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Reactivity of μ-azido and μ-thiocyanato bridged Schiff base palladacycles toward aromatic *N*-heterocycles and phosphines

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ABSTRACT

Reaction of μ-azido bridged Schiff base palladacycles [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-N_3)]$_2$ (R = H; OMe) with 1-methylimidazole generated different conformational mononuclear palladacycles. Complexes [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-N_3)]$_2$ (R = H; OMe) reacted with bidentate 1,2-bis(4-pyridyl)-ethene to give mononuclear palladacycles. Also the reaction of [Pd{C_6H_4CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-N_3)]$_2$ with 4,4′-bipyridine (bpy) produced mononuclear palladacycles. However, the reaction of [Pd{(4-MeO)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-N_3)]$_2$ with 4,4′-bipyridine formed a 4,4′-bipyridine bridged binuclear palladacycle [Pd{(4-OMe)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(N_3)]$_2$(μ-bpy). In contrast, μ-thiocyanato bridged Schiff base palladacycles were relatively unreactive toward aromatic *N*-heterocycles. Only the reaction of [Pd{C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2}(μ-SCN)]$_2$ with imidazole generated a thiocyanato coordinated mononuclear Schiff base palladacycle [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(imidazole)(SCN)]. Moreover, reactions of μ-azido and μ-thiocyanato bridged Schiff base palladacycles with triphenylphosphine and 1,4-bis(diphenylphosphino) butane routinely formed mono- and binuclear terminal azido or isothiocyanato coordinated palladacycles [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(PPh_3)(N_3)], [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(PPh_3)(NCS)], [Pd{(4-R)C_6H_3−CH=N−C_6H_3−2,6-*i*-Pr_2}(N_3)]$_2$(μ-dppb) and [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(NCS)]$_2$(μ-dppb) (R = H; OMe).

1. Introduction

In the last few decades, cyclometallation of C,N-chelating ligands by palladium has remained as one of the major topics in organometallic chemistry [1–8]. Recently, the reactivity of μ-chloro and μ-acetato bridged Schiff base palladacycles toward phosphines has been extensively studied due to their relevance to supramolecular chemistry [9–15]. We also reported mono-, bi- and trinuclear Schiff-base palladacycles by reactions of μ-chloro bridged Schiff base palladacycles with aromatic *N*-heterocycles [16]. However, the reactivity of μ-azido and μ-thiocyanato bridged Schiff base palladacycles is still unexplored, therefor, a novel reactivity due to the azido and thiocyanato group could be introduced into Schiff base palladacycles. Recently, we reported on the synthesis of μ-azido and μ-thiocyanato bridged Schiff base palladacycles [17]. Herein, we describe the reactivity of μ-azido and μ-thiocyanato bridged Schiff base palladacycles toward aromatic *N*-heterocycles and phosphines. This study has allowed the preparation of a series of novel azido, thiocyanato or isothiocyanato coordinated Schiff base palladacycles.

2. Results and discussion

2.1. Reactions of μ-azido and μ-thiocyanato bridged Schiff base palladacycles with aromatic N-heterocycles

μ-Azido and μ-thiocyanato bridged Schiff base palladacycles [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-N_3)]$_2$ (R = H, **1**; OMe, **2**) and [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-SCN)]$_2$ (R = H, **3**; OMe, **4**) were synthesized by metathesis of the corresponding cyclopalladated chloro dimer [Pd{(4-R)C_6H_3CH=N−C_6H_3−2,6-*i*-Pr_2}(μ-Cl)]$_2$ with NaN_3 and NH_4SCN in CH_2Cl_2/CH_3OH, respectively [17]. Subsequently, we examined the reactions of complexes **1**–**4** with monodentate aromatic *N*-heterocycles, such as 1-methylimidazole and imidazole, as shown Schemes 1 and 2. Treatment of complexes **1** and **2** with 2 equiv. 1-methylimidazole in CH_2Cl_2 at room

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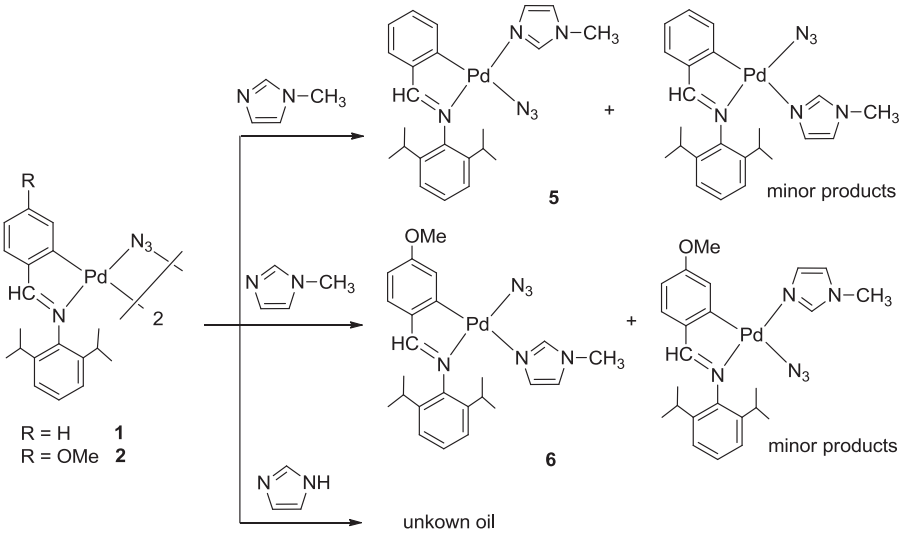
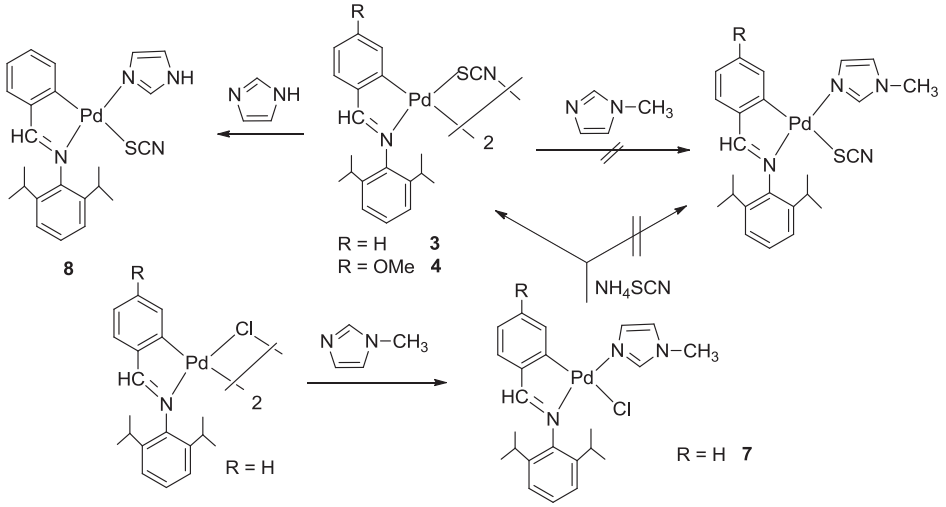


Scheme 1. Reactions of complexes **1** and **2** with monodentate aromatic *N*-heterocycles.

temperature produced yellow mononuclear Schiff base palla dacycles [Pd{(4-R)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(1-methylimidazole)(N_3)] (R = H, **5**; R = OMe, **6**). However, reaction of complexes **1** and **2** with 2 equiv. imidazole in CH_2Cl_2 at room temperature delivered unknown oils, which were not further characterized. Complexes **5** and **6** were characterized by FT-IR, NMR, elemental analysis and single crystal X-ray diffraction. A strong stretch vibration in the FT-IR spectra of **5** and **6** was observed at approximately 2036 cm^{-1} due to the terminal azido group, which was shifted to lower wavenumbers compared to the bridging azido group present in the starting materials (2062 cm^{-1}) [18] indicating that 1-methylimidazole cleaved cyclopalladated azido dimmers. The ^1H NMR spectra of **5** and **6** displayed the resonance for C*H*=N protons at δ 7.89 and δ 7.75 ppm, respectively, indicating a downfield shift compared to the corresponding N_3-bridged cyclopalladated complexes **1** and **2** (δ 7.75 ppm and δ 7.61 ppm, respectively). Moreover, we recognized the presence of two isomers in solution of **5** and **6** according to the ^1H NMR spectra (in the ratio of 1.00:0.16 for **5** and 1.00:0.15 for **6** based on the proton integration) and confirmation was obtained from the molecular structure of **5** and **6**. Interestingly, complexes **3** and **4** showed a distinctive reactivity toward 1-methylimidazole and imidazole comparing to complexes **1** and **2**. Treatment of complexes **3** and **4** with 2 equiv. 1-methylimidazoles in CH_2Cl_2 at room temperature did not produce any mononuclear Schiff base palladacycles. Therefore, we synthesized the chloro coordinated mononuclear Schiff base palladacycle [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2)(1-methylimidazole)(Cl)] (**7**) by reaction of the cyclopalladated chloro dimer [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2)(μ-Cl)]$_2$ with 1-methylimidazole. In an effort to synthesize the thiocyanato or isothiocyanato coordinated mononuclear Schiff base palladacycle by metathesis of **7** with NH_4SCN in CH_2Cl_2/CH_3OH did not produce the expected product but a μ-thiocyanato bridged Schiff base palladacycle **3** was generated. This result suggests that the coordinating ability of the thiocyanato group to Pd is stronger compared to 1-methylimidazole. Unexpectedly, when complex **3** reacted with 2 equiv. imidazole in CH_2Cl_2 at room temperature, thiocyanato coordinated mononuclear Schiff base palladacycle [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(imidazole)(SCN)] (**8**) was isolated. FT-IR spectra of **8** showed a characteristic stretch vibration band at 2108 cm^{-1} due to the S-coordinated thiocyanato group [19], which was shifted to lower wavenumbers compared to the bridged SCN group in complex **3** (2142 cm^{-1}). The molecular



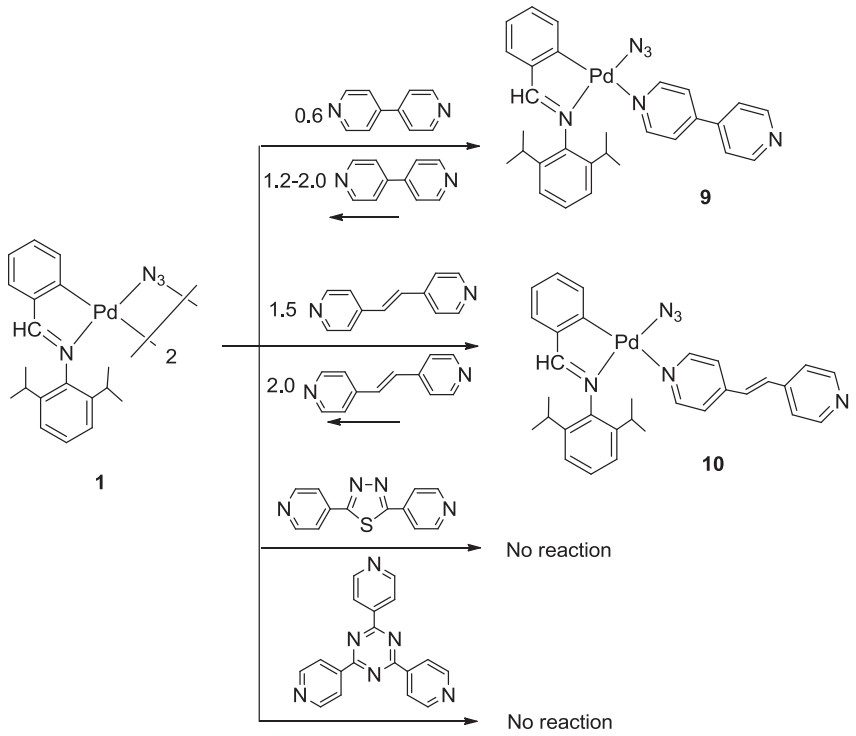
Scheme 2. Reactions of complexes **3** and **4** with monodentate aromatic *N*-heterocycles.

structure of **3** also confirmed that the SCN group coordinates to Pd through the S atom. The ^{1}H NMR spectra of **8** displayed the resonance for C*H*=N protons at δ 7.97 ppm, which was shifted downfield compared to the corresponding SCN-bridged cyclopalladated complex **3** (δ 7.83 ppm). The resonance at δ 10.82 ppm in **3** was assigned to N–*H* protons of coordinating imidazole ring.

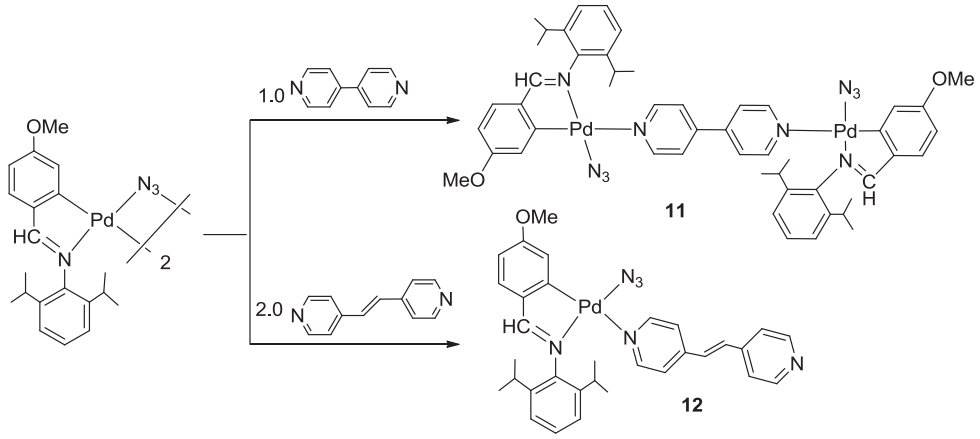
In contrast, we are more interested in reactivity of μ-azido and μ-thiocyanato bridged Schiff base palladacycles toward bi- and tridentate aromatic *N*-heterocycles, expecting the formation of novel bi- and tri-nuclear Schiff base palladacycles. Surprisingly, μ-azido bridged Schiff base palladacycles showed complicated activities (Schemes 3 and 4) and μ-thiocyanato bridged Schiff base palladacycles showed chemical stability with bi- and tri-dentate aromatic *N*-heterocycles. When complex **1** reacted with 0.6 equiv. 4,4′-bipyridyl (bpy) in CH_2Cl_2 at room temperature, yellow mononuclear Schiff base palladacycle [Pd(C_6H_4–CH=NC_6H_3–2,6-*i*-Pr_2)(bpy)(N_3)] (**9**) was obtained. The formation of **9** was confirmed by FT-IR and ^{1}H NMR spectra. FT-IR spectra of **9** showed a strong stretch vibration band at 2044 cm^{-1} assigned to terminal N_3 group instead of bridged N_3 group at 2062 cm^{-1}. Elemental analysis of **9** was consistent with the formula [$C_{29}H_{30}N_6Pd\cdot CH_2Cl_2$] of the mononuclear structure. Single crystal X-ray analysis of **9** also confirmed its mononuclear structure. However, treatment of **1** with 1.2–2.0 equiv. 4,4′-bipyridyl did not yield the expected binuclear Schiff base palladacycle, but produced **9** and **1**. These results indicated that the azido group and 4,4′-bipyridyl competitively coordinate to palladium during reaction. Similarly, when complex **1** reacted with 1.5 equiv. 1,2-bis(4-pyridyl)-ethene (bpe) in CH_2Cl_2 at room temperature, mononuclear Schiff base palladacycle [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2)(bpe)(N_3)] (**10**) was obtained. Treatment of **1** with 2.0 equiv. bpe produced **10** and initially **1**. Complex **10** was characterized by spectroscopic, elemental analysis. Unfortunately, when complex **1** was treated by 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (bpt) or 2,4,6-tris-(4-pyridyl)-1,3,5-triazine (tpt), no mono-, bi- or tri-nuclear Pd complexes were generated. Surprisingly, treatment of **2** with 1.0 equiv. 4,4′-bipyridyl produced the expected binuclear Schiff base palladacycle [Pd{(4-OMe)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(N_3)]$_2$(μ-bpy) (**11**). Single crystal X-ray analysis confirmed the binuclear structure of **11**. However, reaction of **2** with bpe is similar to the reaction of **1** with bpe though only a mononuclear Schiff base palladacycle [Pd{(4-OMe)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(bpe)(N_3)] (**12**) was obtained. The mononuclear structure of **12** was also confirmed by single crystal X-ray analysis.

2.2. Reactions of μ-azido and μ-thiocyanato bridged Schiff base palladacycles with phosphines

Bearing in my mind the above results, as a comparative study, we examined the reactions of complexes **1**, **2**, **3** and **4** with tertiary and chelating phosphines, such as triphenylphosphine and 1,4-bis(diphenylphosphino)butane (dppb) (Scheme 5). Although several cleavage reactions of the μ-chloro bridged Schiff base palladacycles by phosphines to give neutral or ionic complexes are known [9–15], no example associated with μ-azido and μ-thiocyanato bridged Schiff base palladacycles is described in literature. Recently, Kim et al. reported that μ-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 exhibited a labile reactivity toward chelating phosphines [20]. In our study, consistent with the expectation based on stoichiometry, the mononuclear and binuclear Schiff base palladacycles with a terminal N_3 group or NCS group [Pd{(4-R)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(PPh_3)(N_3)] (R = H, **13**; OMe, **14**), [Pd{(4-R)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(PPh_3)(NCS)] (R = H, **15**; OMe, **16**), [Pd{(4-R)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(N_3)]$_2$(μ-dppb) (R = H, **17**; OMe, **18**) and [Pd{(4-R)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(NCS)]$_2$(μ-dppb) (R = H, **19**; OMe, **20**) were formed when complexes **1**–**4** were treated with the stoichiometric amount of PPh_3 or dppb, respectively. Complexes **13**–**20** were characterized by spectroscopic and elemental analysis. The molecular structures



Scheme 3. Reactions of complex **1** with bidentate aromatic *N*-heterocycles.



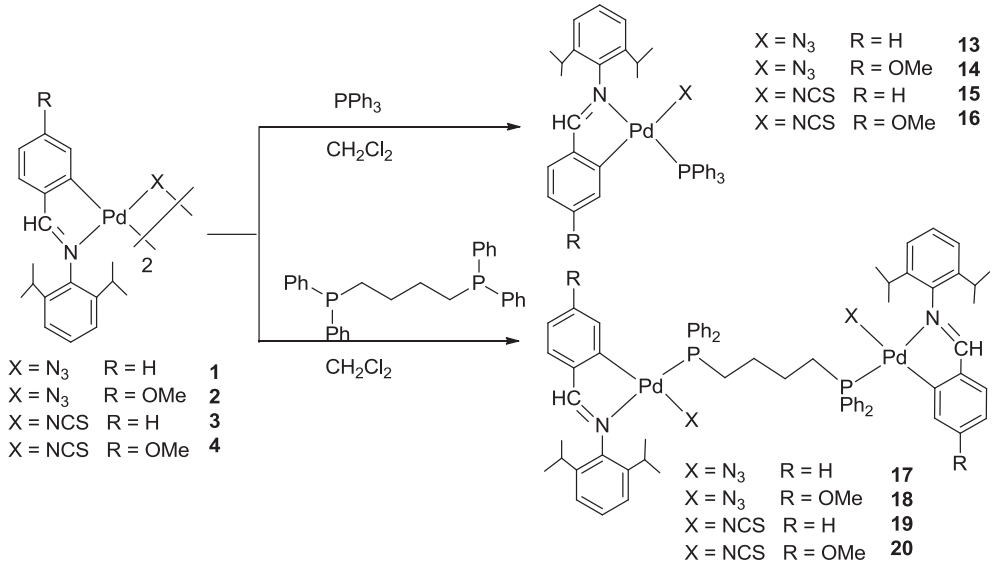
Scheme 4. Reactions of complex **2** with bpy and bpe.

of **14**, **15**, **17** and **20** were determined using X-ray diffraction. The FT-IR spectra of **13** and **14** showed a characteristic stretch vibration band at approximately 2044 cm^{-1} and 2037 cm^{-1}, respectively, due to the terminal azido group, similar to **5** and **6**. Nonetheless, a difference between **5**, **6** and **13**, **14** can be found in the absence of linkage isomers in solution based on ^1H NMR. For **17** and **18**, strong stretching vibration of terminal N_3 also appear at 2038 cm^{-1} and 2037 cm^{-1}, respectively. The presence of strong absorptions at 2091 cm^{-1} (**15**), 2089 cm^{-1} (**16**), 2084 cm^{-1} (**19**) and 2086 cm^{-1} (**20**) can be assigned to the coordinated isothiocyanato group, which is shifted to lower wavenumbers compared to the coordinated thiocyanato group of **8**. ^1H NMR spectra of **13**–**20** are consistent with their structure in solution. Therefor, the resonance of C*H*=N in **13**–**20** splits into doublets due to the coupling between H and P.

2.3. Structures of compounds

Single crystals of **5**, **6**, **8**, **9**, **12**, **14**, **15**, **17** and **20** suitable for X-ray diffraction analysis were obtained from a dichloromethane/hexane solution while single crystals of **11** from a chloroform/hexane solution. Details of **5**, **6**, **11**, **14** and **17** on crystal data, intensity collection, and refinement are given in Table 1, and data of **8**, **9**, **12**, **15** and **20** are in Table S1 (Supplementary Data). In all structures, the coordination of the Pd metal is essentially square-planar.

As shown in Fig. 1, **5** contain a cyclometallated Schiff-base ligand, a 1-methylimidazole and an azido group. The azido group is located on the *trans*-position of Pd–C bond and the 1-methylimidazole is located on the *trans*-position of Pd–N bond. The five-membered chelate ring that contains the imine functionality defined by Pd1, N1, C13, C14 and C15 is essentially planar with the atomic displacements not exceeding 0.0619 Å, to which the diisopropylphenyl ring is almost perpendicular with a dihedral angle 87.7(6)°. The dihedral angle between the cyclometallated ring and the imidazole ring is 51.5°. The Pd1–C15 bond [1.989(2) Å] and Pd1–N1 [2.0372(17) Å] are almost equal to corresponding N_3-bridged cyclopalladated complex **1** [1.983(6) Å] and [2.037(5) Å][3]. Fig. 2 reveals the *cis* disposition of the azido group relative to the metalated carbon atom and the *cis* disposition of the 1-methylimidazole relative to the metalated imine nitrogen atom in compound **6**. This arrangement is unusual in cyclopalladated compounds. The Pd1–C15 bond [1.988(3) Å] of compound **6** is almost equal to that of **5**, but the Pd1–N1bond [2.062(3) Å] is longer compared to **5**. Pd1–N2 bond [2.0343(17) Å] located on the



Scheme 5. Reactions of complexes **1**–**4** with phosphines.

Table 1
X-ray data collection and structure refinement for **5**, **6**, **11**, **14**, **17**.

	5	**6**·CH_2Cl_2	**11**·$2CHCl_3$	**14**·CH_2Cl_2	**17**
Formula	$C_{23}H_{28}N_6Pd$	$C_{25}H_{32}Cl_2N_6OPd$	$C_{52}H_{58}Cl_6N_{10}O_2Pd_2$	$C_{39}H_{41}Cl_2N_4OPPd$	$C_{66}H_{72}N_8P_2Pd_2$
Formula weight	494.91	609.87	1280.64	790.03	1252.06
Temperature (K)	293(2)	296(2)	296(2)	296(2)	296(2)
Crystal size	0.30 × 0.26 × 0.21	0.9 × 0.25 × 0.21	0.33 × 0.28 × 0.21	0.33 × 0.27 × 0.22	0.30 × 0.26 × 0.21
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pca2_1/c$	$P2_1/c$
a, Å	10.088(2)	8.2046(4)	10.812(2)	9.7026(16)	9.3508(7)
b, Å	14.598(3)	11.1509(6)	11.100(2)	21.120(3)	15.1746(11)
c, Å	17.696(5)	16.4366(9)	18.401(4)	19.723(3)	22.2092(17)
a, deg	90.00	98.9790(10)	84.33(3)	90.00	90.00
β, deg	117.79(2)	90.1880(10)	87.96(3)	105.207(7)	90.5810(10)
γ, deg	90.00	110.9250(10)	61.56(3)	90.00	90.00
V, Å^3	2305.4(9)	1384.53(13)	1932.2(7)	3900.1(10)	3151.2(4)
Z	4	2	2	4	2
d_{cal}, g cm^{-3}	1.426	1.463	1.474	1.345	1.320
μ, mm^{-1}	0.826	0.892	1.071	0.688	0.666
F(000)	1016	624	872	1624	1292
T_{min}	0.790	0.784	0.7394	0.811	0.8251
T_{max}	0.855	0.840	0.8261	0.872	0.8727
No. of reflns measured	17,707	19,567	15,443	27,722	23,427
No. of reflns unique	4142	4936	6916	6990	5631
No. of params refined	276	322	436	438	357
Max., in $\Delta\rho$ (eÅ^{-3})	0.564	0.702	1.522	0.698	0.527
Min., in $\Delta\rho$ (eÅ−3)	−0.291	−0.507	−1.453	−0.930	−0.381
GOF on F^2	1.144	1.169	1.193	1.009	1.099
R ($I > 2\sigma(I)$)	0.0266	0.0309	0.0576	0.0724	0.0392
wR_2[a] ($I > 2\sigma(I)$)	0.0736	0.0948	0.1491	0.1953	0.0980
R (all data)	0.0291	0.0366	0.1086	0.1489	0.0681
wR_2[a] (all data)	0.0752	0.1217	0.2366	0.2610	0.1296

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

cis-position of Pd1–C15 bond in **6** is significantly shorter than Pd1–N4 bond [2.137(2) Å] located on the *trans*-position of Pd1–C15 bond in **5**, and Pd1–N5 bond [2.156(3) Å] located on the *trans*-position of Pd1–C15 bond in **6** is considerably longer than Pd1–N2 bond [2.0343(17) Å] located on the *cis*-position of Pd1–C15 bond in **5**. This can be ascribed to a higher *trans* influence of the carbon. For compound **6** N2 is 0.1782 Å out of the molecule planar, defined by N1, Pd1, C15 and N5. The five-membered chelate ring that contains the imine functionality defined by Pd1, N1, C13, C14 and C15 is essentially planar with the atomic displacements not exceeding 0.0264 Å. The dihedral angle between the diisopropylphenyl ring and the five-membered chelate ring turns into 72.05° due to the effect of the coordinated imidazole ring. The dihedral angle between the cyclometallated ring and the imidazole ring is 34.59°. As depicted in Fig. S1 (in Supplementary Data), the palladium atom of complex **8** coordinated with a cyclometallated Schiff-base ligand,

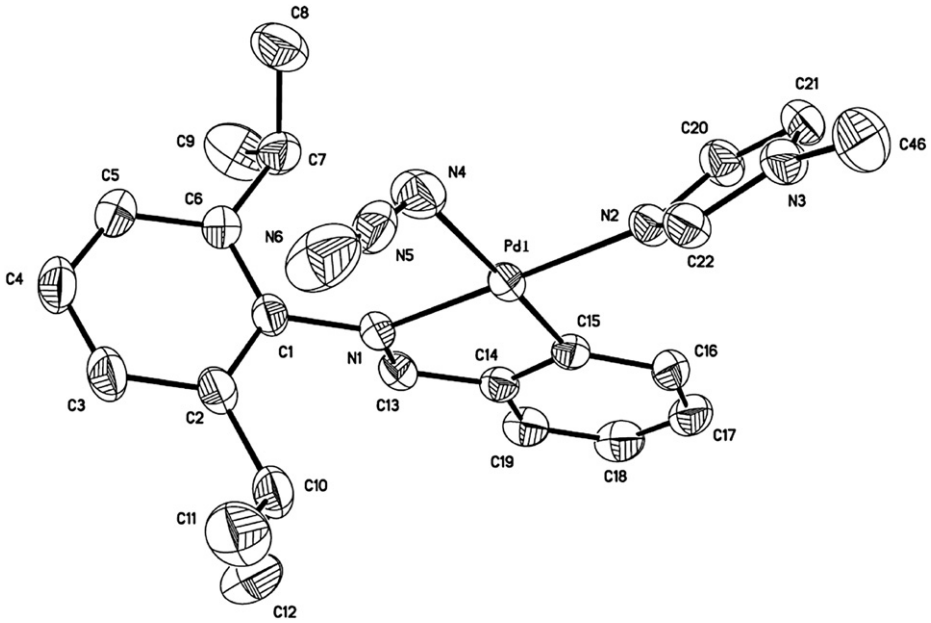


Fig. 1. Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Pd1–C15 1.989(2), Pd1–N1 2.0372(17), Pd1–N2 2.0343(17), Pd1–N4 2.137(2), N4–N5 1.158(3), N5–N6 1.165(4); N1–Pd1–C15 81.21(8), N2–Pd1–C15 94.86(8), N2–Pd1–N1 174.49(6), N2–Pd1–N4 89.03(9), N5–N4–Pd1 128.7(2), N4–N5–N6 176.4(3).

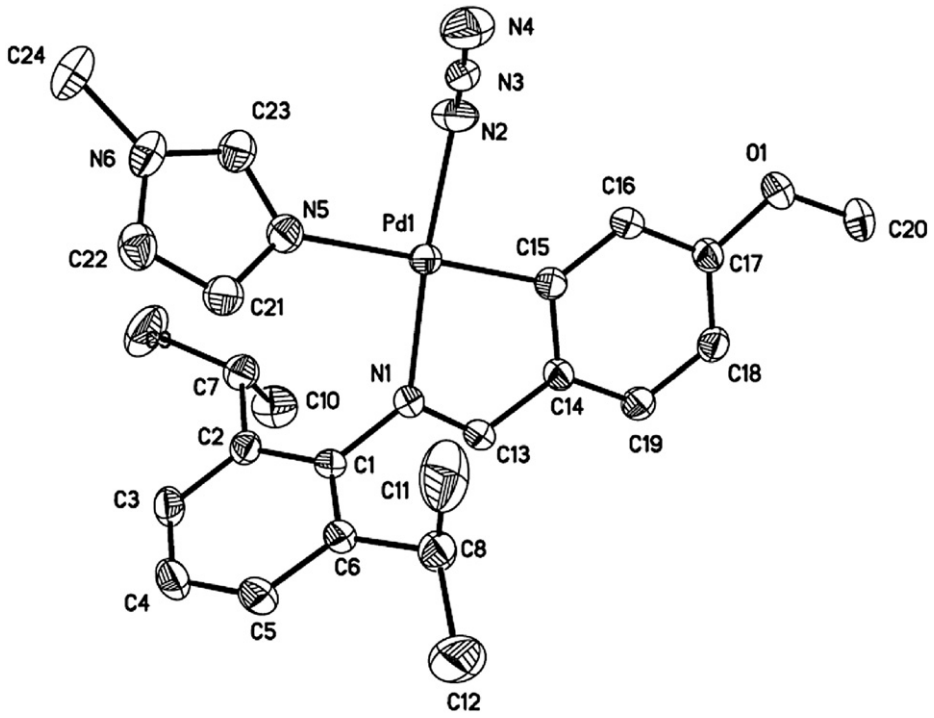


Fig. 2. Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Pd1–C15 1.988(3), Pd1–N1 2.062(3), Pd1–N2 2.038(3), Pd1–N5 2.156(3), N2–N3 1.169(5), N3–N4 1.167(5); N1–Pd1–C15 80.67(12), N1–Pd1–N2 170.78(12), N5–Pd1–C15 178.79(12), N5–Pd1–N1 98.98(11), N3–N2–Pd1 120.0(3), C15–Pd1–N2 91.62(14), N4–N3–N2 176.0(4).

an imidazole and a thiocyanato group. Sulfur and metalated carbon atoms adopt a *trans* arrangement.

Complexes **9** (Fig. 3) and **12** (Fig. S2 in Supplementary Data) have a similar mononuclear structure. Likewise, it is similar to complex **6** where the azido group is in *cis* position relative to metalated carbon atom. For **9**, the coordination plane shows a slight tetrahedral distortion, the deviation from the mean plane being 0.0006, 0.0207, −0.0492, 0.0600 and −0.0399 for Pd1, N1, C15, N2 and N5, respectively. The five-membered chelate ring that contains the imine functionality is almost perpendicular to the diisopropylphenyl ring with a dihedral angle 84.5(1)°. The two pyridyl rings of the bpy ligand are not coplanar but twisted to each other by an angle of 26.3(2)°. For **12**, N4 is 0.2150 Å out of the molecule planar, defined by N1, Pd1, C27 and N3. The dihedral angle between the

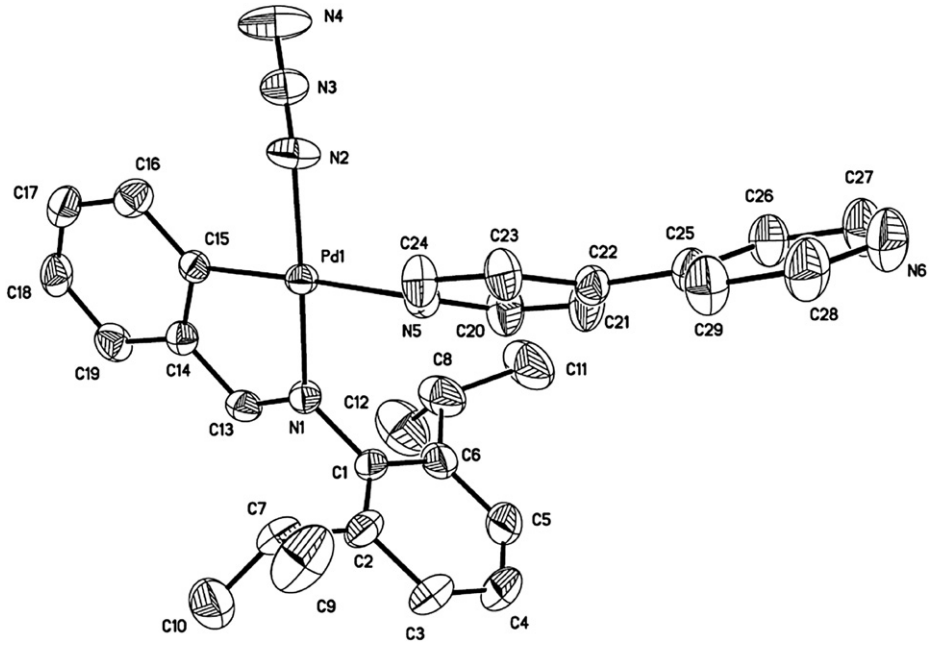


Fig. 3. Molecular structure of **9**. Selected bond lengths (Å) and angles (°): Pd1–C 151.990(4), Pd1–N1 2.051(5), Pd1–N2 2.013(6), Pd1–N5 2.160(3), N2–N3 1.205(9), N3–N4 1.133(9); C15–Pd1–N1 80.7(2), C15–Pd1–N5 177.3(2), C15–Pd1–N2 95.6(3), N1–Pd1–N5 98.5(2), N2–Pd1–N1 175.56(19), N3–N2–Pd1 123.2(5), N4–N3–N2 174.7(7).

diisopropylphenyl ring and the five-membered chelate ring turns into 69.8° due to the effect of coordinated bpe. Fig. 4 reveals that complex **11** has a dimeric structure bridged by μ-bpy. Each Pd center contains a cyclometallated Schiff-base ligand, a bridging bpy ligand and a terminal azido ligand. 4,4′-Bipyridyl links two [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(N_3)] moieties to give a binuclear compound, and the distance of Pd(1)···Pd(1A) is 11.4539(8) Å. The two cyclometallated ligands are in a *trans* arrangement with respect to the Pd···Pd axis. The molecule planar, defined by Pd1, N2, C15, N1 and N3 (plane 1), is relatively planar with the atomic displacements not exceeding 0.0214 Å. Two pyridyl rings of bridging bpy ligand are essentially coplanar.

Fig. 5 shows that complex **14** contains a *C*,*N*-coordinating Schiff-base ligand, one PPh_3, and one terminal azido ligand. The difference with complexes **9** and **12** can be found in the *trans* position of the azido group instead of *cis* relative to the metalated carbon atom. The Pd2–C15 bond [2.026(8) Å] of compound **14** is longer than those of **9** and **12**. Pd2–N2 bond [2.091(8) Å] located on the *trans*-position of Pd2–C15 bond in **14** is significantly longer than Pd1–N2 bond [2.013(6) Å] located on the *cis*-position of Pd1–C15 bond in **9**. Complex **15** (Fig. S3 in Supplementary Data) reveals similarly structure with **14** containing a *C*,*N*-coordinating Schiff-base ligand, one PPh_3, and one terminal isothiocyanato group. The isothiocyanato group is in *trans* position relative to the metalated carbon atom. Also complexes **17** and **20** have a similar dinuclear structure. In complex **17** (Fig. 6) dppb links two [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2}(N_3)] moieties to give a binuclear compound containing a terminal azido group, and the distance of Pd(1)···Pd(1A) is 8.7349(7) Å. In complex **20** (Fig. S4 in Supplementary Data) dppb links two [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-*i*-Pr_2)}(NCS)] moieties to give a binuclear compound containing a terminal isothiocyanato group, and the distance of Pd(1)···Pd(1A) is 9.0591(8) Å. Two cyclometallated ligands are in a *trans* arrangement with respect to the Pd···Pd axis.

In summary, the reactivity of μ-azido and μ-thiocyanato bridged Schiff base palladacycles toward aromatic *N*-heterocycles and phosphines was examined. Due to the lability of μ-azido bridged Schiff base palladacycles toward aromatic *N*-heterocycles mono- and bi-nuclear compounds were generated. Unexpectedly, only one binuclear palladacycle was synthesized by reaction of μ-azido Schiff base palladacycles with bidentate *N*-heterocycles. Furthermore, μ-thiocyanato bridged Schiff base palladacycles were relatively unreactive toward aromatic *N*-heterocycles. Only one thiocyanato coordinated mononuclear Schiff base palladacycle [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2) (imidazole)(SCN)] was produced. Moreover, reactions of μ-azido and μ-thiocyanato bridged Schiff base palladacycles with triphenylphosphine and 1,4-bis(diphenylphosphino) butane regularly formed mono- and bi-nuclear terminal azido or isothiocyanato coordinated palladacycles.

3. Experimental

3.1. General, materials and measurements

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

Caution! No problems were encountered during this work, however heavy metal azides are known to be shock sensitive detonators, therefore it is essential to handle any palladium azide compound carefully.

3.2. Preparations

3.2.1. [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2)(1-methylimidazole)(N_3)] (**5**), [Pd{(4-MeO)C_6H_3–CH=N–C_6H_3–2,6-*i*-Pr_2}(1-methylimidazole)(N_3)] (**6**)

To a 12 mL CH_2Cl_2 solution of complex [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2)(μ-N_3)]$_2$ (**1**) (0.100 g, 0.12 mmol) was added stepwise 1-methylimidazole (20 μL, 0.25 mmol). After stirring for 12 h at room temperature, the solvent was completely evaporated and the resulting residue was washed with ether to give a pale yellow solid. Recrystallization from CH_2Cl_2/hexane gave yellow crystals of [Pd(C_6H_4CH=N–C_6H_3–2,6-*i*-Pr_2)(1-methylimidazole)(N_3)] (**5**, 0.071 g, 59%). IR (KBr, cm^{-1}): 1601 ($\nu_{C=N}$), 2036 ($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 7.89 (s, 1H, –C*H*=N), 7.80 (d, 1H, J = 7.8 Hz), 7.41 (d, 1H, J = 7.5 Hz), 7.34 (t, 1H, J = 6.9 Hz, 8.1 Hz), 7.24–7.29 (m, 1H), 7.16–7.21 (m, 1H), 7.12 (d, 2H, J = 7.8 Hz), 6.83 (s, 1H), 6.55 (s, 1H), 6.13 (s, 1H), 3.47 (s, 1H, N–CH_3), 3.38 (hepta, 2H, –C*H*(CH_3)$_2$), 1.12 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.05 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$); Anal. Calcd for $C_{23}H_{28}N_6Pd$: C, 55.82; H, 5.70; N, 16.98. Found: C, 55.64; H, 5.67; N, 16.61.

Complexes **6**–**20** were prepared in a similar manner as complex **5**.

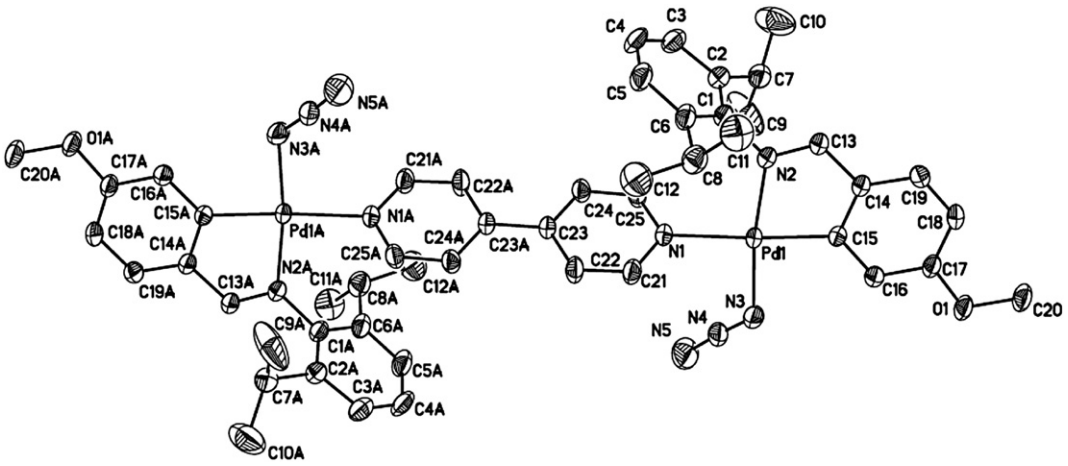


Fig. 4. Molecular structure of **11**. Selected bond lengths (Å) and angles (°): Pd1–C15 1.989(5), Pd1–N1 2.168(4), Pd1–N2 2.055(4), Pd1–N3 2.043(5), N3–N4 1.159(7), N4–N51 153(8); C15–Pd1–N2 80.30(19), C15–Pd1–N1 176.82(18), C15–Pd1–N3 91.6(2), N3–Pd1–N2 171.87(18), N2–Pd1–N1 96.57(17), N4–N3–Pd1 123.3(4), N5–N4–N3 176.3(7).

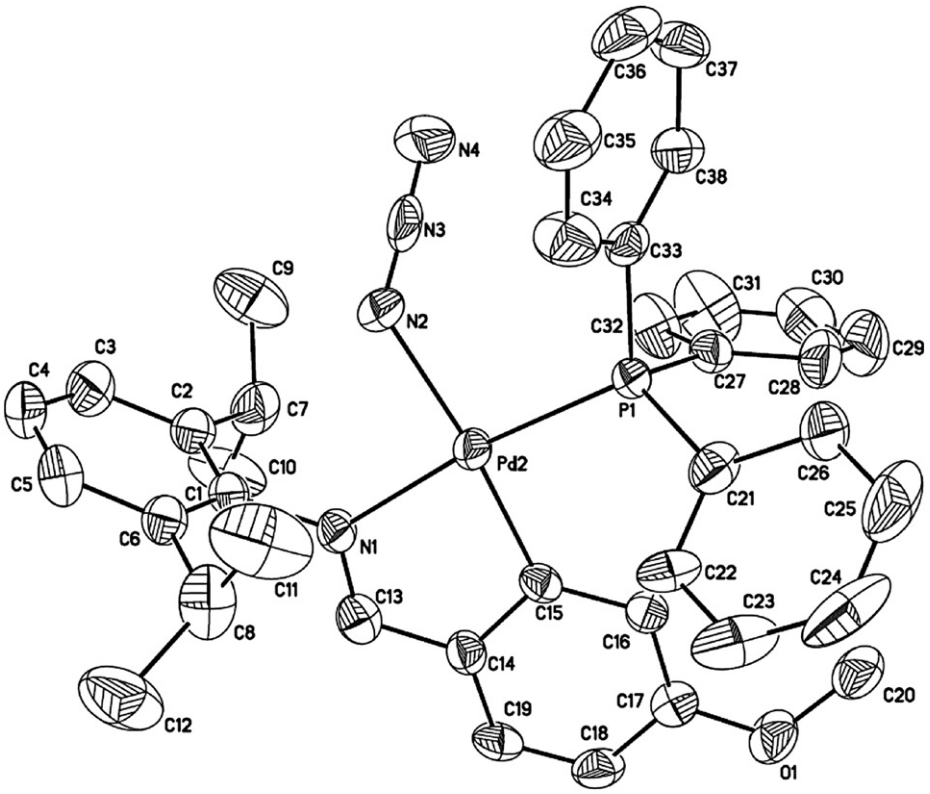


Fig. 5. Molecular structure of **14**. Selected bond lengths (Å) and angles (°): Pd2–C15 2.026(8), Pd2–N1 2.094(7), Pd2–N2 2.091(8), Pd2–P1 2.245(2), N2–N3 1.211(15), N3–N4 1.163(16); C15–Pd2–N1 80.4(3), C15–Pd2–N2 170.7(3), C15–Pd2–P1 94.0(2), N1–Pd2–P1 172.7(2), N2–Pd2–N1 91.8(3), C27–P1–Pd2 108.9(3), C21–P1–Pd2 114.3(4), C33–P1–Pd2 116.9(3), N3–N2–Pd2 122.3(8), N4–N3–N2 176.3(14), C1–N1–Pd2 124.5(5).

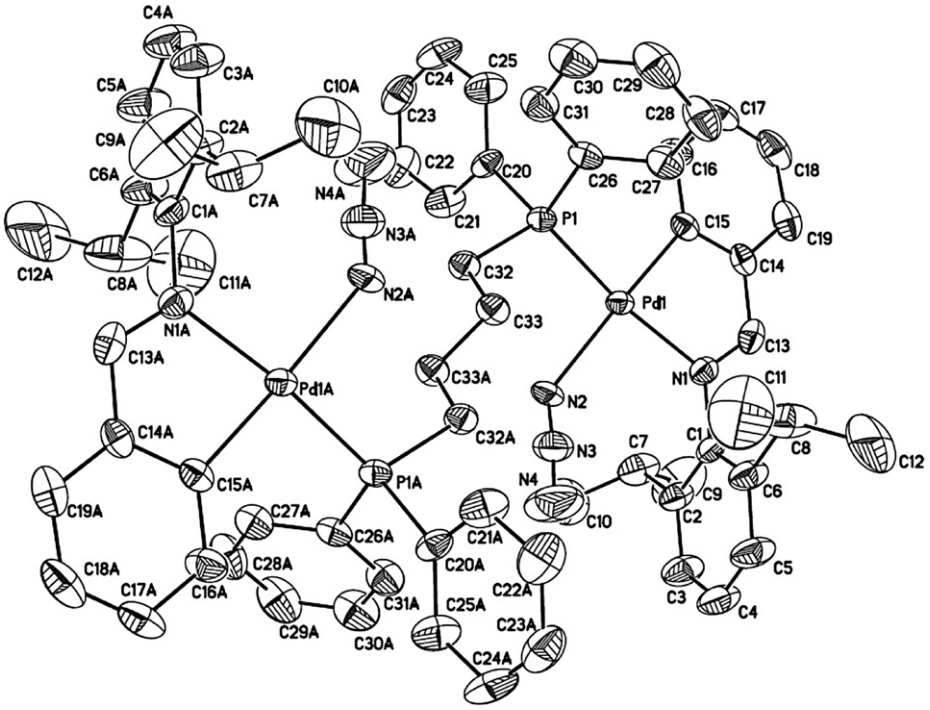


Fig. 6. Molecular structure of **17**. Selected bond lengths (Å) and angles (°): Pd1–C15 2.028(4), Pd1–N1 2.093(4), Pd1–N2 2.122(4), Pd1–P1 2.2548(11), N2–N3 1.136(6), N3–N4 1.178(7); C15–Pd1–N1 80.71(16), C15–Pd1–N2 166.58(17), C15–Pd1–P1 95.52(13), N2–Pd1–P1 92.21(12), N1–Pd1–P1 170.21(10), N3–N2–Pd1 132.4(4), N2–N3–N4 175.6(8), C20–P1–Pd1 116.88(14), C26–P1–Pd1 114.72(16), C32–P1–Pd1 112.22(15), C1–N1–Pd1 124.7(3).

*3.2.2. [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-i-Pr_2}(1-methylimidazole(N_3)] (**6**, 51%)*

IR (KBr, cm^{-1}): 1598 ($\nu_{C=N}$), 2036 ($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 7.75 (s, 1H, –C*H*=N), 7.36 (d, 1H, J = 2.4 Hz, imidazole), 7.32 (d, 1H, J = 8.4 Hz), 7.23 (d, 1H, J = 7.8 Hz), 7.09 (d, 2H, J = 7.5 Hz), 6.82 (s, 1H), 6.67 (dd, 1H, J = 2.4, 2.4 Hz, imidazole), 6.54 (s, 1H), 6.15 (s, 1H), 3.97 (s, 3H, –OCH_3), 3.47 (s, 3H, N–CH_3), 3.39 (hepta, 2H, –C*H*(CH_3)$_2$), 1.10 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$), 1.04 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$); Anal. Calcd for $C_{24}H_{30}N_6OPd$: C, 54.91; H, 5.76; N, 16.01. Found: C, 54.79; H, 5.96; N, 16.35.

*3.2.3. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(imidazole)(SCN)] (**8**, 59%)*

IR (KBr, cm^{-1}): 1603 ($\nu_{C=N}$), 2108($\nu_{S=C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 10.82 (s, 1H, N–*H*), 7.97 (s, 1H, –C*H*=N), 7.37–7.44 (m, 2H), 7.23 (d, 1H, J = 7.5 Hz), 7.19 (d, 1H, J = 6.9 Hz), 7.09–7.15 (m, 3H),6.98 (d, 2H, J = 7.5 Hz), 6.51 (s, 1H), 3.32 (hepta, 2H, –C*H*(CH_3)$_2$), 1.15 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.08 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$); Anal. Calcd for $C_{23}H_{26}N_4PdS$: C, 55.59; H, 5.27; N, 11.27. Found: C, 55.56; H, 5.28; N, 11.05.

*3.2.4. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(bpy)(N_3)] (**9**, 57%)*

IR (KBr, cm^{-1}): 1602 ($\nu_{C=N}$), 2044($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.74 (d, 2H, J = 5.1 Hz), 8.21 (d, 2H, J = 6.0 Hz), 7.94 (s, 1H, –*H*C=N), 7.40 (d, 2H, J = 5.7 Hz), 7.37 (d, 2H, J = 7.8 Hz), 7.31 (d, 2H, J = 6.3 Hz), 7.22 (d, 2H, J = 7.8 Hz), 7.13–7.18 (m, 2H), 7.02 (d, 2H, J = 7.2 Hz), 3.42 (hepta, 2H, –C*H*(CH_3)$_2$),1.11 (dd, 12H, J = 3.0 Hz, –CH(CH_3)$_2$); Anal. Calcd for $C_{29}H_{30}N_6Pd\cdot0.125CH_2Cl_2$: C, 60.35; H, 5.26; N, 14.50. Found: C, 60.30; H, 5.19; N, 14.18.

*3.2.5. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(bpe)(N_3)] (**10**, 49%)*

IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$), 2023 ($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.63 (d, 2H, J = 5.1 Hz), 8.07 (d, 2H, J = 5.4 Hz), 7.93 (s, 1H, –*H*C=N), 7.39–7.44 (m, 3H), 7.35 (d, 2H, J = 5.7 Hz), 7.21 (d, 1H, J = 6.6 Hz), 7.12–7.16 (m, 3H), 7.09 (d, 1H, J = 8.4 Hz), 7.02 (d, 2H, J = 7.5 Hz), 3.42 (hepta, 2H, –C*H*(CH_3)$_2$),1.11 (d, 12H, J = 6.3 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{31}H_{32}N_{10}Pd\cdot0.5CH_2Cl_2$: C, 59.35; H, 5.22; N, 13.18. Found: C, 59.45; H, 5.25; N, 13.13.

*3.2.6. [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-i-Pr_2}(N_3)]$_2$(μ-bpy) (**11**, 54%)*

IR (KBr, cm^{-1}): 1597 ($\nu_{C=N}$), 2035($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.70 (d, 4H, J = 5.7 Hz), 8.17 (d, 4H, J = 5.1 Hz), 7.77 (s, 2H, –*H*C=N), 7.37 (d, 2H, J = 7.8 Hz), 7.18 (d, 4H, J = 7.5 Hz), 7.13 (d, 2H, J = 7.5 Hz), 6.94 (d, 2H, J = 7.8 Hz), 6.73 (d, 2H, J = 8.1 Hz), 3.96(s, 6H, –OCH_3), 3.39 (hepta, 4H, –C*H*(CH_3)$_2$), 1.07 (dd, 24H, J = 2.7 Hz, 3.0 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{50}H_{56}N_{10}O_2Pd_2$: C, 57.64; H, 5.42; N, 13.44. Found: C, 57.36; H, 5.70; N, 13.32.

*3.2.7. [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-i-Pr_2}(bpe)(N_3)] (**12**, 74%)*

IR (KBr, cm^{-1}): 1609 ($\nu_{C=N}$), 2037($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.63 (d, 1H, J = 5.7 Hz), 8.07 (d, 2H, J = 6.3 Hz), 7.79 (s, 1H, –*H*C=N), 7.33–7.36 (m, 3H), 7.29 (d, 1H, J = 8.4 Hz), 7.21 (d, 1H, J = 8.4 Hz), 7.17 (d, 1H, J = 3.9 Hz), 7.13 (d, 2H, J = 7.2 Hz), 7.08 (d, 1H, J = 7.5 Hz), 7.01 (d, 1H, J = 2.7 Hz), 6.99 (d, 1H, J = 3.0 Hz), 6.95 (d, 1H, J = 6.9 Hz), 6.71 (dd, 1H, J = 2.4 Hz), 3.98 (s, 3H, OCH_3), 3.42 (hepta, 2H, –C*H*(CH_3)$_2$),1.09 (dd, 12H, J = 6.3 Hz, 5.4 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{32}H_{34}N_6OPd\cdot0.5CH_2Cl_2$: C, 58.48; H, 5.28; N, 12.59. Found: C, 58.27; H, 5.19; N, 12.22.

*3.2.8. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(PPh_3)(N_3)] (**13**, 70%)*

IR (KBr, cm^{-1}): 1612 ($\nu_{C=N}$) 2044 ($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.08 (d, 1H, J = 7.8 Hz, –C*H*=N), 7.68–7.75 (m, 6H, PPh_3), 7.34–7.49 (m, 10H, PPh_3, H^6), 7.23 (d, 2H, J = 6.9 Hz, $H^{3\prime}$, $H^{5\prime}$), 7.12–7.19 (m, 1H, $H^{4\prime}$), 7.01 (dd, 1H, J = 7.5, 7.2 Hz, H^4), 6.69 (dd, 1H, J = 7.5, 7.8 Hz, H^5), 6.46 (dd, 1H, J = 5.4 Hz, 5.4 Hz, H^3), 3.41 (hepta, 2H, –C*H*(CH_3)$_2$), 1.41 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.22 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{37}H_{37}N_4PPd\cdot0.125CH_2Cl_2$: C, 65.03; H, 5.48; N, 8.17. Found: C, 64.96; H, 5.78; N, 7.90.

*3.2.9. [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-i-Pr_2}(PPh_3)(N_3)] (**14**, 92%)*

IR (KBr, cm^{-1}): 1606 ($\nu_{C=N}$), 2037($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 7.96 (d, 1H, J = 8.1 Hz, –C*H*=N), 7.67–7.75 (m, 6H, PPh_3), 7.32–7.49 (m, 10H, PPh_3, H^6), 7.16–7.26 (m, 3H, $H^{3\prime}$, $H^{4\prime}$, $H^{5\prime}$), 6.51 (dd, 1H, J = 2.4 Hz, 2.4 Hz, H^5), 6.05 (dd, 1H, J = 2.1 Hz, 2.4 Hz, H^3), 3.42 (hepta, 2H, –C*H*(CH_3)$_2$), 3.08 (s, 3H, –OCH_3), 1.40 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.20 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{38}H_{39}N_4OPPd\cdot0.125CH_2Cl_2$: C, 63.98; H, 5.53; N, 7.83. Found: C, 64.17; H, 5.91; N, 7.85.

*3.2.10. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(PPh_3)(NCS)] (**15**, 80%)*

IR (KBr, cm^{-1}): 1610 ($\nu_{C=N}$), 2091 ($\nu_{N=C=S}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.07 (d, 1H, J = 7.8 Hz), 7.66 (dd, 6H, J = 7.2, 7.2 Hz, PPh_3), 7.39–7.51 (m, 10H, PPh_3, H^6), 7.22–7.33 (m, 3H, $H^{3\prime}$, $H^{4\prime}$, $H^{5\prime}$), 7.02 (dd, 1H, J = 7.5, 7.2 Hz, H^4), 6.69 (dd, 1H, J = 7.5, 7.8 Hz, H^5), 6.46 (dd, H, J = 6.0 Hz, 7.2 Hz, H^3), 3.41 (hepta, 2H, –C*H*(CH_3)$_2$), 1.41 (d, 6H, J = 6.9 Hz, –CH(CH_3)$_2$), 1.23 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{38}H_{37}N_2PPdS$: C, 66.03; H, 5.40; N, 4.05; S, 4.64. Found: C, 65.91; H, 5.53; N, 3.90; S, 4.40.

*3.2.11. [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-i-Pr_2}(PPh_3)(NCS)] (**16**, 54%)*

IR (KBr, cm^{-1}): 1606 ($\nu_{C=N}$), 2089 ($\nu_{N=C=S}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 7.95 (d, 1H, J = 7.8 Hz), 7.67 (dd, 6H, J = 7.2 Hz, 7.2 Hz, PPh_3), 7.40–7.52 (m, 9H, PPh_3), 7.35 (d, 1H, J = 8.4 Hz), 7.21–7.32 (m, 3H), 6.53 (dd, 1H, J = 2.1, 2.1 Hz), 6.03 (d, 1H, J = 3.9 Hz), 3.42 (hepta, 2H, –C*H*(CH_3)$_2$), 3.07 (s, 3H, –OCH_3), 1.47 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.23 (d, 6H, J = 6.6 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{39}H_{39}N_2OPPdS\cdot0.25CH_2Cl_2$: C, 63.50; H, 5.36; N, 3.77; S, 4.32. Found: C, 63.80; H, 5.34; N, 3.47; S, 4.05.

*3.2.12. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(N_3)]$_2$(μ-dppb) (**17**, 61%)*

IR (KBr, cm^{-1}): 1611 ($\nu_{C=N}$), 2038 ($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.01 (d, 2H, J = 6.9 Hz, –C*H*=N), 7.73–7.79 (m, 8H, P–Ph), 7.30–7.44 (m, 14H, P–Ph, H^6), 7.22–7.28 (m, 6H, $H^{3\prime}$, $H^{4\prime}$, $H^{5\prime}$), 6.96 (dd, 2H, J = 7.2, 7.5 Hz, H^4), 6.69 (dd, 2H, J = 7.5, 6.9 Hz, H^5), 6.48 (dd, 2H, J = 4.5, 4.5 Hz, H^3), 3.36 (hepta, 4H, –C*H*(CH_3)$_2$), 2.34 (br, 4H, P–CH_2–CH_2–), 1.61 (br, 4H, P–CH_2–CH_2–), 1.37 (d, 12H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.19 (d, 12H, J = 6.9 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{66}H_{72}N_8P_2Pd_2$: C, 63.31; H, 5.80; N, 8.95. Found: C, 63.06; H, 6.21; N, 8.88.

*3.2.13. [Pd{(4-MeO)C_6H_3CH=N–C_6H_3–2,6-i-Pr_2}(N_3)]$_2$(μ-dppb) (**18**, 54%)*

IR (KBr, cm^{-1}): 1606 ($\nu_{C=N}$), 2037($\nu_{N=N=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 7.89 (d, 2H, J = 7.8 Hz, –C*H*=N), 7.77 (dd, 8H, P–Ph), 7.32–7.46 (m, 12H, P–Ph), 7.28 (d, 4H, J = 8.4 Hz, H^6, $H^{4\prime}$), 7.21 (d, 4H, J = 7.5 Hz, $H^{3\prime}$, $H^{5\prime}$), 6.48 (d, 2H, J = 8.4 Hz, H^5), 6.04 (d, 2H, J = 4.2 Hz, H^3), 3.38 (hepta, 4H, –C*H*(CH_3)$_2$), 3.06 (s, 6H, OCH_3), 2.37 (br, 4H, P–CH_2–CH_2–), 1.70 (br, 4H, P–CH_2–CH_2–), 1.36 (d, 12H, J = 6.9 Hz, –CH(CH_3)$_2$), 1.19 (d, 12H, J = 6.9 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{68}H_{76}N_8O_2P_2Pd_2$: C, 62.24; H, 5.84; N, 8.54. Found: C, 62.24; H, 5.79; N, 8.63.

*3.2.14. [Pd(C_6H_4CH=N–C_6H_3–2,6-i-Pr_2)(NCS)]$_2$(μ-dppb) (**19**, 59%)*

IR (KBr, cm^{-1}): 1616 ($\nu_{C=N}$), 2084($\nu_{N=C=S}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 7.99 (d, 2H, J = 7.5 Hz, –C*H*=N), 7.82–7.88 (m, 8H, P–Ph), 7.34–7.44 (m, 14H, P–Ph, H^6), 7.26–7.31 (m, 6H, $H^{3\prime}$, $H^{4\prime}$, $H^{5\prime}$), 6.96 (dd, 2H, J = 7.2, 7.5 Hz, H^4), 6.66 (dd, 2H, J = 7.5, 7.5 Hz, H^5), 6.45 (dd, 2H, J = 5.7, 7.5 Hz, H^3), 3.35 (hepta, 4H, –C*H*(CH_3)$_2$), 2.36 (br,

4H, P–CH_2–CH$_2$–), 1.55 (br, 4H, P–CH$_2$–CH_2–), 1.38 (d, 12H, J = 6.6 Hz, –CH(CH_3)$_2$), 1.20 (d, 12H, J = 6.9 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{68}H_{72}N_4P_2Pd_2S_2 \cdot 0.25CH_2Cl_2$: C, 62.79; H, 5.60; N, 4.29. Found: C, 62.62; H, 5.53; N, 4.00.

*3.2.15. [Pd{(4-MeO)C$_6$H$_3$CH=N–C$_6$H$_3$–2,6-i-Pr$_2$}(NCS)]$_2$(μ-dppb) (**20**, 93%)*

IR (KBr, cm^{-1}): 1607 ($\nu_{C=N}$), 2086($\nu_{N=C=S}$); ^{1}H NMR (300 MHz in $CDCl_3$, δ): 7.84–7.89 (m, 8H, P–Ph), 7.82 (br, 2H, –CH=N), 7.34–7.45 (m, 14H, P–Ph, H^6), 7.23–7.29 (m, 3H, H$^{4\prime}$, H$^{3\prime}$, H$^{5\prime}$), 6.46 (dd, 2H, J = 2.1, 2.1 Hz, H^5), 6.01 (d, 2H, J = 2.4, 2.1 Hz, H^3), 3.36 (hepta, 4H, –CH(CH$_3$)$_2$), 3.02 (s, 6H, –OCH_3), 2.37 (br, 4H, P–CH_2–CH$_2$–), 1.65 (br, 4H, P–CH$_2$–CH_2–), 1.36 (d, 12H, J = 6.9 Hz, –CH(CH_3)$_2$), 1.19 (d, 12H, J = 6.9 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{70}H_{76}N_4O_2P_2Pd_2S_2$: C, 62.54; H, 5.70; N, 4.17. Found: C, 62.57; H, 5.84; N, 3.88.

3.3. X-ray structure determination

Suitable crystals for X-ray analysis of **5**, **6**, **8**, **9**, **12**, **14**, **15**, **17** and **20** were obtained by recrystallization from CH_2Cl_2/hexane except **11**, which was obtained from $CHCl_3$/hexane. X-ray data of complexes **5**, **6**, **8**, **9**, **11**, **12**, **14**, **15**, **17** and **20** were collected on Bruker APEX-II area-detector diffractometer, Rigaku Saturn724 CCD or Rigaku/MSC Mercury CCD. All unit cell determinations and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at room temperature using the ω-scan technique (except **8** at −160 °C). Details of the data collection and refinement are summarized in Table 1 and Table S1. All calculations were carried out with the SHELX-97 programs [21]. The structures were solved by direct methods. The non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods.

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Appendix A. Supplementary material

CCDC 873995–874004 contain the supplementary crystallographic data for this paper. 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 data related to this article can be found online at http://dx.doi.org/10.1016/j.jorganchem.2012.10.033.

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