. (2005) 3722.
[23] C.-L. Chen, Y.-H. Liu, S.-M. Peng, S.-T. Liu, J. Organomet. Chem. 689 (2004) 1806.
[24] H. Onoue, I. Moritani, J. Organomet. Chem. 43 (1972) 431.
[25] Y. Ustynyuk, V.A. Chertov, J.V. Barinov, J. Organomet. Chem. 29 (1971) C53.
[26] H.K. Lee, S.W. Lee, J. Korean Chem. Soc. 50 (2006) 420.
[27] K.-E. Lee, H.-T. Jeon, S.-Y. Han, J. Ham, Y.-J. Kim, S.W. Lee, Dalton Trans. (2009) 6578.
[28] A. Crispini, G.D. Munno, M. Ghedini, F. Neve, J. Organomet. Chem. 427 (1992) 409.
[29] L. Brammer, J.M. Charnock, P.L. Goggin, R.J. Goodfellow, A.G. Orpena, T.F. Koetzle, J. Chem. Soc., Dalton Trans. (1991) 1789.
[30] J. Dupont, N. Beydoun, M. Pfeffer, J. Chem. Soc., Dalton Trans. (1989) 1715.
[31] W.P. Fehlhammer, L.F. Dahl, J. Am. Chem. Soc. 94 (1972) 3377.
[32] G.M. Sheldrick, SHELXL-97, Universität of Gőttingen, Germany, 1997.