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Synthesis, reactivity and characterization of mono-, bi- and tri-nuclear Schiff-base palladacycles with aromatic *N*-heterocycles

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ABSTRACT

Reactions of μ_2-Chloro bridged cyclometallated Pd(II) complexes [Pd{(4-R) $C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(μ-Cl)]$_2$ (R = H, OMe) with aromatic *N*-heterocycles such as 1-methylimidazole, 4,4′-bipyridyl (bpy), 1,2-bis(4-pyridyl)-ethene (bpe), 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (bpt) and 2,4,6-tris-(4-pyridyl)-1,3,5-triazine (tpt), generated mononuclear complexes [Pd{(4-R)$C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(L)(Cl)] (L = 1-methylimidazole, R = H, OMe), binuclear complexes [Pd{(4-R)$C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(Cl)]$_2$(μ-Y) (R = H, OMe; Y = bpy, bpe, bpt) and trinuclear complexes [Pd{(4-R) $C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(Cl)]$_3$(tpt) (R = H, OMe). In contrast, the reaction of μ_2-Chloro bridged cyclometallated Pd(II) complexes [Pd{(4-R) $C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(μ-Cl)]$_2$ (R = H, OMe) with 2 equiv of $AgNO_3$ and followed with bpy, bpe, bpt to produce binuclear cyclometallated Pd(II) nitrato complexes [Pd{(4-R) $C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(O-NO_2)]$_2$(μ-Y) (R = H, OMe; Y = bpy, bpe, bpt). Treatment of [Pd{(4-R)$C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(Cl)]$_3$(tpt) (R = H, OMe) with an excess $AgNO_3$ produced trinuclear cyclometallated Pd(II) nitrato complexes [Pd{(4-R) $C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(ONO_2)]$_3$(tpt) (R = H, OMe). All these complexes were fully characterized by FT-IR, NMR spectroscopy, elemental analysis and/or X-ray crystallography.

1. Introduction

In the last few decades, the assemblies of organometallic supramoleculars have attracted more and more interest because of their potential application as promising molecular materials [1–11]. The square planar species of platinum(II) and palladium(II) have been extensively exploited to generate supramolecular assemblies due to their rigid coordination environment [12–22]. It is worth noticing that in most examples the blocking ligands bound to platinum or palladium centers are symmetric diamines or diphosphines. However, cyclometallated Pd(II) or Pt(II) complexes containing *C,N*-donor ligands as corner species to assemble supramoleculars are very limited [23–26]. In our opinion, readily synthesized μ_2-chloro bridged dinuclear cyclometallated Pd(II) complexes [Pd{(4-R)$C_6H_3CH{=}$N-C_6H_3-2,6-*i*-Pr_2}(μ-Cl)]$_2$ (R = H, **1**; OMe, **2**), with two blocked *cis*-coordination sites, seemed suitable for assembling of metal macrocycles, if one could bridge the [Pd{(4-R)$C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}]$^+$ fragments by appropriate linkers. Interestingly, although Schiff-base palladacycles are one of the most extensively studied areas in Pd-chemistry [27–33], cyclometallated Pd(II) complexes incorporating Schiff-base and aromatic *N*-heterocycles are rarely explored. Herein, we report reactions of μ_2-chloro bridged dinuclear cyclometallated Pd(II) complexes [Pd{(4-R)$C_6H_3CH{=}$N-C_6H_3-2,6-*i*-Pr_2}(μ-Cl)]$_2$ with aromatic *N*-heterocycles. Studies of resulting mono-, bi- and tri-nuclear Schiff-base palladacycles with aromatic *N*-heterocycles as building blocks toward supramolecular construction are in progress.

2. Results and discussion

2.1. Reactions of μ-chloro bridged dinuclear cyclometallated Pd(II) complexes with mono-, bi-, tri-dentate aromatic N-heterocycles

Recently, we reported that μ_2-chloro bridged dinuclear cyclometallated Pd(II) complexes [Pd{(4-R)$C_6H_3CH{=}NC_6H_3$-2,6-*i*-Pr_2}(μ-Cl)]$_2$ (R = H, **1**; OMe, **2**) can readily synthesized by reaction of Na_2PdCl_4 with corresponding Schiff base [34]. Although cleavage of the Cl-bridged cyclopalladated complexes by phosphines giving neutral or ionic complexes is known [29,35,36], the reports of Cl-bridged cyclopalladated complexes cleaved by aromatic *N*-

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heterocycles are rare [37–39]. Consequently, we examined the reactions of μ_2-chloro bridged dinuclear cyclometallated Pd(II) complex **1** and **2** with mono-, bi- and tri-dentate aromatic *N*-heterocycles, as shown in Scheme 1. Treatment of complex **1** and **2** with 2 equiv 1-methylimidazole in CH_2Cl_2 at room temperature produced yellow mononuclear cyclometallated Pd(II) complexes $[Pd\{(4\text{-}R)C_6H_3CH{=}N\text{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(L)(Cl)]$ (L = 1-methylimidazole, R = H, **3**; L = 1-methylimidazole, R = OMe, **4**). The IR spectra of **3** and **4** showed a strengthened stretching at approximately 1602 cm^{-1} and 1599 cm^{-1}, respectively, due to the ν(C=N). The ^1H NMR spectra of **3** and **4** displayed the resonance for C*H*=N protons at δ 7.91 and δ 7.78 ppm, respectively, which was shifted downfield compared to the corresponding Cl-bridged cyclopalladated complexes **1** and **2**, respectively δ 7.74 ppm and δ 7.61 ppm. Moreover, upfield shift of the aromatic proton H_3 of palladated ring in the ^1H NMR spectra of complexes **3** and **4** indicated the *cis* disposition of 1-methylimidazole relative to metalated carbon atom [35]. Interestingly, the ^1H NMR spectra of **3** and **4** revealed the presence of two isomers (in the ratio of 1.00:0.41 for **3** and 1:0.23 for **4** based on the measured intensities of the signals due to the C*H*=N groups), for major isomer, the Cl atom of Pd–Cl bond is located in the *trans*-position of Pd–C bond, and for minor isomer, the Cl atom of Pd–Cl bond is located on the *trans*-position of Pd–N bond. However, the molecular structure of complex **3** only exhibited one of the two isomers (Fig. 1).

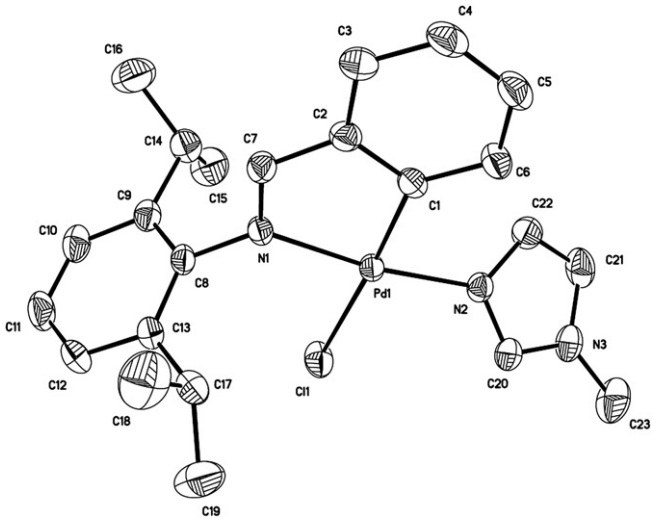
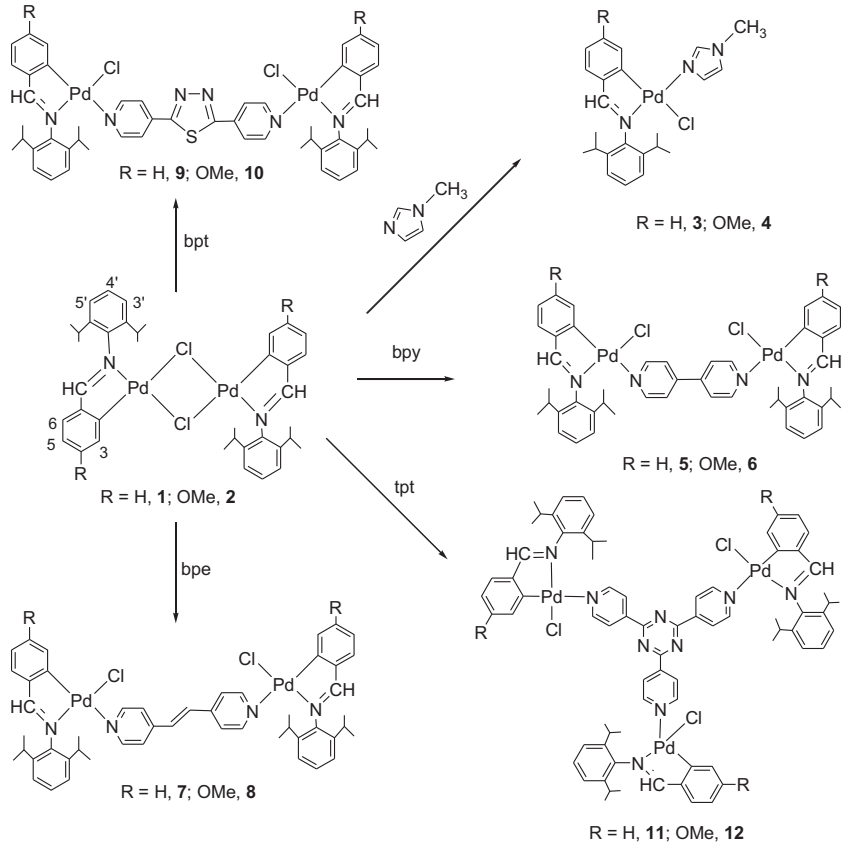


Fig. 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Pd1–C1 1.986(3), Pd1–N1 2.041(2), Pd1–Cl1 2.4017(7), Pd1–N2 2.082(2); N1–Pd1–N2 172.42(8), N1–Pd1–Cl1 94.96(6), N2–Pd1–Cl1 90.02(6), C1–Pd1–Cl1 176.03(8), C1–Pd1–N1 81.14(9).

Bearing in mind that μ-chloro bridged dinuclear cyclometallated Pd(II) complexes **1** and **2** can be readily cleaved by 1-methylimidazole, we decided to extend this cleavage reaction to bidentate and tridentate aromatic *N*-heterocycles. We anticipated that these reactions should afford binuclear and trinuclear cyclometallated Pd(II) complexes containing *C*,*N*-Schiff base ligand as blocking ligand. Therefore, we examined reactions of μ-chloro bridged dinuclear cyclometallated Pd(II) complexes **1** and **2** with bidentate and tridentate aromatic *N*-heterocycles, such as 4,4′-bipyridyl (bpy), 1,2-bis(4-pyridyl)-ethene (bpe), 2,5-Bis(4-pyridyl)-1,3,4-thiadiazole (bpt) and 2,4,6-tris-(4-pyridyl)-1,3,5-triazine(tpt). As shown in Scheme 1, bidentate aromatic *N*-heterocycles (bpy,



Scheme 1. Synthesis of mono-, bi- and tri-nuclear cyclometallated Pd(II) chloro complexes.

bpe, bpt) stoichiometrically cleaved the μ-chloro bridged dinuclear cyclometallated Pd(II) complexes **1** and **2** in CH_2Cl_2 at room temperature to give *N*-heterocycles bridged dinuclear cyclometallated Pd(II) complexes [Pd{(4-R)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(Cl)]$_2$(μ-Y) (R = H, Y = bpy, **5**; R = OMe, Y = bpy, **6**; R = H, Y = bpe, **7**; R = OMe, Y = bpe, **8**; R = H, Y = bpt, **9**; R = OMe, Y = bpt, **10**). Complexes **5**–**10** were characterized by spectroscopy and elemental analysis and the molecular structure of **9** was determined by X-ray crystallography. The ^{1}H NMR spectra of **5**–**10** showed the resonances of dipyridyl protons at δ 8.21 and δ 7.03 ppm, δ 8.27 and δ 7.09 ppm, δ 8.12–8.19 and δ 7.04 ppm, δ 8.14 and δ 7.04 ppm, δ 8.33 and δ 7.59 ppm, δ 8.34 and δ 7.58 ppm, respectively. The aromatic proton H_3 of palladated ring in ^{1}H NMR spectra of complexes **5**–**10** was shifted to downfield compared to that of complexes **3** and **4**, indicating the *trans* disposition of bipyridyl moieties in complexes **5**–**10** relative to metalated carbon atom. Furthermore, this observation was confirmed by the molecular structure of complex **9**. Similarly to complexes **3** and **4**, ^{1}H NMR spectra of **5**–**10** also revealed the presence of two isomers in solution (in the ratio of 1.00:0.30 for **5**, 1.00:0.23 for **6**, 1.00:0.40 for **7**, 1.00:0.27 for **8**, 1.00:0.27 for **9**, 1.00:0.17 for **10** based on the measured intensities of the signals due to the C*H*=N groups). We presumed the minor products were *cis*-isomers, in which the Cl atom in Pd–Cl bond is located on the *trans*-position of Pd–C bond, based on the molecular structure of complex **9** (Fig. 2).

In contrast, the corresponding reactions of μ-chloro bridged dinuclear cyclometallated Pd(II) complexes **1** and **2** with a stoichiometric amount of tpt in CH_2Cl_2 at room temperature produced trinuclear cyclometallated Pd(II) complexes [Pd(C_6H_4CH=N-C_6H_3-2,6-*i*-Pr_2)(Cl)]$_3$(tpt) (**11**) and [Pd{(4-MeO)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(Cl)](tpt) (**12**), respectively. Complex **11** was characterized by FT-IR spectrum and elemental analysis. However, ^{1}H NMR of complex **11** was not possible due to the poor solubility of **11** in common organic solvents. The elemental analysis results were consistent with the formula [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(Cl)]$_3$(tpt). Complex **12** was characterized by FT-IR, ^{1}H NMR and elemental analysis. ^{1}H NMR spectrum of **12** showed the resonance approximately at δ 7.87 ppm which is assigned to the imine proton (C*H*=N group) and the resonances approximately at δ 8.48 and 8.18 ppm which are assigned to pyridyl ring protons in tpt. Noteworthy was that the H_3 proton signal in complex **12** appeared at lower field (δ 7.71 ppm), indicating that molecular of complex **12** adopted a *cis* arrangement, in which the Cl atom in Pd–Cl bond was located on the *trans*-position of Pd–N bond and the pyridyl ring in tpt, coordinating to Pd, was located on the *trans*-position of Pd–C bond. Furthermore, the ^{1}H NMR spectra of **12** also revealed the presence of two isomers (ratio of 1.00:0.23 based on the measured intensities of the signals due to the C*H*=N groups).

Single crystals of **3** and **9** suitable for X-ray diffraction analysis were obtained from a dichloromethane/hexane solution and their molecular structure is depicted in Figs. 1 and 2, respectively. Details on crystal data, intensity collection, and refinement details are given in Table 1. As shown in Fig. 1, **3** shows a slightly distorted square-planar coordination containing a cyclometallated Schiff-base ligand, a 1-methylimidazole and a Cl atom. N1 is 0.2032 Å out of the molecule planar, defined by C1, Pd1, Cl1 and N2. The five-membered chelate ring that contains imine functionality defined by Pd1, C1, C2, C7 and N1 is essentially planar with atomic displacements not exceeding 0.0530 Å, to which the diisopropylphenyl ring is roughly perpendicular with a dihedral angle 80.41(7)°. The smallest angle in coordination sphere of palladium corresponds to the C1–Pd1–N1 bite angle, 81.14(9)°. The Pd1–C1 bond [1.986(3) Å] is slightly longer compared to complex **1** [1.965(2) Å] [30] and shorter than the calculated value of 2.05 Å based on the sum of the covalent radii of carbon and palladium. This is consistent with the values for related complexes where a partial multiple-bond character of Pd–C was assumed [40–43]. An intermolecular C–H…Cl interaction between a proton of the 1-methylimidazole ring and a chlorine atom coordinated to Pd atom is observed, with a H…Cl distance of 2.861 Å and a C…Cl distance of 3.666 Å. Moreover, intramolecular C14–H14…N1 and C17–H17…N1 interactions are observed, with the distance of H14…N1 2.4100 Å, C14…N1 2.9035 Å, H17…N1 2.4000 Å, C17…N1 2.8796 Å. Fig. 2 reveals that molecular of complex **9** has a dimeric structure bridged by μ-bpt. The two Pd atoms are separated by a distance of 15.054(1) Å due to 2,5-bis(4-pyridyl)-1,3,4-thiadiazole with two [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(Cl)] moieties taking the *cis* conformation. Each Pd center adopts a slightly distorted square-planar coordination containing a cyclometallated Schiff-base ligand, a bridging bpt ligand and a chlorine atom, the deviation from the mean plane being 0.0333, 0.0346, −0.0011, 0.0061 and 0.0171 for C13, N5, Pd1, Cl1 and N1, respectively. The molecule plane, defined by Pd1, C13, C18, C19 and N5 (plane 1), is relatively planar with the atomic displacements not exceeding 0.0297 Å. The dihedral is 71.15(8)° between plane 1 and diisopropylphenyl ring, and the dihedral amounts to 48.58(8)° between plane 1 and pyridyl ring coordinated to Pd1. The structure of **9** also reveals that two pyridyl rings of the bridging bpt ligand are not coplanar, being twisted to each other by an angle of 18.07(10)°. The Pd1–C13 bond length [1.989(3) Å] is almost equal to the bond of complex **3**. The Pd1–Cl1 bond [2.2893(9) Å] and Pd2–Cl2 bond [2.3081(9) Å] *trans* to nitrogen in complex **9** are significantly shorter than that of complex **3** [2.4017(7) Å] *trans* to Pd–C bond, indicating a higher *trans* influence of the carbon. The similar C…Cl interaction as in complex **3** between C9 of the pyridyl ring and a chlorine atom coordinated to Pd atom is observed, with a distance of 3.641 Å.

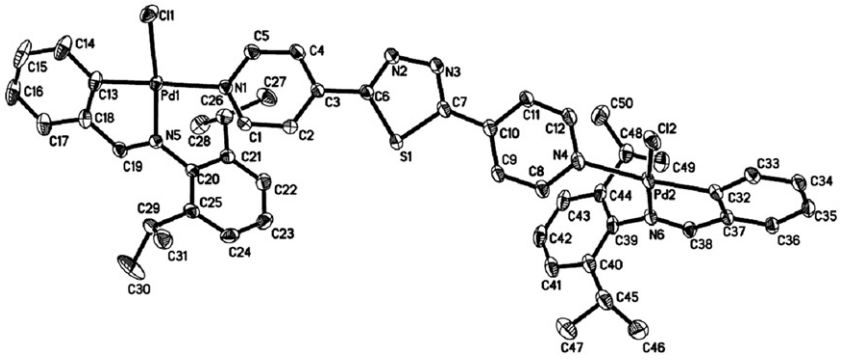


Fig. 2. Molecular structure of **9**. Selected bond lengths (Å) and angles (°): Pd1–C13 1.989(3), Pd1–N1 2.181(3), Pd1–N5 2.051(3), Pd1–Cl1 2.2893(9), Pd2–C32 1.988(3), Pd2–N4 2.156(3), Pd2–N6 2.037(3), Pd2–Cl2 2.3081(9); C13–Pd1–N1 177.42(12), C13–Pd1–N5 80.42(13), N5–Pd1–Cl1 173.61(8), N1–Pd1–Cl1 88.84(7), N5–Pd1–N1 97.43(10), C32–Pd2–N6 81.20(12), C32–Pd2–N4, 172.40(13), N6–Pd2–Cl2 96.94(11), N4–Pd2–Cl2 88.25(8), N6–Pd2–Cl2 174.27(8).

Table 1
X-ray data collection and structure refinement.

	3	**9**·0.5C_6H_{14}·1.25CH_2Cl_2	**13**	**21**·4.775CH_2Cl_2
Formula	$C_{23}H_{28}ClN_3Pd$	$C_{54.25}H_{61.50}Cl_{4.50}N_6Pd_2S$	$C_{21}H_{25}N_3O_3Pd$	$C_{82.77}H_{93.54}Cl_{9.55}N_{12}O_{12}Pd_3$
Formula weight	488.33	1201.98	473.84	2106.05
Temperature (K)	296(2)	113(2)	293(2)	113(2)
Crystal size	0.33 × 0.27 × 0.21	0.22 × 0.14 × 0.12	0.30 × 0.27 × 0.22	0.24 × 0.22 × 0.16
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, Å	9.9869(7)	20.517(3)	8.7730(18)	15.1786(17)
b, Å	14.5976(10)	11.6920(13)	28.821(6)	17.2424(19)
c, Å	15.6445(10)	25.107(3)	9.1457(18)	20.398(2)
α, deg	90	90	90	77.838(11)
β, deg	93.8620(10)	105.116(7)	112.87(3)	87.736(12)
γ, deg	90	90	90	69.511(11)
V, Å^3	2275.6(3)	5814.4(12)	2130.7(7)	4885.0(9)
Z	4	4	4	2
d_{cal}, g cm^{-3}	1.425	1.373	1.477	1.432
μ, mm^{-1}	0.945	0.900	0.896	0.867
$F(000)$	1000	2454	968	2141
T_{min}	0.338	0.8266	0.7748	0.8188
T_{max}	0.475	0.8997	0.8272	0.8737
No. of reflns measured	16,872	55,635	14,054	49,077
No. of reflns unique	4057	13,791	3823	22,777
No. of params refined	258	676	258	1239
Max., in $\Delta\rho$ (e·Å^{-3})	0.274	1.114	0.763	1.530
Min., in $\Delta\rho$ (e·Å^{-3})	−0.563	−0.796	−1.299	−1.936
GOF on F^2	1.171	1.064	1.078	1.058
R ($I > 2\sigma(I)$)	0.0227	0.0479	0.0447	0.0531
wR_2[a] ($I > 2\sigma(I)$)	0.0783	0.1290	0.1028	0.1296
R (all data)	0.0272	0.0587	0.0993	0.0586
wR_2[a] (all data)	0.0949	0.1363	0.1617	0.1337

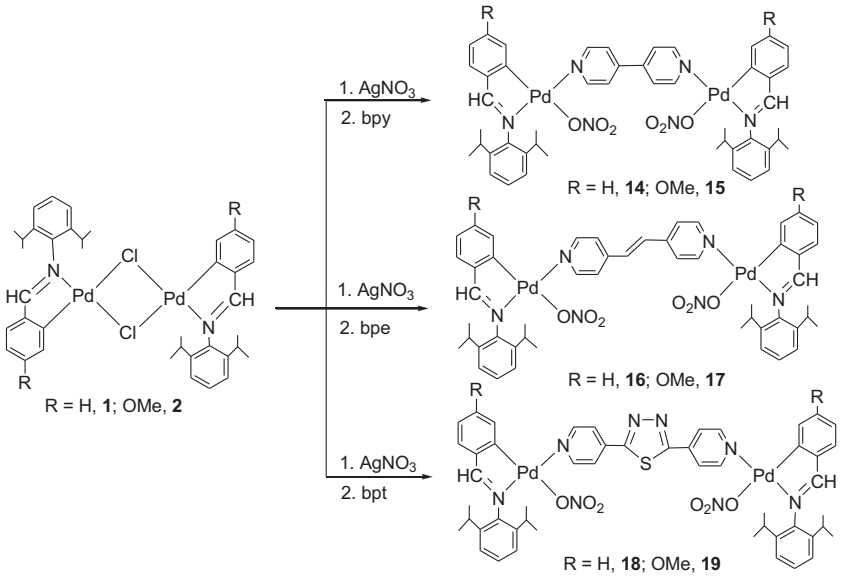
[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Moreover, there are disordered crystallization solvent molecules are found in molecular structure of complex **9**.

2.2. Bi- and tri-nuclear cyclometallated Pd(II) nitrato complexes with aromatic N-heterocycle

Since nitrato ligand coordinated to Pd atom could be readily substituted by other ligands for further supramolecular construction, bi- and tri-nuclear cyclometallated Pd(II) nitrato complexes, as shown in Scheme 2 and Scheme 3 were prepared. Reacting complexes **1** and **2** with 2 equiv of $AgNO_3$ in CH_3CN followed by reaction with 4,4′-bipyridyl or 1,2-bis(4-pyridyl)-ethene or 2,5-bis(4-pyridyl)-1,3,4-thiadiazole in a 1:1 molar ratio in CH_2Cl_2 at room temperature produced the binuclear cyclometallated Pd(II) nitrato complexes [Pd{(4-R)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(ONO_2)]$_2$(μ-Y) (R = H, Y = bpy, **14**; R = OMe, Y = bpy, **15**; R = H, Y = bpe, **16**; R = OMe, Y = bpe, **17**; R = H, Y = bpt, **18**; R = OMe, Y = bpt, **19**). Reacting complexes **11** and **12** with an excess of $AgNO_3$ in CH_2Cl_2/CH_3OH at room temperature generated [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(ONO_2)]$_3$(tpt) (**20**) and [Pd{(4-MeO)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(ONO_2)]$_3$(tpt) (**21**), respectively. Moreover, the fully characterized complex **20** confirmed the formation of complex **11**. Additionally, we were interested in the process of above reactions, therefore the intermediate [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)$(NCCH_3)(ONO_2)$] (**13**) was isolated (Scheme 4). The molecular structure of complex **13** confirmed that it was a neutral monomeric compound bearing one C,N-chelating Schiff-base ligand, one CH_3CN and one O-bound nitrato group, see Fig. 3. Complexes **13**–**21** were characterized by FT-IR, NMR and elemental analysis; moreover the molecular structure of **13** and **21** was determined by X-ray crystallography. The FT-IR spectra of **13**–**19** showed a strong band at approximately 1384 cm^{-1} due to the ν_{N-O}. The formation of complexes **20** and **21** also was easily confirmed by characteristic stretching band at 1384 cm^{-1} deriving from the nitrato group. The ^{1}H NMR spectra of **14**–**19** and **21** displayed the resonance of pyridyl protons at δ 9.12 and δ 7.69 ppm, δ 9.07 and δ 7.64 ppm, δ 9.01 and δ 7.93 ppm, δ 9.00 and δ 7.93 ppm, δ 9.17 and δ 8.09 ppm, δ 9.13 and δ 8.28 ppm, δ 9.28 and δ 8.57 ppm, respectively, which were shifted downfield compared to those of the corresponding chloro coordinated cyclopalladated complexes **5**–**10** and **12**. The resonance of the H_3 protons in complexes **14**–**19** and **21** shifted upfield compared to those of the corresponding chloro coordinated cyclopalladated complexes **5**–**10** and **12**. All these indications prove that the configuration of complexes **14**–**21** was different from corresponding complexes **5**–**12**. The molecular structure of complex **21** confirmed that the pyridyl fragments are located in *trans*-position of Pd–N bond and the O-bound nitrato groups are located in *trans*-position of Pd–C bond. Moreover, in contrast with the spectra of **5**–**12**, no isomers of the complexes **14**–**21** could be detected in ^{1}H NMR spectra.

Single crystals of **13** and **21** suitable for X-ray diffraction analysis were obtained from dichloromethane/hexane solutions and their molecular structures are presented in Figs. 3 and 4, respectively. Details on crystal data, intensity collection, and refinement details are given in Table 1. Fig. 3 shows that palladium atom of complex **13** is in a square-planar environment containing a *C,N*-coordinating Schiff-base ligand, one CH_3CN, and one nitrato ligand. The coordination plane shows a tetrahedral distortion, the deviation from the mean plane being −0.0012, −0.0609, 0.1794, 0.1163 and −0.0904 for Pd1, N1, C15, O1 and N3, respectively. The five-membered chelate ring that contains imine functionality defined by Pd1, N1, C13, C14 and C15 is essentially planar with the atomic displacements not exceeding 0.0174 Å, to which the diisopropylphenyl ring is roughly perpendicular with a dihedral angle 74.1(2)°. Pd1–N1 bond [2.025(6) Å] and Pd1–N3 bond [2.022(7) Å] lengths are almost equal to each other. An intramolecular C–H…Pd between the proton of isopropyl and palladium atom is observed, with a H…Pd bond distance of 2.793 Å and C…Pd distance of 3.639 Å. As presented in Fig. 4, complex **21** reveals that each Pd center has one cyclometallated Schiff-base ligand, one terminal O-bound nitrato



Scheme 2. Synthesis of binuclear cyclometallated Pd(II) nitrato complexes **14**–**19**.

ligand and one tpt ligand. 2,4,6-Tris(4-pyridyl)-1,3,5-triazine links three [Pd{(4-MeO)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2} (ONO_2)] moieties to give three-dentate "clip" structure, the separation of Pd1…Pd2, Pd2…Pd3 and Pd1… Pd3 is 12.761(1) Å, 13.169(2) Å and 13.126(2) Å, respectively. The coordination sphere of each Pd can be described as slightly distorted square planar. The five-membered chelate ring that contains the imine functionality defined by Pd1, N6, C21, C22 and C27 is essentially planar with the atomic displacements not exceeding 0.0339 Å, to which the diisopropylphenyl ring is roughly perpendicular with a dihedral angle 83.9(1)°. The pyridyl rings are not coplanar with the triazine ring but they are twisted to an angle of 12.1(9)°, 3.5(9)° and 6.6(9)°, respectively.

In summary, we prepared a number of mono-, bi- and trinuclear cyclometallated Pd(II) chloro complexes containing C,N-coordinating Schiff-base ligand by reactions of Cl-bridged cyclopalladated complexes with aromatic *N*-heterocycles. As well bi- and tri-nuclear cyclometallated Pd(II) nitrato complexes were synthesized. We found that bi- and tri-nuclear cyclometallated Pd(II) nitrato complexes possess a different *cis* conformation with corresponding bi- and tri-nuclear cyclometallated Pd(II) chloro complexes in solid state. This kind of *cis* conformation should be beneficial for assembling macrocycles based on bi- and tri-nuclear cyclometallated Pd(II) nitrato complexes. Two kinds of interconversion isomers occurred in solution of bi- and tri-nuclear cyclometallated Pd(II) chloro complexes. However, no isomers were observed in solution of bi- and tri-nuclear cyclometallated Pd(II) nitrato complexes.

3. Experimental

3.1. General, materials and measurements

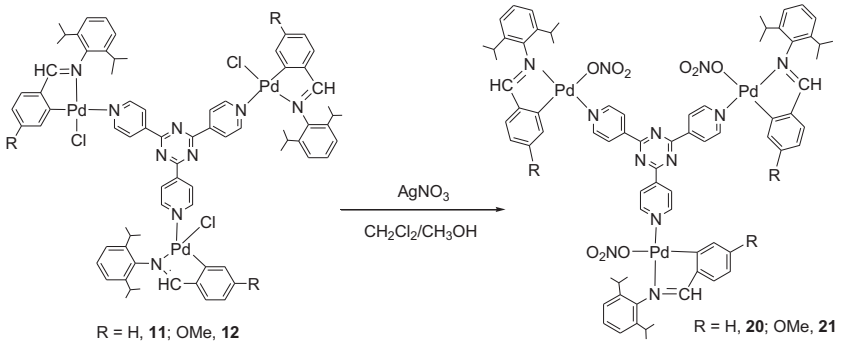
All manipulations of air-sensitive compounds were performed under nitrogen by using standard Schlenk techniques. All solvents were purified and degassed by standard procedure, other regents were used as supplied. ^{1}H NMR spectra were obtained using a Mercury-300 spectrophotometer (Varian), $CDCl_3$ or [d_6]-DMSO was applied for all compounds using TMS as an internal standard. FT-IR spectra were recorded on a Nicolet AVATAR 330 FT-IR spectrometer. Elemental analyses were performed on a Thermo Flash EA1112 Analyzer. ESI-MS was determined by Varian 500-MS ion trap mass spectrometer equipped with an electrospray ionization (ESI) source in positive ion mode, with data acquisition using the Varian MS Workstation (Varian, Palo Alto, CA, USA).

[Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(μ-Cl)]$_2$ and [Pd{(4-MeO)C_6H_3CH=NC_6H_3-2,6-*i*-Pr_2}(μ-Cl)]$_2$ were prepared according to literature methods [34].

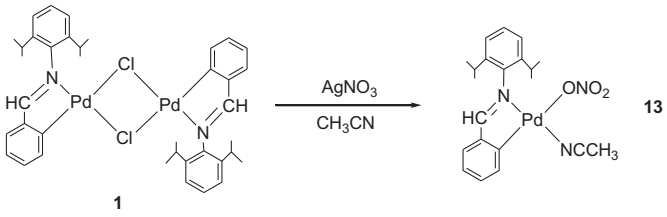
3.2. Preparations

3.2.1. [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(L)(Cl)](L = 1-methylimidazole) (**3**)

To a 10 mL CH_2Cl_2 solution of complex [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(μ-Cl)]$_2$ (**1**, 0.075 g, 0.092 mmol) was added stepwise 1-methylimidazole (16 μL, 0.200 mmol). After stirring for 12 h at



Scheme 3. Synthesis of trinuclear cyclometallated Pd(II) nitrato complexes **20**, **21**.



Scheme 4. Synthesis of mononuclear cyclometallated Pd(II) nitrato complex **13**.

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 generated pale yellow crystals of [Pd($C_6H_4CH{=}NC_6H_3$-2,6-*i*-Pr_2)(L)(Cl)](L = 1-methylimidazole) (**3**, 0.054 g, 60%). IR (KBr, cm^{-1}): 1602 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.18 (d, 1H, J = 8.4 Hz), 7.91 (s, 1H, −C*H*=N), 7.37 (d, 1H, J = 7.5 Hz), 7.18–7.24 (m, 2H), 7.15 (br, 1H), 7.11 (d, 3H, J = 7.5 Hz), 6.49 (s, 1H), 6.15 (s, 1H), 3.40–3.55 (m, 5H, −C*H*(CH_3)$_2$, N−C*H*$_3$), 1.12 (d, 6H, J = 6.9 Hz, −CH(C*H*$_3$)$_2$), 1.04 (d, J = 6.6 Hz, 6H, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{23}H_{28}ClN_3Pd$: C, 56.57; H, 5.78; N, 8.60. Found: C, 56.79; H, 5.96; N, 8.55.

Complex **4** was prepared in a similar manner as complex **3**.

*3.2.2. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(L)(Cl)](L = 1-methylimidazole) (**4**, 45%)*

IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$); m.p.: 108–110 °C; ^1H NMR (300 MHz in $CDCl_3$, δ): 7.78 (s, 1H, −C*H*=N), 7.76 (d, 1H, J = 2.7 Hz, imidazole), 7.29 (d, 1H, J = 8.4 Hz, H^6), 7.22 (d, 1H, J = 8.1 Hz, $H^{4'}$), 7.08 (d, 2H, J = 7.5 Hz, $H^{3'}$, $H^{5'}$), 7.01 (s, 1H, imidazole), 6.63 (dd, 1H, J = 2.4, 2.4 Hz, imidazole), 6.48 (s, 1H, H^5), 6.18 (s, 1H, H^3), 3.92 (s, 3H, −OC*H*$_3$), 3.40–3.56 (m, 5H, −C*H*(CH_3)$_2$, N−C*H*$_3$), 1.10 (d, 6H, J = 6.9 Hz, −CH(C*H*$_3$)$_2$), 1.03 (d, 6H, J = 6.9 Hz, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{24}H_{30}ClN_3OPd\cdot CH_2Cl_2$: C, 49.77; H, 5.35; N, 6.96. Found: C, 50.03; H, 5.29; N, 6.80.

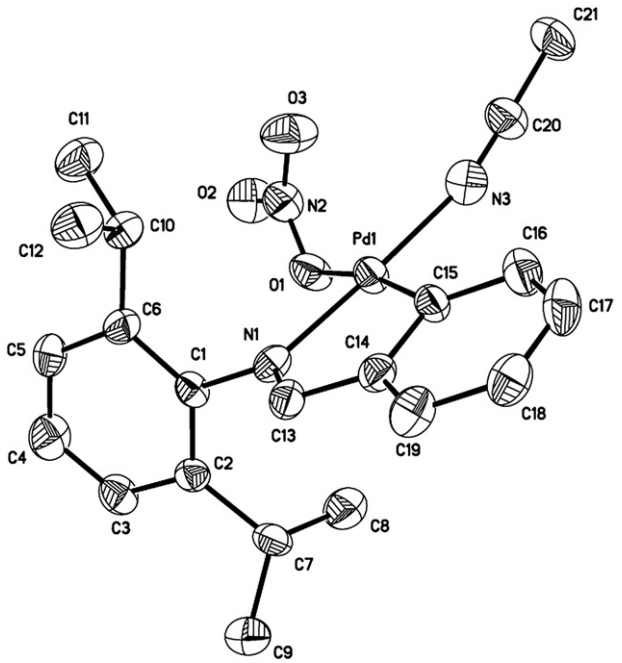


Fig. 3. Molecular structure of **13**. Selected bond lengths (Å) and angles (°): Pd1–N1 2.025(6), Pd1–C15 1.964(7), Pd1–N3 2.022(7), Pd1–O1 2.194(5), N2–O3 1.242(9), N2–O2 1.250(8), N2–O1 1.247(8); N1–Pd1–N3 173.4(2), N1–Pd1–C15 81.7(2), N1–Pd1–O1 92.5(2), C15–Pd1–O1 169.7(3), Pd1–O1–N2 117.3(5), Pd1–N3–C20 166.3(7).

*3.2.3. [Pd($C_6H_4CH{=}NC_6H_3$-2,6-i-Pr_2)(Cl)]$_2$(μ-bpy) (**5**)*

To a 10 mL CH_2Cl_2 solution of complex **1** (0.130 g, 0.160 mmol) was dropwise added a CH_2Cl_2 solution of 4,4′-Bipyridyl (0.037 g, 0.192 mmol). After stirring for 22 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 generated pale yellow crystals of [Pd($C_6H_4CH{=}NC_6H_3$-2,6-*i*-Pr_2)(Cl)]$_2$(μ-bpy) (**5**, 0.090 g, 58%). IR (KBr, cm^{-1}): 1600 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.21 (d, 4H, J = 5.7 Hz, pyridyl), 8.06 (d, 2H, J = 7.8 Hz, H^3), 7.91 (s, 2H, −*H*C=N), 7.34 (d, 2H, J = 7.2 Hz, H^6), 7.17–7.26 (m, 2H, $H^{4'}$), 7.08 (d, 4H, J = 7.8 Hz, H^4, H^5), 7.03 (d, 4H, J = 5.7 Hz, pyridyl), 6.91 (d, 4H, J = 7.5 Hz, $H^{3'}$, $H^{5'}$), 3.37 (hepta, 4H, −C*H*(CH_3)$_2$), 1.02 (dd, 24H, J = 7.2 Hz, 7.2 Hz, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{48}H_{52}Cl_2N_4Pd_2$: C, 59.51; H, 5.41; N, 5.78. Found: C, 59.33; H, 5.49; N, 5.69.

Complexes **6**–**12** were prepared in a similar manner as complex **5**.

*3.2.4. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(Cl)]$_2$(μ-bpy) (**6**, 63%)*

IR (KBr, cm^{-1}): 1598 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.27 (d, 4H, J = 6.0 Hz, pyridyl), 7.83 (s, 2H, −C*H*=N), 7.70 (d, 2H, J = 2.1 Hz, H^3), 7.32 (d, 2H, J = 8.1 Hz, H^6), 7.14–7.19 (m, 2H, $H^{4'}$), 7.09 (m, 4H, J = 5.7 Hz, pyridyl), 6.97 (d, 4H, J = 7.8 Hz, $H^{3'}$, $H^{5'}$), 6.67 (dd, J = 2.1, 2.1 Hz, 2H, H^5), 3.93 (s, 6H, −OC*H*$_3$), 3.40–3.53 (m, 4H, −C*H*(CH_3)$_2$), 1.08 (dd, 24H, J = 7.5 Hz, 7.5 Hz, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{50}H_{56}Cl_2N_4O_2Pd_2$: C, 58.38; H, 5.45; N, 5.39. Found: C, 58.65; H, 5.67; N, 5.41.

*3.2.5. [Pd($C_6H_4CH{=}NC_6H_3$-2,6-i-Pr_2)(Cl)]$_2$(μ-bpe) (**7**, 65%)*

IR (KBr, cm^{-1}): 1600 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.12–8.19 (m, 6H, pyridyl, H^3), 7.96 (s, 2H, −C*H*=N), 7.39 (d, 2H, J = 7.5 Hz, H^6), 7.23–7.29 (m, 2H, $H^{4'}$), 7.18 (d, 1H, J = 7.2 Hz, H^4), 7.14 (d, 4H, J = 8.4 Hz, −C*H*=C*H*−, H^5), 7.04 (d, 4H, J = 6.6 Hz, pyridyl), 7.00 (d, 4H, J = 7.8 Hz, $H^{3'}$, $H^{5'}$), 3.45 (hepta, 4H, −C*H*(CH_3)$_2$), 1.09 (dd, 24H, J = 6.3 Hz, 5.4 Hz, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{50}H_{54}Cl_2N_4Pd_2$: C, 60.37; H, 5.47; N, 5.63. Found: C, 60.25; H, 5.43; N, 5.61.

*3.2.6. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(Cl)]$_2$(μ-bpe) (**8**, 83%)*

IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.14 (d, 4H, J = 6.0 Hz, pyridyl), 7.82 (s, 2H, −C*H*=N), 7.72 (d, 2H, J = 2.4 Hz, H^3), 7.31 (d, 2H, J = 8.4 Hz, H^6), 7.10–7.19 (m, 4H, −C*H*=C*H*−, $H^{4'}$), 7.04 (d, 4H, J = 6.0 Hz, pyridyl), 6.98 (d, 4H, J = 7.5 Hz, $H^{3'}$, $H^{5'}$), 6.67 (dd, J = 2.4, 2.4 Hz, 2H, H^5), 3.93 (s, 6H, −OC*H*$_3$), 3.47 (hepta, 4H, −C*H*(CH_3)$_2$), 1.09 (dd, 24H, J = 6.0 Hz, 5.7 Hz, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{52}H_{58}Cl_2N_4O_2Pd_2\cdot 0.5C_6H_{14}$: C, 60.17; H, 5.97; N, 5.10. Found: C, 60.03; H, 5.70; N, 5.32.

*3.2.7. [Pd($C_6H_4CH{=}NC_6H_3$-2,6-i-Pr_2)(Cl)]$_2$(μ-bpt) (**9**, 58%)*

IR (KBr, cm^{-1}): 1600 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.33 (d, 4H, J = 6.3 Hz, pyridyl), 8.13 (d, 2H, J = 7.5 Hz, H^3), 7.99 (s, 2H, −C*H*=N), 7.59 (d, 4H, J = 6.3 Hz, pyridyl), 7.42 (d, 2H, J = 7.5 Hz, H^6), 7.23–7.28 (m, 2H, $H^{4'}$), 7.18 (d, 4H, J = 7.5 Hz, $H^{3'}$, $H^{5'}$), 7.01 (d, 4H, J = 7.8 Hz, H^5), 3.45 (hepta, 4H, −C*H*(CH_3)$_2$), 1.10 (dd, 24H, J = 3.0 Hz, −CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{50}H_{52}Cl_2N_6Pd_2S$: C, 57.04; H, 4.98; N, 7.98; S, 3.05. Found: C, 56.72; H, 5.08; N, 7.76; S, 3.27. ESI-MS: m/z = 1018.5 (MH^+ − Cl). $C_{50}H_{52}ClN_6Pd_2S$ (M_r = 1017.3).

*3.2.8. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(Cl)]$_2$(μ-bpt) (**10**, 65%)*

IR (KBr, cm^{-1}): 1598 ($\nu_{C=N}$); ^1H NMR (300 MHz in $CDCl_3$, δ): 8.34 (d, 4H, J = 6.3 Hz, pyridyl), 7.84 (s, 2H, −CC*H*=N), 7.71 (d, 2H, J = 2.1 Hz, H^3), 7.58 (d, 4H, J = 6.6 Hz, pyridyl), 7.33 (d, 2H, J = 8.4 Hz, H^6), 7.11–7.19 (m, 2H, $H^{4'}$), 6.99 (d, 4H, J = 7.5 Hz, $H^{3'}$, $H^{5'}$), 6.68 (dd, 2H, J = 2.4 Hz, 2.7 Hz, H^5), 3.93 (s, 6H, −OC*H*$_3$), 3.47 (hepta, 4H,

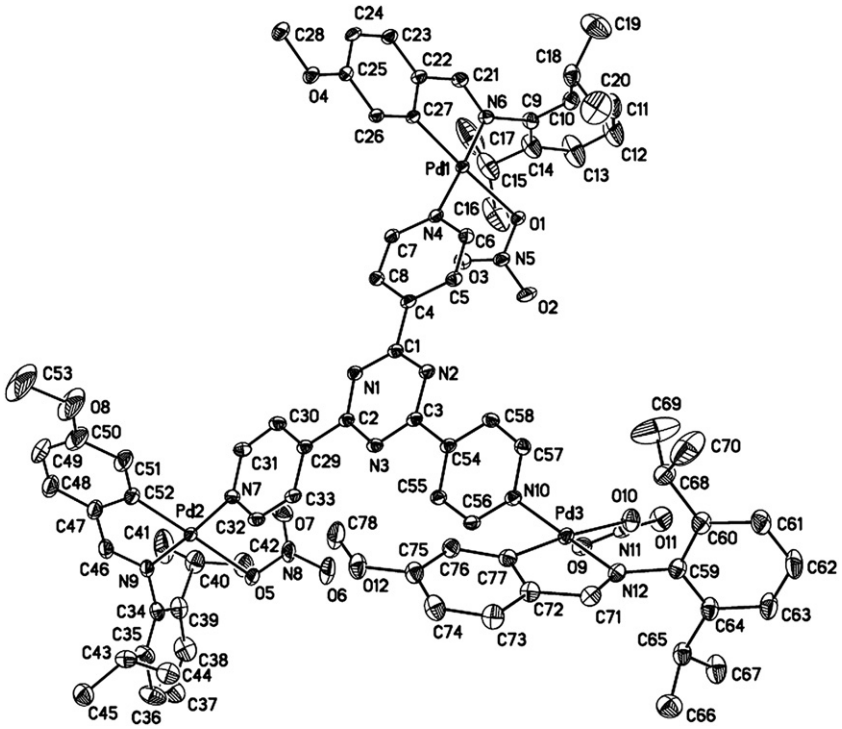


Fig. 4. Molecular structure of **21**. Selected bond lengths (Å) and angles(°): Pd1–N6 2.030(3), Pd1–N4 2.037(3), Pd1–O1 2.154(2), Pd1–C27 1.977(3), Pd2–N9 2.030(3), Pd2–N7 2.037(3), Pd2–O5 2.146(2), Pd2–C52 1.978(4), Pd3–N10 2.032(3), Pd3–N12 2.041(3), Pd3–O10 2.143(3), Pd3–C77 1.992(3); N6–Pd1–N4 177.22(11), C27–Pd1–N6 81.71(12), C27–Pd1–O1 177.41(12), C27–Pd1–N4 95.63(12), N4–Pd1–O1 85.85(10), N9–Pd2–N7 176.54(12), C52–Pd2–N9 82.79(16), C52–Pd2-O5 178.53(14), C52–Pd2–N7 93.77(15), N7–Pd2–O5 87.32(11), N10–Pd3–N12 174.14(11), C77–Pd3–N12 81.65(13), C77–Pd3–O10 174.04(13), N10–Pd3–O10 91.62(11).

–C*H*(CH_3)$_2$), 1.09–1.12 (m, 24H, –CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{52}H_{56}Cl_2N_6O_2Pd_2S$: C, 56.12; H, 5.07; N, 7.55; S, 2.88. Found: C, 55.97; H, 4.66; N, 7.58; S, 2.94.

*3.2.9. [Pd(C_6H_4CH=NC_6H_3-2,6-i-Pr_2)(Cl)]$_3$(tpt) (**11**, 83%)*

IR (KBr, cm^{-1}): 1601 ($\nu_{C=N}$); Anal. Calcd for $C_{75}H_{78}Cl_3N_9Pd_3$: C, 58.83; H, 5.13; N, 8.23. Found: C, 58.39; H, 4.84; N, 8.36. ESI-MS: *m*/*z* = 1491.2 (M – Cl). $C_{75}H_{78}Cl_2N_9Pd_3$ (M_r = 1492.3). ^{1}H NMR was not performed due to their poor solubility in common organic solvents.

*3.2.10. [Pd{(4-MeO)C_6H_3CH=NC_6H_3-2,6-i-Pr_2}(Cl)]$_3$(tpt) (**12**, 75%)*

IR (KBr, cm^{-1}): 1598 ($\nu_{C=N}$); m.p.: 280–282 °C; ^{1}H NMR (300 MHz in $CDCl_3$, δ): 8.48 (d, 4H, *J* = 5.7 Hz, pyridyl), 8.18 (dd, 4H, *J* = 6.0, 6.0 Hz, pyridyl), 7.87 (s, 2H, –C*H*=N), 7.74 (d, 2H, *J* = 2.1 Hz, H^3), 7.35 (d, 2H, *J* = 8.1 Hz, H^6), 7.15 (dd, 2H, *J* = 7.5, 7.5 Hz, $H^{4'}$), 7.02 (d, 4H, *J* = 7.8 Hz, $H^{3'}$, $H^{5'}$), 6.69 (d, 2H, *J* = 8.4 Hz, H^5), 3.95 (s, 3H, OCH_3), 3.54 (hepta, 4H, –C*H*(CH_3)$_2$), 1.14 (dd, 24H, *J* = 3.0, 3.0 Hz, –CH(CH_3)$_2$). Anal. Calcd for $C_{78}H_{84}Cl_3N_9O_3Pd_3$: C, 57.79; H, 5.22; N, 7.78. Found: C, 57.93; H, 5.14; N, 8.08.

*3.2.11. [Pd(C_6H_4CH=NC_6H_3-2,6-i-Pr_2)(NCCH_3)(ONO_2)] (**13**)*

To a 20 mL CH_3CN solution of complex **1** (0.200 g, 0.246 mmol) was added $AgNO_3$ (0.093 g, 0.547 mmol). After stirring for 10 h in dark at room temperature, insoluble materials were filtered off. The solvents of the filtrate were fully removed by evaporation. The resulting residue was solidified with hexane to give crude solids. Recrystallization from CH_2Cl_2/hexane gave pale yellow crystals of [Pd(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)(NCCH_3)(ONO_2)] (**13**, 0.161 g, 69%). IR (KBr, cm^{-1}): 1601 ($\nu_{C=N}$), 1384 (ν_{NO}); m.p.: 114–116 °C; ^{1}H NMR (300 MHz in $CDCl_3$, δ): 7.76 (d, 1H, *J* = 2.1 Hz, –C*H*=N), 7.33–7.37 (m, 1H), 7.24–7.30 (m, 1H), 7.15–7.18 (m, 5H), 3.43 (hepta, 2H, –C*H*(CH_3)$_2$), 1.85 (br, 3H, CH_3CN), 1.36 (dd, 6H, *J* = 1.5, 2.4 Hz, –C*H*(CH_3)$_2$), 1.14 (d, 6H, *J* = 6.6 Hz, –C*H*(CH_3)$_2$). Anal. Calcd for $C_{21}H_{25}N_3O_3Pd$: C, 53.23; H, 5.32; N, 8.87. Found: C, 53.11; H, 5.50; N, 8.76.

*3.2.12. [Pd(C_6H_4CH=NC_6H_3-2,6-i-Pr_2)(ONO_2)]$_2$(μ-bpy) (**14**)*

To a 20 mL CH_3CN solution of complex **1** (0.092 g, 0.113 mmol) was added $AgNO_3$ (0.039 g, 0.230 mmol). After stirring for 10 h in dark at room temperature, insoluble materials were filtered off. The solvents of the filtrate were fully removed by evaporation. To the resulting pale yellow oil was 10 mL CH_2Cl_2 and 4,4′Bipyridyl (0.026 g, 0.135 mmol). After stirring for 14 h at room temperature, the solvent was removed completely. The resulting residue was washed with ether to give a pale yellow solid. Recrystallization from CH_2Cl_2/hexane gave pale yellow needles of [Pd_2(C_6H_4CH=NC_6H_3-2,6-*i*-Pr_2)$_2$(μ-bpy)(ONO_2)$_2$] (**14**, 0.082 g, 71%). IR (KBr, cm^{-1}): 1603 ($\nu_{C=N}$), 1384 (ν_{NO}); ^{1}H NMR (300 MHz in $CDCl_3$, δ): 9.12 (d, 4H, *J* = 6.3 Hz, pyridyl), 7.89 (s, 2H, –C*H*=N), 7.69 (d, 4H, *J* = 6.6 Hz, pyridyl), 7.45 (d, 2H, *J* = 7.5 Hz, H^6), 7.29–7.35 (m, 2H, $H^{4'}$), 7.20 (dd, 6H, *J* = 8.4, 8.4 Hz, $H^{3'}$, $H^{5'}$, H^4), 7.10 (dd, 2H, *J* = 7.8, 7.5 Hz, H^5), 6.40 (d, 2H, *J* = 7.8 Hz, H^3), 3.53 (hepta, 4H, –C*H*(CH_3)$_2$), 1.44 (d, 12H, *J* = 6.6 Hz, –C*H*(CH_3)$_2$), 1.18 (d, 12H, *J* = 6.9 Hz, –C*H*(CH_3)$_2$). Anal. Calcd for $C_{48}H_{52}N_6O_6Pd_2$: C, 56.42; H, 5.13; N, 8.22. Found: C, 56.09; H, 5.08; N, 8.14.

Complexes **15**–**19** were prepared in a similar way as complex **14**.

*3.2.13. [Pd{(4-MeO)C_6H_3CH=NC_6H_3-2,6-i-Pr_2}(ONO_2)]$_2$(μ-bpy) (**15**, 80%)*

IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$), 1384 (ν_{NO}); ^{1}H NMR (300 MHz in $CDCl_3$, δ): 9.07 (d, 4H, *J* = 5.7 Hz, pyridyl), 7.75 (s, 2H, –C*H*=N), 7.64 (d, 4H, *J* = 5.4 Hz, pyridyl), 7.39 (d, 2H, *J* = 8.1 Hz, H^6), 7.30 (d, 2H, *J* = 7.5 Hz, $H^{4'}$), 7.19 (d, 4H, *J* = 7.5 Hz, $H^{3'}$, $H^{5'}$), 6.66 (d, 2H, *J* = 8.1 Hz, H^5), 5.87 (s, 2H, H^3), 3.71 (s, 6H, –OCH_3), 3.54 (hepta, 4H, –C*H*(CH_3)$_2$), 1.43 (d, 12H, *J* = 6.6 Hz, –CH(CH_3)$_2$), 1.18 (d, 12H,

$J = 6.6$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{50}H_{56}N_6O_8Pd_2$: C, 55.51; H, 5.22; N, 7.77. Found: C, 55.12; H, 5.64; N, 7.45.

*3.2.14. [Pd($C_6H_4CH{=}NC_6H_3$-2,6-i-Pr_2)(ONO_2)]$_2$(μ-bpe) (**16**, 75%)*

IR (KBr, cm^{-1}): 1603 ($\nu_{C=N}$), 1384 (ν_{NO}); ^1H NMR (300 MHz in [d_6]-DMSO, δ): 9.01 (br, 4H, pyridyl), 8.52 (s, 2H, $-CH{=}N$), 7.93 (br, 4H, pyridyl), 7.85 (br, 2H, $-CH{=}CH-$), 7.61 (d, 2H, $J = 7.2$ Hz, H^6), 7.41 (t, 2H, $J = 7.2$ Hz, $H^{4'}$), 7.33 (d, 4H, $J = 7.2$ Hz, $H^{3'}$, $H^{5'}$), 7.23 (t, 2H, $J = 7.2$ Hz, H^5), 7.15 (dd, 2H, $J = 8.1$, 7.8 Hz, H^4), 6.28 (br, 2H, H^3), 3.42 (m, 4H, $-CH(CH_3)_2$), 1.39 (d, 12H, $J = 6.6$ Hz, $-CH(CH_3)_2$), 1.18 (d, 12H, $J = 6.6$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{50}H_{54}N_6O_6Pd_2 \cdot 0.75CH_2Cl_2$: C, 54.84; H, 5.03; N, 7.56. Found: C, 54.92; H, 4.88; N, 7.49.

*3.2.15. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(ONO_2)]$_2$(μ-bpe) (**17**, 78%)*

IR (KBr, cm^{-1}): 1600 ($\nu_{C=N}$), 1384 (ν_{NO}); ^1H NMR (300 MHz [d_6]-DMSO, δ): 9.00 (br, 4H, pyridyl), 8.34 (s, 2H, $-CH{=}N$), 7.93 (br, 4H, pyridyl), 7.86 (br, 2H, $-CH{=}CH-$), 7.58 (d, 2H, $J = 8.4$ Hz, H^6), 7.39 (dd, 2H, $J = 8.4$, 6.9 Hz, $H^{4'}$), 7.31 (d, 4H, $J = 7.5$ Hz, $H^{3'}$, $H^{5'}$), 6.80 (d, 2H, $J = 8.4$ Hz, H^5), 5.67 (br, 2H, H^3), 3.68 (s, 6H, $-OCH_3$), 3.45 (m, 4H, $-CH(CH_3)_2$), 1.37 (d, 12H, $J = 6.6$ Hz, $-CH(CH_3)_2$), 1.17 (d, 12H, $J = 6.6$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{52}H_{58}N_6O_8Pd_2 \cdot 0.5CH_2Cl_2$: C, 54.81; H, 5.17; N, 7.31. Found: C, 54.73; H, 4.98; N, 7.04.

*3.2.16. [Pd($C_6H_4CH{=}NC_6H_3$-2,6-i-Pr_2)(ONO_2)]$_2$(μ-bpt) (**18**, 79%)*

IR (KBr, cm^{-1}): 1602 ($\nu_{C=N}$), 1384 (ν_{NO}); ^1H NMR (300 MHz in $CDCl_3$, δ): 9.17 (d, 4H, $J = 6.3$ Hz, pyridyl), 8.09 (d, 4H, $J = 6.3$ Hz, pyridyl), 7.88 (s, 2H, $-CH{=}N$), 7.45 (d, 2H, $J = 7.2$ Hz, H^6), 7.31 (dd, 2H, $J = 7.2$, 7.2 Hz, $H^{4'}$), 7.17–7.22 (m, 6H, $H^{3'}$, $H^{5'}$, H^5), 7.09 (dd, 2H, $J = 7.5$, 7.5 Hz, H^4), 6.39 (d, 2H, $J = 7.5$ Hz, H^3), 3.52 (hepta, 4H, $-CH(CH_3)_2$), 1.44 (d, 12H, $J = 6.6$ Hz, $-CH(CH_3)_2$), 1.18 (d, 12H, $J = 6.9$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{50}H_{52}N_8O_6Pd_2S \cdot 0.25CH_2Cl_2$: C, 53.55; H, 4.69; N, 9.94; S, 2.84. Found: C, 53.58; H, 4.81; N, 10.03, S, 3.03. ESI-MS: $m/z = 1106.5$ (MH^+). $C_{50}H_{52}N_8O_6Pd_2S$ ($M_r = 1105.9$).

*3.2.17. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(ONO_2)]$_2$(μ-bpt) (**19**, 56%)*

IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$), 1384 (ν_{NO}); ^1H NMR (300 MHz in [d_6]-DMSO, δ): 9.13 (br, 4H, pyridyl), 8.35 (s, 2H, $-CH{=}N$), 8.28 (br, 4H, pyridyl), 7.58 (d, 2H, $J = 8.4$ Hz, H^6), 7.40 (dd, 2H, $J = 7.8$, 7.2 Hz, $H^{4'}$), 7.32 (d, 4H, $J = 7.2$ Hz, $H^{3'}$, $H^{5'}$), 6.82 (d, 2H, $J = 8.4$ Hz, H^5), 5.76 (s, 2H, H^3), 3.72 (s, 6H, $-OCH_3$), 3.46 (hepta, 4H, $-CH(CH_3)_2$), 1.37 (d, 12H, $J = 6.3$ Hz, $-CH(CH_3)_2$), 1.16 (d, 12H, $J = 6.6$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{52}H_{56}N_8O_8Pd_2S \cdot 0.5CH_2Cl_2$: C, 52.18; H, 4.75; N, 9.27. Found: C, 51.88; H, 4.66; N, 7.04.

*3.2.18. [Pd($C_6H_4CH{=}NC_6H_3$-2,6-i-Pr_2)(ONO_2)]$_3$(tpt) (**20**)*

To a 15 mL CH_2Cl_2 suspension of complex **11** (0.103 g, 0.067 mmol) was added $AgNO_3$ (0.044 g, 0.259 mmol) solution dissolved in 5 mL methanol. After stirring for 10 h in dark at room temperature, insoluble materials were filtered off, the filtrate was evaporated to remove the solvents. The residue was isolated with ether giving a yellowish green solid. After recrystallization from CH_2Cl_2/hexane yellowish green crystals of [$Pd_3(C_6H_4CH{=}NC_6H_3$-2,6-i-$Pr_2)_3$(tpt)$(ONO_2)_3$] (**20**, 0.071 g, 66%) were obtained. IR (KBr, cm^{-1}): 1602 ($\nu_{C=N}$), 1384 (ν_{NO}); ^1H NMR (300 MHz in $CDCl_3$, δ): 9.28 (d, 6H, $J = 6.6$ Hz, pyridyl), 8.61 (d, 6H, $J = 6.6$ Hz, pyridyl), 7.90 (s, 3H, $-CH{=}N$), 7.46 (d, 3H, $J = 7.2$ Hz, H^6), 7.29–7.34 (m, 3H, $H^{4'}$), 7.17–7.22 (m, 9H, $H^{3'}$, $H^{5'}$, H^5), 7.05–7.11 (m, 3H, H^4), 6.41 (d, 3H, $J = 7.2$ Hz, H^3), 3.55 (hepta, 6H, $-CH(CH_3)_2$), 1.45 (d, 18H, $J = 6.6$ Hz, $-CH(CH_3)_2$), 1.19 (d, 18H, $J = 6.6$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{75}H_{78}N_{12}O_9Pd_3 \cdot 0.5CH_2Cl_2$: C, 54.85; H, 4.82; N, 10.17. Found: C, 54.73; H, 5.11; N, 10.11.

Complex **21** was prepared in a similar way as complex **20**.

*3.2.19. [Pd{(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-Pr_2}(ONO_2)]$_3$(tpt) (**21**, 71%)*

IR (KBr, cm^{-1}): 1600 ($\nu_{C=N}$), 1384 (ν_{NO}); ^1H NMR (300 MHz in $CDCl_3$, δ): 9.28 (d, 6H, $J = 5.4$ Hz, pyridyl), 8.57 (d, 6H, $J = 5.7$ Hz, pyridyl), 7.77 (s, 3H, $-CH{=}N$), 7.40 (d, 3H, $J = 8.1$ Hz, H^6), 7.30 (dd, 3H, $J = 7.8$, 7.8 Hz, $H^{4'}$), 7.19 (d, 6H, $J = 7.8$ Hz, $H^{3'}$, $H^{5'}$), 6.68 (d, 3H, $J = 8.1$ Hz, H^5), 5.91 (s, 3H, H^3), 3.69 (s, 9H, $-OCH_3$), 3.57 (hepta, 6H, $-CH(CH_3)_2$), 1.45 (d, 18H, $J = 6.6$ Hz, $-CH(CH_3)_2$), 1.19 (d, 18H, $J = 6.9$ Hz, $-CH(CH_3)_2$). Anal. Calcd for $C_{78}H_{84}N_{12}O_{12}Pd_3 \cdot CH_2Cl_2$: C, 53.13; H, 4.85; N, 9.41. Found: C, 53.29; H, 5.28; N, 9.28.

3.3. X-ray structure determination

Suitable crystals for X-ray analysis of **3**, **9**, **13** and **21** were obtained by recrystallization from CH_2Cl_2/hexane. X-ray data of complexes **3**, **9**, **13** and **21** 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). The data of complexes **3** and **13** were collected at room temperature while the data of complex **9** and **21** were collected at 113 K using the ω-scan technique. Details of the data collection and refinement are summarized in Table 1. All calculations were carried out with the SHELX-97 programs [44]. All structures were solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods.

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Appendix A. Supporting material

CCDC 842514–842517 contains the supplementary crystallographic data for **3**, **9**, **13** and **21**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/deposit.

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