Journal of Organometallic Chemistry 861 (2018) 112–124

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Cyclopalladation of azobenzenes and their reactivity towards N-substituted imidazolidine-2-thiones and allied ligands: Synthesis, structures, spectroscopy and ESI-mass studies

Amanpreet K. Sandhu [a], Tarlok S. Lobana [a, *], Balkaran S. Sran [a], Geeta Hundal [a], Jerry P. Jasinski [b]

[a] Department of Chemistry, Guru Nanak Dev University, Amritsar, 143 005, India
[b] Department of Chemistry, Keene State College, Keene, NH 03435-2001, USA

ARTICLE INFO

Article history:
Received 30 December 2017
Received in revised form
15 February 2018
Accepted 21 February 2018
Available online 26 February 2018

Keywords:
Cyclopalladation
N-methyl-imidazolidine-2-thione
N-ethyl-imidazolidine-2-thione
N-(n-propyl)imidazolidine-2-thione
N-(n-butyl)imidazolidine-2-thione
N-phenyl-imidazolidine-2-thione
Thiazolidine-2-thione

ABSTRACT

Reactions of palladium(II) chloride with azobenzene (azbH), p-methoxyazobenzene (mazbH) and 4, 4′-diethoxyazobenzene (deazbH) in methanol yielded halogen bridged dinuclear precursors $[Pd_2(\kappa^2\text{:C,N-L})_2(\mu\text{-Cl})_2]$ (here L = azb$^-$, mazb$^-$ and deazb$^-$). These precursors were further reacted with a series of N, S- donor thio-ligands, namely, 1,3-imidazolidine-2-thiones (imdzSH-NR; R = H, Me, Et, Pr^n, Bu^n, Ph), N-methyl-imidazoline-2-thione (imzSH-NMe), 1,3-benzimidazoline-2-thione (bzimSH-NH) and 1, 3-thiazolidine-2-thione (tzdSH). Nineteen dinuclear organometallic compounds synthesized are listed as follows: (a) $[Pd_2(\kappa^2\text{:C, N-azb})_2(\mu\text{-N, S-imdzS-NR})_2]$ (R = H, **1**; Me, **2**; Et **3**; Pr^n **4**; Bu^n **5**; Ph **6**), (b) $[Pd_2(\kappa^2\text{:C, N-mazb})_2(N, S\text{-imdzS-NR})_2]$ (R = Me, **7**; Et, **8**; Pr^n **9**; Bu^n **10**), (c) $[Pd_2(\kappa^2\text{:C, N-deazb})_2(N, S\text{-imdzS-NR})_2]$ (R = Et, **11**; Pr^n **12**; Bu^n **13**; Ph **14**), (d) $[Pd_2(\kappa^2\text{:C, N-azb})_2(\mu\text{-N, S-L})_2]$ (L = bzimS-NH **15**; imzS-NMe **16**; tzdS **17**), and (e) $[Pd_2(\kappa^2\text{:C, N-deazb})_2(N, S\text{-L})_2]$ (L = bzimS-NH **18**; imzS-NMe **19**). All these compounds have been characterized with the help of analytical data, electron absorption, NMR and fluoresecence spectroscopy, ESI-mass spectrometry and single crystal X-ray crystallography. The loss of one C-H proton of an azobenzene and one N-H proton of a thio-ligand occurred per palladium metal center in dinuclear complexes synthesized, which have C, N-chelating azobenzenes and N, S-bridging heterocyclic thiolates.

1. Introduction

The chemistry of cyclopalladated compounds [1,2] of azobenzenes has invited interest of several researchers owing to their importance in organic synthesis [3–6], catalysis [7–17], photochemistry [18–22] and metallomesogen chemistry [23,24]. The cyclopalladated complexes containing N-donor ligands are important because of their potential applications as model compounds for photoactive units in different optical devices [1,25–27], as differential chromogenic and fluorescent chemosensors [17,28–32], and in catalysts [7–17]. Recently, it was observed that coordination chemistry of cyclopalladated azobenzenes bonded to N, S-donor atoms was poorly investigated [33,34], and in this context we reported a few complexes of cyclopalladated azobenzenes with the thio-ligands, namely, pyridine-2-thione and pyrimidine-2-thione with azobenzenes [34]. Keeping in view the importance of cyclopalladated compounds of azobenzenes, and our experience in palladium-heterocyclic-2-thione chemistry [35], in this paper we are reporting cyclopalladated azobenzenes (see Chart 1) and their coordination to imidazolidine-2-thiones and allied thio-ligands (see Chart 2).

Heterocyclic -2- thiones as shown in Chart 2 above possess chemically active groups such as, –N(H)–C(=S)– ↔ –N=C(–SH)–, and are expected to coordinate to the metal center as anions through N, S- donor atoms, after deprotonation of one –N-H group. This is expected on the pattern of pyridine-2-thione/pyrimidine-2-thione as reported earlier [35]. A major interest lies in the anticipation of formation of N,S-bridged dinuclear complexes which could be useful molecules in terms of higher flexibility of dinuclear moieties from catalysis point of view and enhanced fluorescent property due to binding of hard-soft (N,S) donors to metal centere which could of importance for optical materials [7–22]. Chart 1

* Corresponding author.
E-mail address: tarlokslobana@yahoo.co.in (T.S. Lobana).

https://doi.org/10.1016/j.jorganchem.2018.02.037
0022-328X/

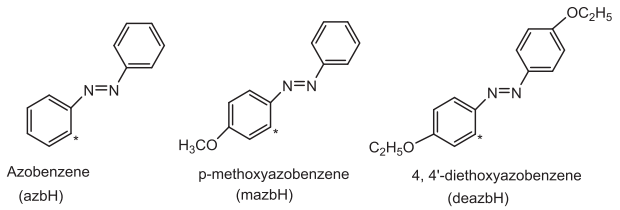

Chart 1. Azobenzene, p-methoxyazobenzene and 4, 4′-diethoxyazobenzene; *indicates metallation site.

shows various azobenzenes which will be first reacted with palladium(II) followed by their reactions with thio-ligands as listed in Chart 2. The substitution in rings of azobenzenes is arbitrarily incorporated.

2. Experimental

2.1. Materials and techniques

Palladium(II) chloride, 1, 3-imidazolidine-2-thione (imdzSH-NH), N-methyl-imidazoline-2-thione (imzSH-NMe), thiazolidine-2-thione (tzdSH), benzimidazoline-2-thione (bzimSH-NH), azobenzene (azbH), p-methoxy- azobenzene (mazbH) and 4, 4′-diethoxyazobenzene (deazbH) were procured from Sigma–Aldrich Ltd. The N-substituted imidazolidine-2-thiones were prepared as follows. For example, N-methyl-imidazolidine-2-thione prepared by the addition of carbon disulfide dropwise to a cooled solution of 1-methyl-ethylenediamine in ethanol and water. The reaction mixture was heated under reflux (110 °C) for 1 h and conc. HCl was added. The mixture was heated under reflux for a further period 10 h. The reaction mixture was cooled and stored in a freezer. The resulting precipitate were filtered and washed with cold acetone to give the desired ligand. N-ethyl-imidazolidine-2-thione, N-(n-propyl)-imidazolidine-2-thione, N-(n-butyl)-imidazolidine-2-thione (imzdSH-Bu^n) and N-phenylimidazolidine-2-thione (imzdSH-Ph) were prepared [36] (see Supporting Information). The precursor, namely, [$Pd_2(\kappa^2$: C, N-azb$)_2(\mu$-Cl$)_2$] was prepared by the addition of an azobenzene (azbH) to a suspension of $PdCl_2$ in methanol followed by overnight stirring [37]. Similarly, precursors [$Pd_2(\kappa^2$: C, N-mazb$)_2(\mu$-Cl$)_2$] and [$Pd_2(\kappa^2$: C, N-deazb$)_2(\mu$-Cl$)_2$] were prepared. The melting point was determined with a Gallenkamp electrically heated apparatus. Elemental analysis for C, H and N were carried out using a thermoelectron FLASHEA1112 analyzer. The IR spectra were recorded using KBr pellets on a Varian 660 FT IR Spectrometer in the 4000-200 cm^{-1} range. The ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker Avance 500 NMR spectrometer at 500 MHz using TMS as an internal reference. ESI-MS mass spectrometer was micro TOF-QII 10356 in positive mode. UV–visible spectra of complexes were recorded using UV-1800 Shimadzu spectrophotometer and fluorescence spectra of complexes were recorded with a Varian Cary Eclipse and Perkin Elmer Fluorescence spectrophotometers.

2.2. Synthesis of complexes

2.2.1. [$Pd_2(\kappa^2$:C, N-azb$)_2(\mu$-N, S-imdzS-NH$)_2$] ·2H_2O **1**

To an orange suspension of [$Pd_2(\kappa^2$:C, N-azb$)_2(\mu$- Cl$)_2$] (0.025 g, 0.040 mmol) in dichloro-methane (5 mL), imidazolidine-2-thione (0.009 g, 0.080 mmol) was added in presence of Et_3N base (0.5 mL). The color of the reaction mixture became dark red brown and it was stirred for 5–6 h. The solution was filtered, toluene (1 mL) was added and left to evaporate slowly. The dark red brown crystals of compound **1** were obtained along with the formation of $Et_3NH^+Cl^-$ after a period of 4–5 d. Yield 0.021 g, 68%, m.p. 190–192 °C. Anal. found: C, 44.33; H, 3.90; N, 13.75%; $C_{30}H_{32}N_8O_2Pd_2S_2$ requires: C, 44.29; H, 3.96; N, 13.77%. IR bands (KBr pellets, cm^{-1}): ν(N-H) + ν(O-H), 3418s, 3400s; ν(C-H), 3043 m, 2935 m, 2871 m; δ(O-H)+ δ(N-H),1671s; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1574w, 1534s, 1481w, 1426s, 1391s; other bands, 1302s, 1275 m, 1257w, 1237w, 1216 m; ν(C-S), 1188s; other bands, 1095w, 1072w, 1036 m, 1017 m, 916w, 770s, 714 m, 694s, 619w, 591w, 547w, 527w, 497w, 445w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 8.04 (bs, 2H, NH), 7.65 (m, 6H, H$^{9, 10, 14}$), 7.50 (d, 2H, *J*, 5 Hz, H^6), 7.45 (m, 6H, H$^{11, 13, 12}$), 7.10 (m, 4H, H$^{7, 8}$), 3.86 (m, 2H, C^{4}H$_2$), 3.70 (m, 2H, C^{4}H$_2$), 3.44 (m, 2H, C^{5}H$_2$), 3.32 (m, 2H, C^{5}H$_2$). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 459 (0.47 × 10^4), 341 (1.28 × 10^4), 242 (3.84 × 10^4). Fluorescence data (λ^{em}_{max} = 652 nm, λ^{ex}_{max} = 270 nm). Compounds **2**–**6**, **16** and **19** were prepared by the method used for compound **1**.

2.2.2. [$Pd_2(\kappa^2$:C, N-azb$)_2(\mu$-N, S-imdzS-NMe$)_2$] **2**

Compound **2** was prepared by following a method used for compound **1**. Yield 0.025 g, 81%, m.p. 190–192 °C. Anal. found: C, 47.65; H, 4.11; N, 13.85; $C_{32}H_{32}N_8Pd_2S_2$ requires: C, 47.71; H, 4.00; N, 13.91%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3041w, 2997w, 2933 m, 2832 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1597 m, 1579s, 1552 m, 1524s, 1501 m, 1483w, 1457 m, 1424 m, 1375s; other bands, 1326 m, 1300 m, 1254s, 1218 m, 1201 m, 1173w, 1157 m; ν(C-S), 1124 m; other bands, 1105s, 1082w, 1034s, 1024s, 956w, 876w, 831 m, 798w, 787w, 763s, 723w, 711w, 694 m, 672w, 649w, 633w, 530 m, 497w, 444w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.65 (m, 6H, H$^{9, 10, 14}$), 7.49 (d, 2H, *J*, 10 Hz, H^6), 7.42 (m, 6H, H$^{11, 12, 13}$), 7.09 (m, 4H, H^{7,8}), 3.56 (m, 4H, *J*, 9.34 Hz, C^{4}H$_2$), 3.32 (m, 2H, C^{5}H$_2$), 3.11 (m, 2H, C^{5}H$_2$), 1.58 (s, 6H, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 450 (1.09 × 10^4), 361 (1.80 × 10^4), 245 (3.96 × 10^4). Fluorescence data (λ^{em}_{max} = 651 nm, λ^{ex}_{max} = 270 nm).

2.2.3. [$Pd_2(\kappa^2$:C, N-azb$)_2(\mu$-N, S-imdzS-NEt$)_2$] **3**

Compound **3** was prepared by following a method used for compound **1**. Yield 0.026 g, 81%, m.p. 210–212 °C. Anal. found: C, 48.78; H, 4.60; N, 13.32; $C_{34}H_{38}N_8Pd_2S_2$ requires: C, 48.87; H, 4.58; N, 13.41%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3051w, 2965 m, 2927 m, 2854 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1578w, 1552w, 1523s, 1483 m, 1457 m, 1440 m, 1396s, 1376 m; other bands, 1355w, 1316 m, 1290 m, 1259s, 1234s, 1207 m, 1178w, 1153w; ν(C-S), 1124 m; other bands, 1108w, 1084 m, 1074 m, 1042w, 1022 m, 971w, 957w, 945w, 916w, 832w, 771s, 759 m, 706 m, 697s, 649 m, 622w,

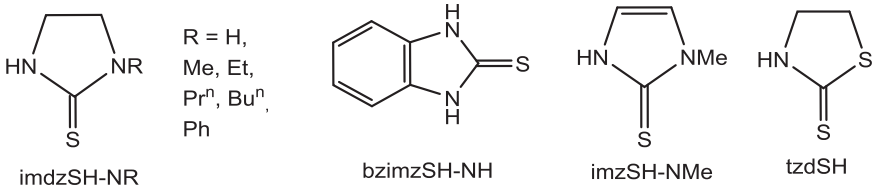

Chart 2. The thio-ligands used for synthesis.

592w, 548w, 525w, 499w, 439w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.66 (m, 6H, $H^{9, 10, 14}$), 7.47 (d, 2H, *J*, 5 Hz, H^6), 7.42 (m, 6H, $H^{11, 12, 13}$), 7.14 (t, 2H, *J*, 7.5 Hz, H^8), 7.07 (t, 2H, *J*, 7.5 Hz, H^7), 3.60 (m, 4H, C^4H_2), 3.27 (m, 8H, C^5H_2, N-CH_2), 0.95 (s, 6H, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 452 (0.558×10^4), 353 (1.24×10^4), 242 (3.99×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 270$ nm).

2.2.4. [$Pd_2(\kappa^2$:C, N-azb)$_2(\mu$-N, S-imdzS-NPr^n)$_2$] **4**

Compound **4** was prepared by following a method used for compound **1**. Yield 0.025 g, 76%, m.p. 180–182 °C. Anal. found: C, 50.24; H, 4.70; N, 13.20; $C_{36}H_{40}N_8Pd_2S_2$ requires: C, 50.18; H, 4.68; N, 13.00%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3050 m, 2956 m, 2922 m, 2854 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1577 m, 1523s, 1480 m, 1455 m, 1396s; other bands, 1298s, 1254 m, 1221s; ν(C-S), 1130 m; other bands, 1088w, 1072w, 1028w, 965w, 911w, 768s, 695w, 670w, 638w, 592w, 544w, 526w, 499w, 454w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.66 (m, 6H, $H^{9, 10, 14}$), 7.47 (d, 2H, *J*, 5 Hz, H^6), 7.42 (m, 6H, $H^{11, 12, 13}$), 7.13 (t, 2H, *J*, 5 Hz, H^8), 7.07 (t, 2H, *J*, 5 Hz, H^7), 3.59 (m, 4H, C^4H_2), 3.24 (m, 8H, C^5H_2, N-CH_2), 1.40 (m, 4H, -CH_2-), 0.85 (t, 6H, *J*, 7.5 Hz, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 451 (0.66×10^4), 348 (1.50×10^4), 252 (3.96×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 270$ nm).

2.2.5. [$Pd_2(\kappa^2$:C, N-azb)$_2(\mu$-N, S-imdzS-NBu^n)$_2$] **5**

Compound **5** was prepared by following a method used for compound **1**. Yield 0.027 g, 79%, m.p. 190–192 °C. Anal. found: C, 51.32; H, 4.90; N, 12.50; $C_{38}H_{44}N_8Pd_2S_2$ requires: C, 51.29; H, 4.98; N, 12.59%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3046 m, 2956s, 2926s, 2854s; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1575 m, 1526s, 1478 m, 1453 m, 1392s, 1376s; other bands, 1294s, 1254s, 1234 m, 1205s, 1179 m; ν(C-S), 1130s; other bands, 1113 m, 1088w, 1071w, 1025 m, 964w, 938w, 911w, 864w, 838w, 767s, 732w, 709w, 693 m, 654w, 590w, 546w, 525w, 497w, 443w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.66 (m, 6H, $H^{9, 10, 14}$), 7.47 (dd, 2H, *J*, 5 Hz, H^6), 7.41 (m, 6H, $H^{11, 12, 13}$), 7.13 (t, 2H, *J*, 7.5 Hz, H^8), 7.07 (t, 2H, *J*, 5 Hz, H^7), 3.58 (m, 4H, C^4H_2), 3.20 (m, 8H, C^5H_2, N-CH_2), 1.32 (m, 8H, -CH_2CH_2-), 0.94 (t, 6H, *J*, 7.5 Hz, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 448 (0.37×10^4), 344 (1.03×10^4), 244 (3.89×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 270$ nm).

2.2.6. [$Pd_2(\kappa^2$:C, N-azb)$_2(\mu$-N, S-imdzS-NPh)$_2$] **6**

Compound **6** was prepared by following a method used for compound **1**. Yield 0.028 g, 78%, m.p. 230–232 °C. Anal. found: C, 54.32; H, 3.82; N, 12.20; $C_{42}H_{36}N_8Pd_2S_2$ requires: C, 54.26; H, 3.90; N, 12.05%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3030 m, 2960w, 2925w, 2858 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1597s, 1577 m, 1550w, 1521s, 1496s, 1450 m, 1389 m, 1370s; other bands, 1337w, 1317 m, 1297s, 1255w, 1297s, 1255w, 1218s; ν(C-S), 1108w; other bands, 1075w, 1043 m, 1022 m, 956w, 916w, 832w, 764s, 715w, 707w, 692s, 665w, 635w, 589w, 550 m, 529w, 507w, 465w, 438w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.71 (m, 4H, $H^{9, 10}$), 7.66 (d, 2H, *J*, 5 Hz, H^{14}), 7.48 (m, 8H, $H^{6, 12}$, m-H(Ph)), 7.33 (t, 4H, *J*, 7.5 Hz, $H^{11, 13}$), 7.20 (d, 4H, *J*, 10 Hz, o-H (Ph)), 7.14 (t, 4H, *J*, 7.5 Hz, H^8, p-H (Ph)), 6.99 (t, 2H, *J*, 7.5 Hz, H^7), 3.82 (m, 8H, C^4H_2, C^5H_2). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 453 (0.34×10^4), 351 (0.85×10^4), 245 (3.03×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 270$ nm).

2.2.7. [$Pd_2(\kappa^2$:C, N-mazb)$_2(\mu$-N, S-imdzS-NMe)$_2$] **7**

To an orange suspension of [$Pd_2(\kappa^2$:C, N-mazb)$_2(\mu$-Cl)$_2$] (0.025 g, 0.040 mmol) in dichloromethane (5 mL), N-methylimidazolidine-2-thione (0.012 g, 0.080 mmol) was added in presence of Et_3N base (0.5 mL). The color of the reaction mixture became red brown and was stirred for 5–6 h. The solution was filtered and methanol (5 mL) was added and was left to evaporate slowly. The red brown crystals of compound 7 were obtained after a period of 4–5 d. Yield 0.023 g, 76%, m.p. 158–160 °C. Anal. found: C, 47.30; H, 4.22; N, 12.90%; $C_{34}H_{36}N_8O_2Pd_2S_2$ requires: C, 47.17; H, 4.19; N, 12.90%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 2930 m, 2832 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1598s, 1580s, 1552w, 1528s, 1482w, 1458w; other bands, 1376 m, 1298 m, 1257s, 1157 m; ν(C-S), 1106s; other bands, 1032s, 955w, 830 m, 799w, 761 m, 722w, 693w, 647w, 586w, 529 m, 496w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.63 (m, 6H, $H^{9, 10, 14}$), 7.44 (m, 6H, $H^{11, 12, 13}$), 7.07 (m, 2H, H^7), 6.90 (d, 2H, *J*, 5 Hz, H^6), 3.88 (d, 6H, -OCH_3), 2.88 (m, 8H, C^4H_2, C^5H_2), 1.58 (s, 6H, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 444 (1.51×10^4), 367 (2.10×10^4), 244 (3.99×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm). Compounds **8**–**15**, and **18** were prepared by the method used for compound **7**.

2.2.8. [$Pd_2(\kappa^2$:C, N-mazb)$_2(\mu$-N, S-imdzS-NEt)$_2$] **8**

Compound **8** was prepared by following a method used for compound **7**. Yield 0.025 g, 78%, m.p. 160–162 °C. Anal. found: C, 48.35; H, 4.50; N, 12.51%; $C_{36}H_{40}N_8O_2Pd_2S_2$ requires: C, 48.38; H, 4.51; N, 12.54%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3054w, 2965 m, 2928 m, 2859 m, 2834 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1579s, 1553s, 1523s, 1483w, 1458 m, 1426w, 1398w, 1375 m; other bands, 1326w, 1310 m, 1253s, 1235s, 1218s, 1202 m, 1173 m; ν(C-S), 1124s; other bands, 1073w, 1034s, 958w, 915w, 876w, 833w, 789w, 763 m, 724w, 694 m, 673w, 649w, 623w, 593w, 527 m, 500w, 443w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.62 (m, 6H, $H^{9, 10, 14}$), 7.48 (t, 2H, *J*, 5 Hz, H^{12}), 7.40 (m, 4H, $H^{11, 13}$), 7.07 (m, 2H, H^8), 6.83 (d, 2H, *J*, 10 Hz, H^6), 3.88 (d, 6H, -OCH_3), 3.42 (m, 12H, C^4H_2, C^5H_2, N-CH_2), 0.99 (m, 6H, CH_3).·UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 455 (0.94×10^4), 369 (1.48×10^4), 249 (3.85×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm).

2.2.9. [$Pd_2(\kappa^2$:C, N-mazb)$_2(\mu$-N, S-imdzS-N Pr^n)$_2$] **9**

Compound **9** was prepared by a method used for compound **7**. Yield 0.025 g, 79%, m.p. 210–212 °C. Anal. found: C, 49.54; H, 4.80; N, 12.20%; $C_{38}H_{44}N_8O_2Pd_2S_2$ requires: C, 49.51; H, 4.81; N, 12.16%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3000w, 2957 m, 2927 m, 2859 m, 2834 m; ν(C=C) + ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1597 m, 1574s, 1552 m, 1520s, 1500 m, 1479 m, 1456 m, 1428 m, 1398 m, 1371 m; other bands, 1300 m, 1250s, 1231s, 1220s, 1154 m; ν(C-S), 1108s; other bands, 1122s, 1024s, 967w, 910w, 859w, 829w, 814w, 798w, 762 m, 722w, 688w, 643w, 587w, 526 m, 496w, 466w, 440w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.63 (m, 6H, $H^{9, 10, 14}$), 7.43 (m, 6H, $H^{11, 12,13}$), 7.07 (m, 2H, H^8), 6.89 (d, 2H, *J*, 10 Hz, H^6), 3.89 (d, 6H, -OCH_3), 3.60 (m, 4H, C^4H_2), 3.22 (m, 8H, C^5H_2, N-CH_2), 1.43 (m, 4H, -CH_2-), 0.87 (m, 6H, CH_3). UV–vis. data, DCM, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 451 (1.27×10^4), 368 (1.87×10^4), 249 (4.00×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm).

2.2.10. [$Pd_2(\kappa^2$:C, N-mazb)$_2(\mu$-N, S-imdzS-NBu^n)$_2$] **10**

Compound **10** was prepared by a method used for compound 7. Yield 0.025 g, 75%, m.p. 110–112 °C. Anal. found: C, 50.52; H, 5.10; N, 11.78%; $C_{40}H_{48}N_8O_2Pd_2S_2$ requires: C, 50.58; H, 5.09; N, 11.80%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3105w, 3040w, 2999w, 2952 m, 2925 m, 2857 m, 2832 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1598 m, 1578s, 1552 m, 1523s, 1500 m, 1482w, 1456 m, 1426 m, 1377 m; other bands, 1325w, 1297 m, 1251s, 1235s, 1214s, 1175 m; other bands, 1158 m, 1121 m; ν(C-S), 1109 m; other bands, 1087w, 1031s, 939w, 910w, 886w, 865w, 830 m, 797w, 761s, 722w, 711w, 692 m, 671w, 646w, 634w, 588w, 526 m, 503w, 467w, 443w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.63 (m, 6H, $H^{9, 10, 14}$), 7.48 (m, 2H, H^{12}), 7.39 (m, 4H, $H^{11, 13}$), 7.07 (m, 2H, H^8), 6.96 (d, 2H, *J*, 5 Hz, H^6), 3.89 (d, 6H, -OCH_3), 3.60 (m, 4H, C^4H_2), 3.22 (m, 8H, C^5H_2, N-CH_2), 1.43 (m, 8H, -CH_2CH_2-), 0.87 (m, 6H, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L

$mol^{-1}cm^{-1}$: [10^{-4} M] 453 (0.68×10^4), 351 (1.45×10^4), 246 (3.98×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm).

*2.2.11. [$Pd_2(\kappa^2$:C, N-deazb)$_2(\mu$-N, S-imdzS-NEt)$_2$] **11***

Compound **11** was prepared by a method used for compound **7**. Yield 0.024 g, 78%, m.p. 160–162 °C. Anal. found: C, 49.80; H, 5.21; N, 11.15%; $C_{42}H_{52}N_8O_4Pd_2S_2$ requires: C, 49.95; H, 5.19; N, 11.10%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3057w, 2975s, 2926s, 2862s; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1600s, 1578s, 1551s, 1522s, 1500s, 1477 m, 1441 m, 1392s; other bands, 1373s, 1316s, 1246s, 1201s, 1158 m; ν(C-S), 1115s; other bands, 1085 m, 1069 m, 1043s, 960w, 925 m, 887w, 861w, 830 m, 798 m, 772w, 674w, 644 m, 624w, 590w, 553 m, 535 m, 497w, 440w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.55 (d, 4H, $H^{10,14}$), 7.40 (d, 2H, *J*, 7.5 Hz, H^9), 7.13 (d, 2H, *J*, 15 Hz, H^6), 6.83 (m, 4H, $H^{11,13}$), 6.55 (dd, 2H, *J*, 5 Hz, H^8), 4.09 (m, 8H, C^4H_2, C^5H_2), 3.49 (m, 12H, N-CH_2, -OCH_2-), 1.46 (t, 12H, *J*, 7.5 Hz, CH_3), 1.02 (t, 6H, *J*, 7.5 Hz, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 449 (1.90×10^4), 375 (2.03×10^4), 250 (3.92×10^4). Fluorescence data ($\lambda^{em}_{max} = 561$ nm, $\lambda^{ex}_{max} = 275$ nm).

*2.2.12. [$Pd_2(\kappa^2$:C, N-deazb)$_2(\mu$-N, S-imdzS-NPr^n)$_2$] **12***

Compound **12** was prepared by a method used for compound **7**. Yield 0.024 g, 76%, m.p. 190–192 °C. Anal. found: C, 50.95; H, 5.40; N, 10.82%; $C_{44}H_{56}N_8O_4Pd_2S_2$ requires: C, 50.92; H, 5.44; N, 10.80%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3044w, 2959 m, 2926 m, 2857 m, 2822 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1598s, 1576s, 1551s, 1524s, 1500s, 1475 m, 1454 m, 1439 m, 1390s; other bands, 1368s, 1321s, 1296 m, 1244s, 1217s, 1202s, 1159 m; other bands, 1126s; ν(C-S), 1114s; other bands, 1086 m, 1045s, 967w, 921 m, 879w, 872w, 835 m, 825 m, 796 m, 772w, 759w, 672w, 641w, 588 m, 557 m, 534 m, 490w, 436w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.57 (d, 4H, *J*, 10 Hz, $H^{10,14}$), 7.40 (d, 2H, *J*, 10 Hz, H^9), 7.14 (d, 2H, *J*, 5 Hz, H^6), 6.84 (d, 4H, *J*, 10 Hz, $H^{11,13}$), 6.55 (dd, 2H, *J*, 5 Hz, H^8), 4.08 (m, 8H, C^4H_2, C^5H_2), 3.64 (m, 4H, N-CH_2), 3.29 (m, 4H, -CH_2-), 1.58 (s, 8H, -OCH_2-), 1.46 (m, 12H, CH_3), 0.89 (t, 6H, *J*, 7.5 Hz, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 448 (2.34×10^4), 375 (2.46×10^4), 257 (3.91×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm).

*2.2.13. [$Pd_2(\kappa^2$:C, N-deazb)$_2(\mu$-N, S-imdzS-N Bu^n)$_2$] **13***

Compound **13** was prepared by a method used for compound **7**. Yield 0.025 g, 78%, m.p. 158–160 °C. Anal. found: C, 51.75; H, 5.60; N, 10.48%; $C_{46}H_{60}N_8O_4Pd_2S_2$ requires: C, 51.83; H, 5.67; N, 10.51%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3050w, 2974 m, 2956 m, 2925 m, 2865 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1600s, 1578s, 1552s, 1524s, 1500s, 1476 m, 1455 m, 1439 m, 1392 m; other bands, 1369 m, 1314 m, 1298 m, 1243s, 1230s, 1214s, 1200s, 1156 m; other bands, 1128 m; ν(C-S), 1111 m; other bands, 1088w, 1045s, 924 m, 890w, 860w, 834 m, 824 m, 797 m, 771w, 729w, 671w, 639w, 588w, 556w, 548 m, 534 m, 497w, 440w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.56 (d, 4H, *J*, 10 Hz, $H^{10,14}$), 7.40 (d, 2H, *J*, 5 Hz, H^9), 7.14 (d, 2H, *J*, 5 Hz, H^6), 6.84 (d, 4H, *J*, 5 Hz, $H^{11,13}$), 6.55 (d, 2H, *J*, 5 Hz, H^8), 4.09 (m, 8H, C^4H_2, C^5H_2), 3.59 (m, 4H, N-CH_2), 3.30 (m, 8H, -CH_2CH_2-), 1.30 (s, 8H, -OCH_2-), 1.47 (t, 12H, *J*, 6.25 Hz, CH_3), 0.95 (t, 6H, *J*, 7.5 Hz, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 449 (1.62×10^4), 375 (1.72×10^4), 248 (3.96×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm).

*2.2.14. [$Pd_2(\kappa^2$:C, N-deazb)$_2(\mu$-N, S-imdzS-NPh)$_2$] **14***

Compound **14** was prepared by a method used for compound **7**. Yield 0.026 g, 80%, m.p. 210–212 °C. Anal. found: C, 54.29; H, 4.70; N, 10.15%; $C_{50}H_{52}N_8O_4Pd_2S_2$ requires: C, 54.30; H, 4.74; N, 10.13%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3047w, 2975w, 2928w, 2853w; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1597 m, 1577s, 1553 m, 1476 m, 1444 m; other bands, 1365 m, 1317 m, 1297 m, 1248s, 1231s, 1202s, 1157 m; ν(C-S), 1109 m; other bands, 1045s, 958w, 923w, 858w, 824 m, 756w, 690w, 592w, 544 m. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.60 (d, 4H, *J*, 10 Hz, $H^{10,14}$), 7.41 (d, 2H, *J*, 10 Hz, H^9), 7.31 (m, 8H, o-H, m-H(Ph)), 7.14 (m, 4H, H^6, p-H(Ph)), 6.88 (d, 4H, *J*, 10 Hz, $H^{11,13}$), 6.56 (d, 2H, *J*, 5 Hz, H^8), 4.09 (m, 8H, C^4H_2, C^5H_2), 3.85 (m, 8H, -OCH_2-), 1.48 (m, 12H, *J*, 6.25 Hz, CH_3). UV–vis. data, DMSO, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 444 (1.79×10^4), 375 (1.93×10^4), 257 (4.00×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 275$ nm).

*2.2.15. [$Pd_2(\kappa^2$:C, N-azb)$_2(\mu$-N, S- bzimS-NH)$_2$] **15***

Compound **15** was prepared by a method used for compound **7**. Yield 0.027 g, 81%, m.p. 230–232 °C. Anal. found: C, 52.35; H, 3.42; N, 12.60%; $C_{38}H_{28}N_8Pd_2S_2$ requires: C, 52.24; H, 3.23; N, 12.83%. IR bands (KBr pellets, cm^{-1}): ν(N-H), 3417s; ν(C-H), 3047 m, 2966 m; ν(C=C) + ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1575 m, 1552w, 1483 m, 1429s, 1417s, 1387s; other bands, 1357 m, 1316w, 1295s, 1277s, 1199 m, 1160w; ν(C-S), 1107w; other bands, 1021 m, 919w, 805w, 742s, 767s, 711s, 690s, 607w, 591w, 550w, 525w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 8.27 (s, 2H, NH), 7.91 (d, 2H, *J*, 10 Hz, H^{11}), 7.77 (d, 2H, *J*, 5 Hz, H^{12}), 7.55 (d, 2H, *J*, 10 Hz, H^{16}), 7.29 (m, 4H, $H^{4,7}$), 7.20 (m, 10 H, $H^{5,6,13,14,15}$), 7.03 (t, 2H, *J*, 7.5 Hz, H^{10}), 6.98 (t, 2H, *J*, 10 Hz, H^9), 6.90 (d, 2H, *J*, 10 Hz, H^8). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 454 (0.05×10^4), 364 (1.26×10^4), 308 (2.87×10^4), 243 (3.98×10^4). Fluorescence data ($\lambda^{em}_{max} = 645$ nm, $\lambda^{ex}_{max} = 270$ nm).

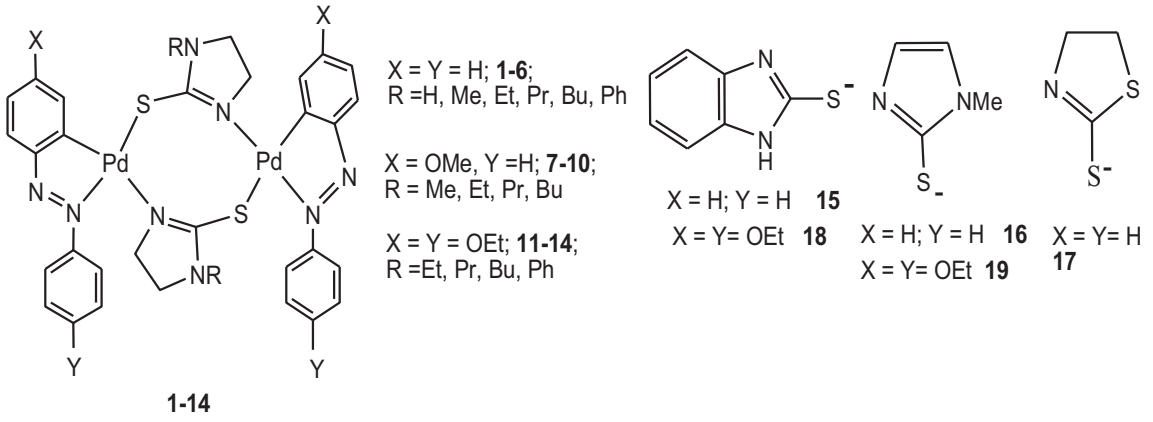

Chart 3. A chem draw view of structures of complexes.

Table 1
Crystallographic data for complexes **1**–**5**, **7**–**9**, **11**–**13** and **15**–**19**.

CCDC	1	2	3	4
	1586210	1586208	1586199	1586205
Empirical formula	$C_{30}H_{32}N_8O_2Pd_2S_2$	$C_{32}H_{32}N_8Pd_2S_2$	$C_{34}H_{38}N_8Pd_2S_2$	$C_{36}H_{40}N_8Pd_2S_2$
M	813.56	805.60	835.66	861.70
T/K	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/n	C 2/c	C 2/c	C 2/c
a(Å)	11.7896(5)	23.9164(5)	24.340(4)	17.893(3)
b(Å)	17.8469(8)	10.8069(2)	10.9758(18)	16.029(3)
c(Å)	15.2663(6)	14.0908(3)	14.054(2)	14.666(2)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.715(2)	117.8840(10)	115.893(7)	119.570(4)
γ (°)	90.00	90.00	90.00	90.00
V(Å^3)	3211.9(2)	3219.10(12)	3377.6(9)	3658.5(11)
Z	4	4	4	4
D_{calcd} (g.cm^{-3})	1.682	1.662	1.643	1.564
μ (mm^{-1})	1.292	1.283	1.226	1.135
F(000)	1632	1616	1688	1744
Reflections collected	76730	15835	14527	17873
Unique reflections	9768 (R_{int}, 0.0458)	4147 (R_{int}, 0.0201)	4507 (R_{int}, 0.0689)	4490 (R_{int}, 0.0281)
Data/restraints/parameters	9768/0/407	4147/0/200	4507/0/208	4490/0/217
Reflens with [I > 2σ(I)]	7429	3645	3008	3939
R indices [I > 2σ(I)]				
R_1	0.0429	0.0215	0.0832	0.0282
wR_2	0.0871	0.0551	0.1928	0.0746
R indices (all data)				
R_1	0.0679	0.0263	0.1250	0.0333
wR_2	0.1060	0.0582	0.2319	0.0804
Largest diff. Peak and hole	0.902 and 0.709 e.Å^{-3}	0.228 and −0.640 e.Å^{-3}	2.042 and −1.934 e.Å^{-3}	0.883 and −0.868 e.Å^{-3}
	5	**7**	**8**	**9**
CCDC	1586206	1586204	1586207	1586203
Empirical formula	$C_{38}H_4N_8Pd_2S_2$	$C_{34}H_{36}N_8O_2Pd_2S_2$	$C_{36}H_{40}N_8O_2Pd_2S_2$	$C_{38}H_{44}N_8O_2Pd_2S_2$
M	889.75	865.65	893.70	921.75
T/K	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/c	P 2_1/c	C 2/c	C 2/c
a(Å)	17.8636(8)	21.6585(12)	18.2527(11)	19.1230(13)
b(Å)	16.4959(8)	12.3518(7)	16.3634(10)	16.1995(11)
c(Å)	14.5533(6)	13.9936(7)	14.2858(7)	14.4318(7)
α (°)	90.00	90.00	90.00	90.00
β (°)	119.4870(10)	97.671(2)	116.449(2)	116.148(3)
γ (°)	90.00	90.00	90.00	90.00
V(Å^3)	3733.0(3)	3710.1(3)	3820.2(4)	4013.2(4)
Z	4	4	4	4
D_{calcd} (g.cm^{-3})	1.583	1.550	1.554	1.526
μ (mm^{-1})	1.115	1.123	1.094	1.044
F(000)	1808	1744	1808	1872
Reflections collected	13101	27613	17014	13073
Unique reflections	3554 (R_{int}, 0.0289)	7446 (R_{int}, 0.0408)	4648 (R_{int}, 0.0233)	3658 (R_{int}, 0.0376)
Data/restraints/parameters	3554/0/227	7446/0/437	4648/1/228	3658/1/237
Reflens with [I > 2σ(I)]	3072	5092	3522	2231
R indices [I > 2σ(I)]				
R_1	0.0354	0.0622	0.0414	0.0953
wR_2	0.0857	0.1651	0.1052	0.2232
R indices (all data)				
R1	0.0431	0.0947	0.0625	0.1482
wR_2	0.0941	0.1889	0.1212	0.2630
Largest diff. Peak and hole	0.982 and −0.859 e.Å^{-3}	1.963 and −0.710 e.Å^{-3}	1.632 and −0.872 e.Å^{-3}	3.508 and −1.831 e.Å^{-3}
	11	**12**	**13**	**15**
CCDC	1559369	1559372	1559370	1586196
Empirical formula	$C_{42}H_{52}N_8\ O_4Pd_2\ S_2$	$C_{87}H_{109}\ N_{16}O_8Pd_4\ S_4$	$C_{46}H_{60}N_8O_4Pd_2S_2$	$C_{38}H_{28}N_8Pd_2S_2$
M	1009.83	2060.74	1065.94	873.62
T/K	173(2)	173(2)	173(2)	296(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2_1/n	P −1	P 2_1/n	P 2/c
a(Å)	15.3507(2)	14.9498(5)	15.0869(7)	26.2740(18)
b(Å)	14.88128(17)	15.3528(5)	17.4305(6)	14.3731(9)

Table 1 (*continued*)

	1	2	3	4
CCDC	1586210	1586208	1586199	1586205
c(Å)	37.8108(5)	20.6048(7)	18.9673(8)	15.1744(11)
α (°)	90	80.278(3)	90	90.00
β (°)	96.0707(11)	79.442(3)	106.299(5)	92.762(3)
γ (°)	90	89.394(3)	90	90.00
V(Å^3)	8589.00(19)	4581.4(3)	4787.4(4)	5723.8(7)
Z	8	2	4	6
D_{calcd} (g.cm^{-3})	1.562	1.494	1.479	1.521
μ (mm^{-1})	0.986	7.586	0.889	1.090
F(000)	4128	2110	2192	2616
Reflections collected	120420	36159	64491	55502
Unique reflections	29526 (R_{int}, 0.0395)	17305 (R_{int}, 0.0436)	16482 (R_{int}, 0.0447)	13936 (R_{int}, 0.0393)
Data/restraints/parameters	29526/0/1057	17305/0/1084	16482/90/588	13936/3/685
Reflens.with [I > 2σ(I)]	23880	14565	12569	9116
R indices [I > 2σ(I)]				
R_1	0.0408	0.0414	0.0409	0.0546
wR_2	0.0760	0.1057	0.0885	0.1395
R indices (all data)				
R_1	0.0554	0.0514	0.0679	0.0998
wR_2	0.0816	0.1136	0.1074	0.1688
Largest diff. Peak and hole	0.969 and −1.493 e.Å^{-3}	1.990 and −1.325 e.Å^{-3}	1.026 and −0.633 e.Å^{-3}	1.919 and −0.775 e.Å^{-3}
	16	**17**	**18**	**19**
CCDC	1586197	1586200	1559371	1586209
Empirical formula	$C_{32}H_{28}N_8Pd_2S_2$	$C_{30}H_{26}N_6Pd_2S_4$	$C_{46}H_{42}N_8O_4Pd_2S_2$	$C_{40}H_{44}N_8O_4Pd_2S_2$
M	801.56	811.65	1047.80	977.77
T/K	296(2)	296(2)	173(2)	100(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	C 2/c	P b c a	P −1	P −1
a(Å)	22.8542(15)	18.2830(5)	11.8002(5)	14.699(4)
b(Å)	10.8604(7)	15.3470(4)	13.4399(6)	15.097(5)
c(Å)	14.0090(10)	22.6650(6)	16.1828(4)	21.085(6)
α (°)	90.00	90.00	110.070(3)	96.374(3)
β (°)	116.401(3)	90.00	94.720(3)	103.979(5)
γ (°)	90.00	90.00	97.643(4)	113.931(2)
V(Å^3)	3114.5(4)	6359.6(3)	2366.56(16)	4033(2)
Z	6	8	2	4
D_{calcd} (g.cm^{-3})	1.521	1.695	1.470	1.610
μ (mm^{-1})	1.090	1.425	0.898	1.047
F(000)	2616	3232	1060	1984
Reflections collected	55502	52581	29746	24788
Unique reflections	13936 (R_{int}, 0.0393)	12472 (R_{int}, 0.0372)	15528 (R_{int}, 0.0394)	13357 (R_{int}, 0.0753)
Data/restraints/parameters	13936/3/685	12472/0/379	15528/0/563	13357/6/1002
Reflens.with [I > 2σ(I)]	9116	7816	11590	8877
R indices [I > 2σ(I)]				
R_1	0.0546	0.0381	0.0439	0.0559
wR_2	0.1395	0.0888	0.1038	0.1116
R indices (all data)				
R1	0.0998	0.0837	0.0636	0.0940
wR_2	0.1688	0.1211	0.1174	0.1261
Largest diff. Peak and hole	1.919 and −0.775 e.Å^{-3}	1.020 and - 0.540 e.Å^{-3}	1.372 and −1.602 e.Å^{-3}	0.628 and −0.759 e.Å^{-3}

*2.2.16. [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S- imzS-NMe)$_2$] **16***

Compound **16** was prepared by following a method used for compound **1**. Yield 0.024 g, 77%, m.p. 200–202 °C. Anal. found: C, 48.20; H, 3.60; N, 13.85%; $C_{32}H_{28}N_8Pd_2S_2$ requires: C, 47.95; H, 3.52; N, 13.98%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3154, 3048 m, 2968 m, 2940 m; ν(C-H, CH_3), 2854 m, 2808 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1591w, 1576 m, 1552w, 1523s, 1480s, 1445s, 1413 m, 1396s, 1375s; other bands, 1313 m, 1296s, 1282 m, 1260 m, 1233 m, 1201 m, 1178w, 1165w, 1145s; ν(C-S), 1104s; other bands, 1076s, 1040w, 1017 m, 1002w, 968w, 953w, 938w, 919w, 862w, 826w, 773s, 758s, 721s, 697s, 686s, 651 m, 591 m, 546 m, 525w, 521w, 509w, 496w, 440w, 424w, 412w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.62 (m, 6H, H$^{9, 10, 14}$), 7.43 (m, 6H, H$^{11, 12, 13}$), 7.13 (m, 4H, H$^{7, 8}$), 6.69 (d, 2H, *J*, 5 Hz, H^6), 3.36 (s, 2H, C^{4}H), 2.83 (s, 2H, C^{5}H), 1.58 (s, 6H, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 452 (0.68 × 10^4), 333 (1.79 × 10^4), 245 (3.98 × 10^4). Fluorescence data (λ^{em}_{max} = 652 nm, λ^{ex}_{max} = 270 nm).

*2.2.17. [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S- tzdS)$_2$] **17***

To an orange suspension of [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ- Cl)$_2$] (0.025 g, 0.040 mmol) in dichloromethane (5 mL), thiazolidine-2-thione (0.010 g, 0.080 mmol) was added in presence of Et_3N base (0.5 mL). The color of the reaction mixture became dark red brown and contents were stirred for 5–6 h. The solution was filtered and toluene (1 mL) was added and left to evaporate slowly. The dark red brown crystalline compound was obtained along with the formation of $Et_3NH^+Cl^-$ after a period of 4–5 d. Crystalline compound formed was recrystallized from dichloromethane and methanol.

The dark red brown crystals of compound **17** were obtained after a period of 4–5 days. Yield 0.022 g, 71%, m.p. 192–194 °C. Anal. found: C, 44.20; H, 3.15; N, 10.42%; $C_{30}H_{26}N_6Pd_2S_4$ requires: C, 44.39; H, 3.23; N, 10.35%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3048 m, 2977 m, 2940 m, 2849 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1589w, 1574 m, 1551w, 1524s, 1481w, 1456w, 1445w, 1432w, 1392 m; other bands, 1315w, 1300 m, 1253w, 1236 m, 1194 m, 1154w; ν(C-S), 1104s; other bands, 1109w, 1073w, 1036s, 973s, 940 m, 913 m, 860w, 836w, 765s, 711 m, 691s, 589w, 547w, 520w, 437w, 417w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.61 (d, 2H, *J*, 10 Hz, H^9), 7. 56 (d, 4H, *J*, 5 Hz, $H^{10, 14}$), 7.48 (m, 8H, $H^{6, 11, 12, 13}$), 7.13 (m, 4H, $H^{7, 8}$), 4.27 (m, 2H, C^4H_2), 4.07 (m, 2H, C^4H_2), 3.28 (m, 4H, C^5H_2). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 451 (0.26×10^4), 387 (0.41×10^4), 329 (1.29×10^4), 248 (2.45×10^4). Fluorescence data ($\lambda^{em}_{max} = 652$ nm, $\lambda^{ex}_{max} = 270$ nm).

2.2.18. [Pd_2(κ^2:C, N-deazb)$_2$(μ-N, S- bzimS-NH)$_2$] ***18***

Compound **18** was prepared by following a method used for compound **7**. Yield 0.024 g, 76%, m.p. 222–224 °C. Anal. found: C, 52.60; H, 4.25; N, 10.62%; $C_{46}H_{44}N_8O_4Pd_2S_2$ requires: C, 52.63 H, 4.22; N, 10.67%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 2974 m, 2927 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1579s, 1553s, 1500 m, 1454 m, 1391 m; other bands, 1361 m, 1322 m, 1257s, 1222 m, 1200 m, 1160 m; other bands, 1131 m; ν(C-S), 1112 m; other bands, 1044 m, 923w, 876w, 839 m, 802 m, 731w, 699w, 591w, 560 m, 536, 432s. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 8.32 (s, 2H, NH), 7.95 (d, 2H, *J*, 10 Hz, H^{11}), 7.47 (d, 4H, *J*, 10 Hz, $H^{12,16}$), 7.28 (s, 4H, $H^{4,7}$), 7.17 (t, 4H, *J*, 7.5 Hz, $H^{5,6}$), 7.05 (m, 4H, $H^{13,15}$), 6.67 (dd, 2H, *J*, 10 Hz, H^{10}), 6.42 (d, 2H, *J*, 10 Hz, H^8), 4.20 (m, 4H, -OCH_2-), 3.91 (m, 4H, -OCH_2-), 1.54 (t, 6H, *J*, 7.5 Hz, CH_3), 1.36 (t, 6H, *J*, 7.5 Hz, CH_3). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L $mol^{-1}cm^{-1}$: [10^{-4} M] 454 (1.05×10^4), 375

Table 2
Important bond lengths (Å) and angles (°) of complexes **1–5, 7–9, 11–13** and **15–19**.

Complex No.	Pd-C[a]	Pd-N[a]	Pd-N[b]	Pd-S[b]	Pd-Pd	C-S
1	1.986(4), 1.978(4)	2.070(3), 2.065(3)	2.106(3), 2.111(3)	2.3055(10), 2.3063(11)	2.9851(4)	1.734(4), 1.733(4)
2	1.9838(19)	2.0676(15)	2.1140(14)	2.3082(5)	2.9408(3)	1.7287(19)
3	1.985(8)	2.062(6)	2.085(7)	2.312(2)	2.9355(13)	1.737(9)
4	1.979(2)	2.0601(18)	2.0909(19)	2.3097(7)	2.9659(5)	1.742(3)
5	1.986(4)	2.067(3)	2.110(3)	2.2997(9)	2.9428(5)	1.735(4)
7	1.958(9), 1.975(7)	2.083(6), 2.055(7)	2.103(7), 2.112(6)	2.306(2), 2.276(2)	2.9524(7)	1.720(9), 1.734(8)
8	1.989(4)	2.064(3)	2.096(3)	2.3109(11), 2.3110(11)	2.9563(6)	1.735(5)
9	2.019(15)	2.064(12)	2.074(13)	2.299(4)	2.9596(16)	1.759(15)
11	1.975(2), 1.979(2)	2.0745(17), 2.0988(18)	2.1086(18), 2.1061(18)	2.3108(5), 2.3043(5)	2.9229(2)	1.733(2), 1.728(2)
12	1.982(3), 1.977(3)	2.074(3), 2.094(3)	2.118(3), 2.105(3)	2.3105(8), 2.3029(8)	2.9128(3)	1.729(3), 1.731(3)
13	1.978(3), 1.978(3)	2.097(2), 2.079(2)	2.105(2), 2.102(2)	2.3061(7), 2.3021(7)	2.9444(3)	1.736(3), 1.739(3)
15	1.979(6), 1.985(6)	2.061(5)	2.108(5)	2.3088(19)	3.0019(9)	1.721(6)
16	1.9815(17)	2.0662(14)	2.1197(14)	2.3075(5)	2.9672(3)	1.7270(18)
17	1.972(3), 1.979(3)	2.068(3), 2.070(3)	2.112(3), 2.118(3)	2.3052(8), 2.3130(9)	2.9656(3)	1.719(3), 1.757(3)
18	1.971(2), 1.984(3)	2.068(2), 2.082(2)	2.139(2), 2.150(2)	2.3019(7), 2.2956(8)	3.0633(3)	1.729(2), 1.731(2)
19	1.977(6), 1.996(7)	2.085(5), 2.059(6)	2.113(5), 2.119(5)	2.298(2), 2.294(2)	4.702	1.737(7), 1.739(7)
	N[a]-Pd-C	**N[a]-Pd-S**	**N[b]-Pd-C**	**N[b]-Pd-S**		
1	78.73(14), 78.61(15)	171.65(9), 171.17(9)	173.52(14), 174.10(15)	90.61(9), 90.83(9)		
2	78.45(7)	170.85(5)	174.02(7)	92.21(4)		
3	79.5(3)	172.2(2)	174.3(3)	91.72(18)		
4	78.88(8)	172.55(6)	172.29(9)	91.54(6)		
5	78.77(13)	170.66(9)	171.37(13)	93.48(8)		
7	78.5(3), 79.1(3)	170.1(2), 171.1(2)	176.8(3), 175.9(3)	90.76(19), 90.4(2)		
8	79.39(16)	172.10(10)	173.73(16)	91.21(10)		
9	79.6(6)	171.9(4)	174.6(5)	91.6(3)		
11	78.95(8), 78.81(8)	172.34(5), 168.09(5)	172.89(8), 177.20(8)	90.78(5), 91.44(5)		
12	78.97(12), 78.95(12)	171.26(8), 169.15(7)	174.37(12), 176.93(12)	90.49(7), 91.67(8)		
13	79.35(10), 78.56(10)	170.05(7), 171.23(6)	179.40(10), 177.44(10)	88.96(7), 89.52(6)		
15	78.6(3)	171.67(16)	175.4(2)	89.64(14)		
16	78.57(7)	171.69(4)	172.34(6)	92.76(4)		
17	78.86(13), 78.47(13)	170.83(8), 171.76(8)	176.34(12), 175.53(13)	90.65(8), 90.45(8)		
18	79.05(10), 78.82(11)	169.49(6), 167.79(7)	176.80(9), 178.05(11)	88.84(6), 89.03(7)		
19	79.6(2), 79.2(3)	168.00(15), 167.87(17)	171.2(2), 170.0(2)	93.44(15), 94.93(16)		

[a] Azobenzenes.
[b] Thio-ligands.

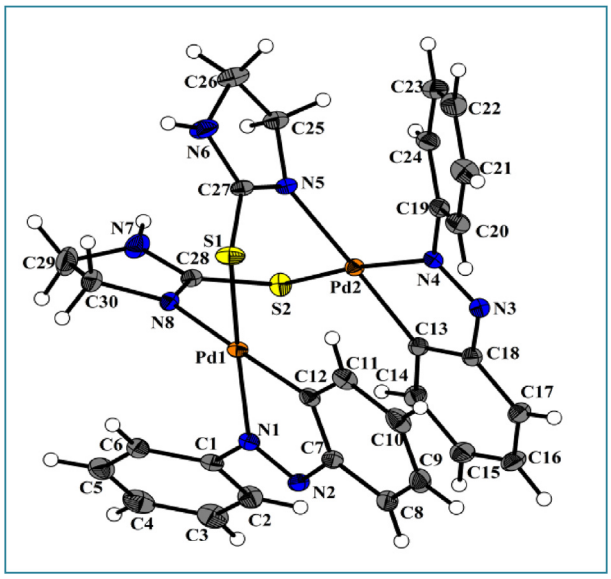

Fig. 1. Molecular structure of $[Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S-imdzS-NH)$_2$] **1**·2H$_2$O (**1**) (Disordered oxygens O1W and O2W of lattice water are omitted for clarity).

(1.09 × 10^4), 302 (1.76 × 10^4), 251 (2.36 × 10^4). Fluorescence data (λ^{em}_{max} = 653 nm, λ^{ex}_{max} = 275 nm.

2.2.19. *[Pd$_2$(κ^2:C, N-deazb)$_2$(μ-N, S- imzS-NMe)$_2$]* ***19***

Compound **19** was prepared by a method used for compound **1**. Yield 0.022 g, 75%, m.p. 218–220 °C. Anal. found: C, 49.10; H, 4.51; N, 11.38%; $C_{40}H_{44}N_8O_4Pd_2S_2$ requires: C,49.13; H, 4.54; N, 11.46%. IR bands (KBr pellets, cm^{-1}): ν(C-H), 3177 m, 3060 m, 2976 m, 2925 m; ν(N=N) + ν(C-N) + ν(C-C) + δ(C-H), 1576s, 1552 m, 1500 m, 1432 m, 1390 m; other bands, 1363 m, 1320 m, 1246s, 1201s, 1159 m; ν(C-S), 1112 m; other bands, 1044s, 926w, 835 m, 799w, 793 m, 706w, 590w, 535 m, 434w. ^{1}H NMR (δ, ppm, J, Hz, $CDCl_3$): 7.45 (d, 2H, *J*, 10 Hz, H^9), 7.33 (d, 4H, *J*, 10 Hz, H^{10,14}), 7.14 (d,

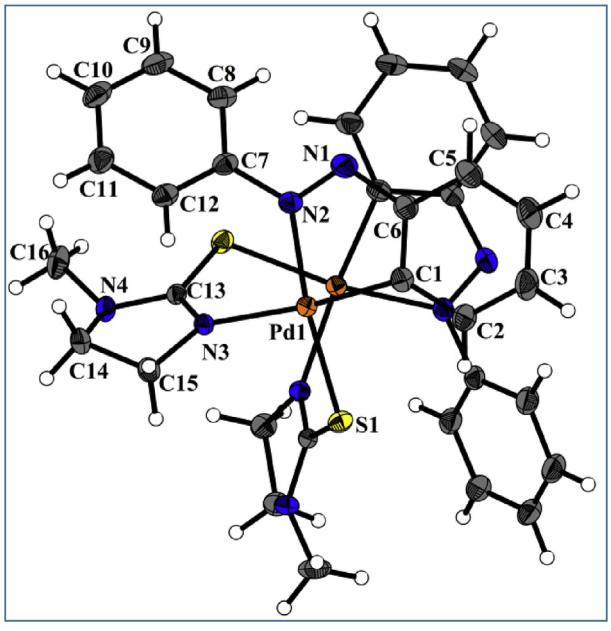

Fig. 2. Molecular structure of $[Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S-imdzS-NMe)$_2$] **2** (Molecular structures of **3**–**5**, see Supporting Information).

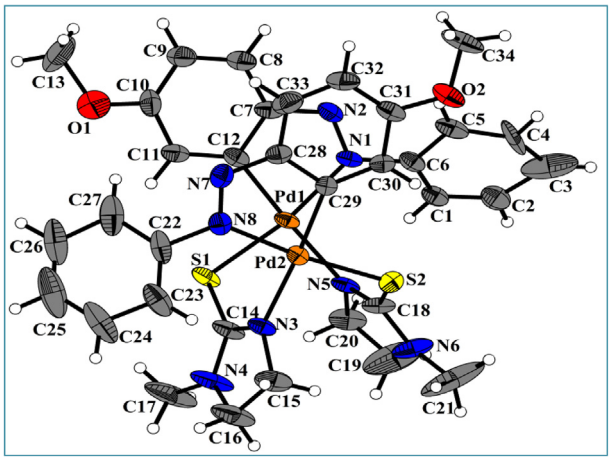

Fig. 3. Molecular structure of $[Pd_2(\kappa^2$:C, N-mazb)$_2$(μ-N, S-imdzS-NMe)$_2$] **7** (Molecular structure of **8**–**9**, see Supporting Information).

2H, H^6), 6.66 (d, 4H, *J*, 10 Hz, H^{11,13}), 6.43 (d, 2H, *J*, 5 Hz, H^8), 4.09 (m, 12H, C^{4}H$_2$, C^{5}H$_2$, -OCH$_2$-), 1.58 (s, 12H, CH$_3$), 1.49 (t, 3H, *J*, 7.5 Hz, CH$_3$), 1.42 (t, 3H, *J*, 7.5 Hz, CH$_3$). UV–vis. data, CH_2Cl_2, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-4} M] 451 (1.39 × 10^4), 374 (1.51 × 10^4), 258 (2.52 × 10^4). Fluorescence data (λ^{em}_{max} = 652 nm, λ^{ex}_{max} = 275 nm).

2.3. X-ray crystallography

The X-ray data of the complexes (**1**–**5, 7**–**9, 15**–**17, 19**) were collected on a Bruker's Apex-II CCD diffractometer using Mo Kα (λ = 0.71069 Å) at room temperature except for the complex **19**, which is done at 100 K. The data were processed by SAINT and Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. The structures were solved by direct methods, using SIR-92 [38] and refined by full-matrix least squares refinement methods based on F^2, using SHELX-2015 [39]. The hydrogen atoms of water molecules were located from the difference Fourier synthesis and were refined isotropically with distance of 0.82(0.02) Å with U_{iso} values 1.2 times that of their carrier oxygen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of methane, methylene and phenylene carbon atoms and 1.5 times that of methyl carbon atoms The hydrogens of the disordered water molecules in**1**, could not be located. Complex 7and 15 showed disorder in some aromatic carbons and the C of the terminal methyl group, which could not be resolved. These atoms were refined with constraints.Some structures showed residual peaks (~1–2 eÅ^3) very close to the Pd(II) ion which may be due to the series termination error because of the heavy metal. All calculations were performed using Wingx package [40].

The data for complexes **11**–**13** and **18** were collected using Agilent, Eos, Gemini and Rigaku Oxford diffraction diffractometer equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å, for **11, 13** and **18**, or Cu- Kα radiation; λ = 1.54184 Å, for **12**). The unit cell dimensions and intensity data were measured at 173(2) (**11**–**13** and **18**). The data were processed with *CrysAlisPro* (data collection, cell refinement), *CrysAlisRED* (data reduction). The structure was solved by direct methods using the program SHELXS-97, SIR-92 or *SHELXL-2015* (**13**, **19**) and *SUPERFLIP* and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 or *SHELXL-2012,* SHELXL-2014 and *SHELXL-2015* [39,41–46].

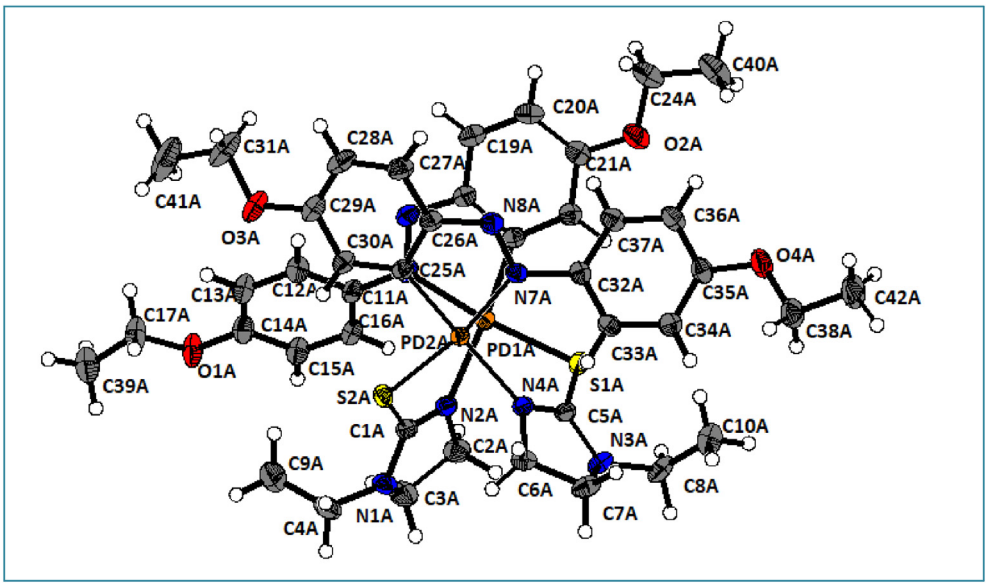

Fig. 4. Molecular structure of $[Pd_2(\kappa^2\text{:C, N-deazb})_2(\mu\text{-N, S-imdzS-NEt})_2]$ **11** {Molecular structures, **12** and **13** see SI}.

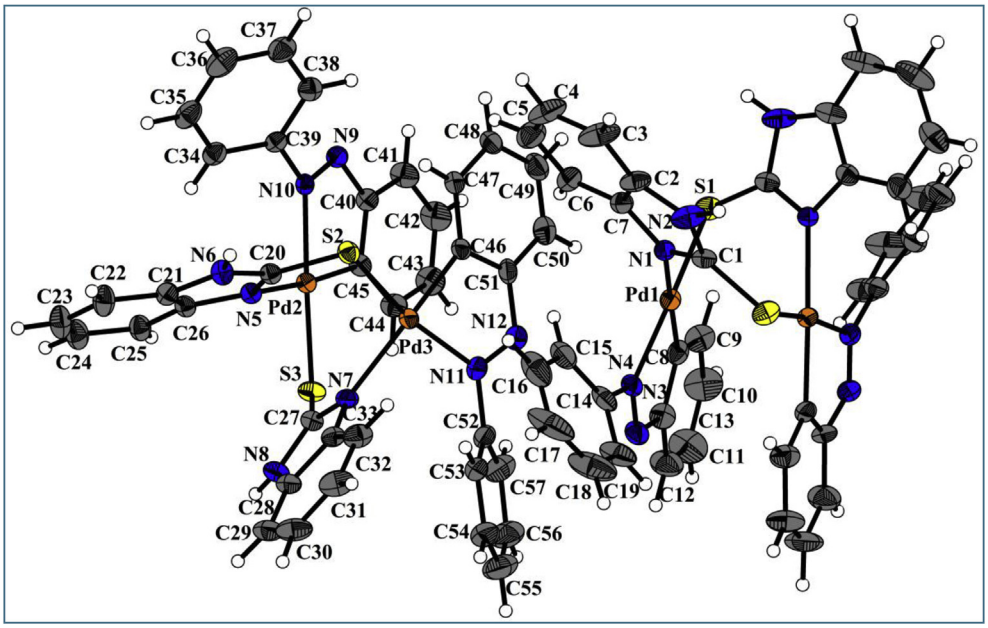

Fig. 5. Molecular structure of complex $[Pd_2(\kappa^2\text{:C, N-azb})_2(\mu\text{-N, S-bzimS-NH})_2]$ **15**.

3. Result and discussion

3.1. Synthetic comments and IR spectroscopy

Cyclopalladated precursors, $[Pd_2(\kappa^2\text{:C, N-azb})_2(\mu\text{-Cl})_2]$, $[Pd_2(\kappa^2\text{:C, N-mazb})_2(\mu\text{-Cl})_2]$ and $[Pd_2(\kappa^2\text{:C, N-deazb})_2(\mu\text{-Cl})_2]$ were prepared initially, which were then reacted with the thio-ligands (Chart 2) in the presence of Et_3N base and the color change occurred from a light yellow solution to red-brown. The Et_3N base deprotonated the thio-ligands (N-H protons) with the formation of $Et_3NH^+Cl^-$ salt. The addition of toluene or methanol assisted in the formation of crystals. The palladium activated C-H bond of one phenyl ring of azobenzene, or p-ethoxy phenyl ring of 4, 4′-diethoxyazobenzene, but in case of p-methoxy azobenzene, the preferential C-H bond activation of methoxy phenyl ring occurred instead of phenyl ring. Complexes **1**–**14** have N, S-bridged imidazolidine-2-thiolate ligands while complexes **15**–**19** have similarly bonded other anionic thio-lgands shown in Chart 3. Complexes are soluble in the organic solvents such as chloroform, dichloromethane and dimethylsulfoxide.

A brief commentary on the IR spectral data of complexes is provided here. The thio-lgands, 1,3-imidazolidine-2-thiones (imdzSH-NR; R = Me, Et, Pr^n, Bu^n, Ph) showed the ν(N–H) stretching bands in the region, 3188 to 3204 cm^{-1}, which disappeared in their complexes **2**–**14**, supporting that the thio-ligands are coordinating as anionic ligands. The ν(N–H) bands of free tzdSH and imzSH-NMe ligands at 3138 and 3106 cm^{-1} respectively disappeared in their complexes, $[Pd_2(\kappa^2\text{:C, N-azb})_2(\mu\text{-N, S- tzdS})_2]$ **17**,

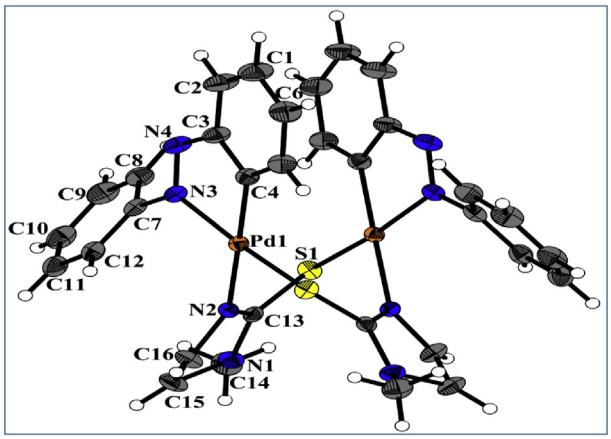

Fig. 6. Molecular structure of complex [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S-imzS-NMe)$_2$] **16**.

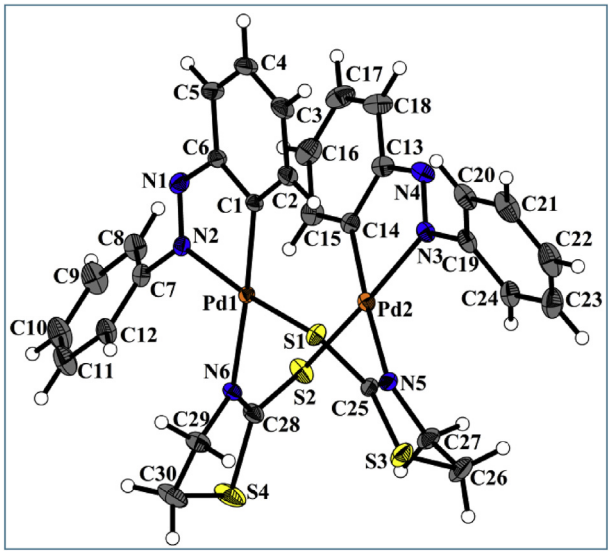

Fig. 7. Molecular structure of complex [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S-tzdS)$_2$] **17** (See SI for molecular structures of **18** and **19**).

[$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S- imzS-NMe)$_2$] **16** and [$Pd_2(\kappa^2$:C, N-deazb)$_2$(μ-N, S- imzS-NMe)$_2$] **19**, which again supported coordination by the thio-ligands as anions. The free ligand (imdzSH-NR, R = H) with two N-H hydrogens showed the ν(N–H) band at 3247 cm^{-1} which appeared at 3230 cm^{-1} in its complex **1**. The presence of water in complex **1** is shown by an intense ν(O–H) band at 3418 cm^{-1}. Finally, the ν(N–H) stretching band of free bzimSH-NH (at 3153 cm^{-1}) shifted to 3118 cm^{-1} and 3200 cm^{-1} in its complexes, [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S- bzimS-NH)$_2$] **15** and [$Pd_2(\kappa^2$:C, N-deazb)$_2$(μ-N, S- bzimS-NH)$_2$] **18**, respectively. The free thio-ligands showed another diagnostic band due to ν(C-S) stretching frequency in the region, 1150 to 1205 cm^{-1} which shifted to low energy region, 1104 to 1178 cm^{-1}, supporting coordination through S-donor atom of the thio-ligands in their complexes (see experimental and Supporting Information).

3.2. Molecular structures

Complexes crystallized in triclinic (P-1, **12**, **18** and **19**), monoclinic ($P2_1/n$, **1, 11, 13**; C 2/c, **2**–**5**, **8**, **9** and **16**; $P2_1/c$, **7**; P 2/c, **15**) and orthorhombic (Pbca, **17**) crystal systems. The crystal data are given in Table 1 and important bond lengths and angles given in Table 2. Among the nineteen complexes, crystal structures of **16** complexes (except **6**, **10** and **14**) have been obtained and only representative structures are discussed below, while others are placed in Supporting Information.

The molecular structure of azobenzene (azbH) complex, [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S-imdzS-NH)$_2$] **1** is shown in Fig. 1. Each azobenzene binds in C, N-chelation mode to one Pd(II) ion forming Pd(κ^2:C, N-azb) moiety (Fig. 1). Two such moieties are then connected with two N, S-bridging imidazolidine-2-thiolates (imdzS-NH^-). The trans bond angles, {C-Pd-N, 173.52(14), 174.10(15)°; N-Pd-S, 171.65(9), 171.17(9)°} suggest that the geometry of each Pd metal is distorted square planar (Table 2). The C-Pd-N bite angle of angle of ca. 79° was the shortest bond angle of Pd metal center.The metal-ligand bond distances in complex **1** {Pd-C, 1.986(4), 1.978(4) Å; Pd-S, 2.3055(10), 2.3063(11) Å and Pd-N, 2.070(3), 2.065(3), 2.106(3), 2.111(3) Å} are less than the sum of covalent radii of Pd and donor atoms {Pd-C, 2.10–2.22 Å; Pd-S, 2.35–2.47 Å and Pd-N, 2.08–2.20 Å} which suggest shortening of the bonds on complexation [47].

It was noted that Pd-$N_{(azobenzene)}$ bond distance was marginally shorter than Pd-$N_{(thio\text{-}ligand)}$ bond distance. The Pd···Pd bond distance of 2.9851(4) Å is less than the sum of van der Waals radii of Pd atoms (3.20 Å), which is indicative of close metal-metal contact [47]. The Pd-donor atom bond distances are comparable to the literature bond distances {Pd-C, 1.990(2); Pd-S, 2.3052(6), 2.3781(7), 2.7113(8), Pd-N, 2.0353(19) Å}, as for example, noted in complex, [Pd(κ^2-C,N-azb)(κ^3-S,S,S-L)][PF_6] {L = 1, 4, 7-trithiocyclononane} [48]. Complex **1** has disordered oxygens O1W and O2W of water in the crystal lattice (Fig. 1). The molecular structures of complexes **2**–**5** with N-R substituents of imdzS-NR moiety (R = Me to Bu^n) made marginal effect on the bond distances/bond angles (Table 2) and structures are similar to that of complex **1**. Thus the molecular structure of representative complex **2** (R = Me) is shown in Fig. 2 and those of others are placed in SI.

Complexes **7**–**9** have one methoxy substitution in phenyl group of azobenzene (mazbH). The crystal structures of these three complexes have shown that it is methoxy substituted ring which is metallated and not the phenyl ring. The thio-ligands are N, S-bridging as was the case for dinuclear complexes, **1**–**5**. Molecular structure of a representative complex, namely, [$Pd_2(\kappa^2$:C, N-mazb)$_2$(μ-N, S-imdzS-NMe)$_2$] **7** is shown in Fig. 3. Complexes **11**–**13** have ethoxy substitution in both the azobenzene rings, but one ring per metal is metallated as found in complex **1.** Molecular structure of representative complex **11** is shown in Fig. 4. The unit cell has two crystallographically independent dimeric molecules in the asymmetric unit with marginal differences in the bond parameters. The bond distances/angles are similar to those found for complexes **1**–**5** or **7**–**9.**

The thio-ligands, bzimSH-NH, imzSH-NMe and tzdSH have formed complexes, [$Pd_2(\kappa^2$:C, N-azb)$_2$(μ-N, S-L)$_2$] (L = bzimS-NH **15**; imzS-NMe **16**; tzdS **17),** and [$Pd_2(\kappa^2$:C, N-deazb)$_2$(N, S-L)$_2$] (L = bzimS-NH **18**; imzS-NMe **19)**, whose crystal structures have shown N, S-bridged anioinic ligands with chelating azobenzenes as was the case for imidazolidine-2-thiones. The unit cell of complex **15** has two crystallographically independent molecules in the asymmetric unit (Fig. 5). Similarly, molecular structures of complexes **16** and **17** are shown in Figs. 6 and 7 respectively.

3.3. Molecular spectroscopy (NMR, UV–visible, fluorescence)

Proton NMR spectra of complexes **1**–**19** were recorded in $CHCl_3$-D and the NMR data are listed in the experimental section (see Charts 4 and 5 for numbering; Tables S2–SI). The free imdzSH-NH ligand showed a broad signal at δ 10.0 ppm due to NH protons,

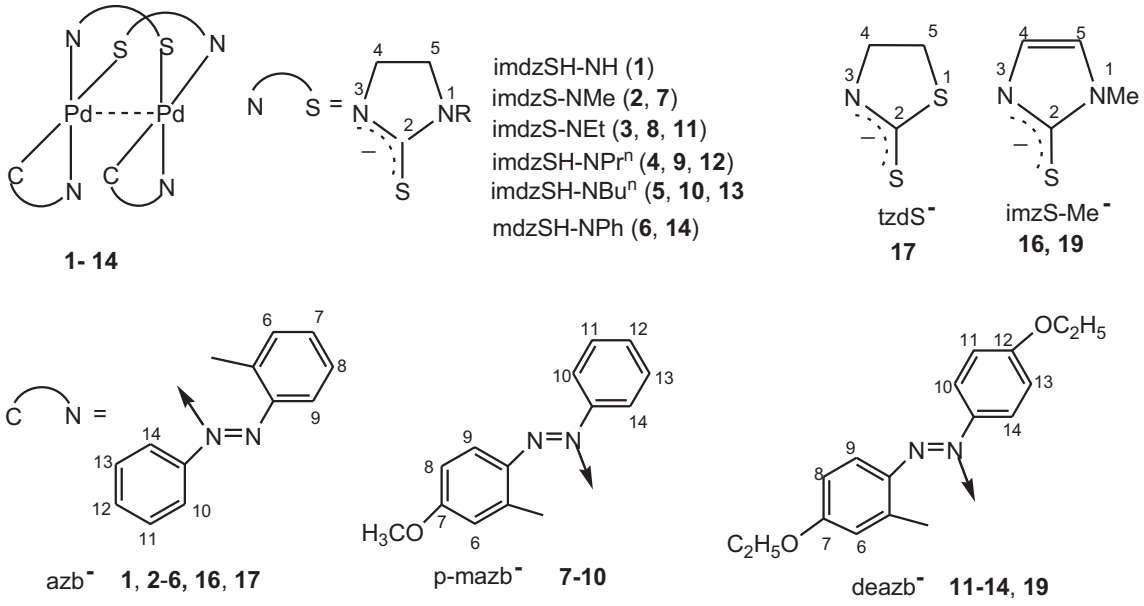

Chart 4. Numbering of various atoms for NMR.

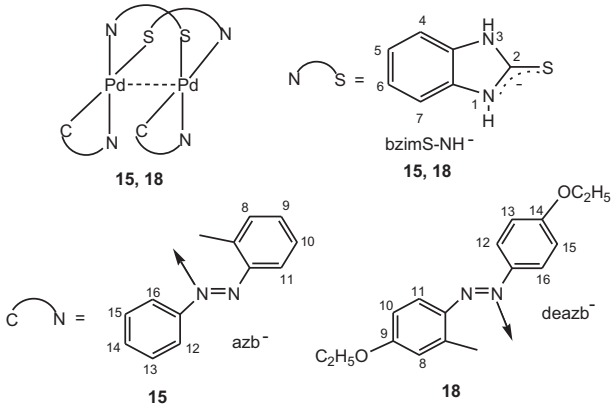

Chart 5. Numbering scheme of bzimS-NH⁻ complexes.

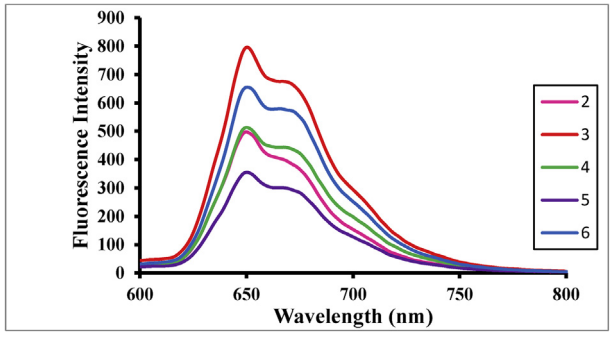

Fig. 8. Fluorescence spectra of complexes **2**–**6**.

which shifted to the low energy region at δ 8.04 ppm in complex **1** (Chart 4). The $C^{4,5}H_2$ protons of free imdzSH-NH ligand appeared as a singlet at δ 3.59 ppm, however, in its complex the C^4H proton signal shifted to low field at δ 3.70–3.86 ppm while C^5H proton signal shifted to high field at δ 3.32–3.44 ppm, as these protons face different chemical environments. The signals due to the anionic azb⁻ protons in complex are assigned at $\delta = 7.50$ (H^6) (doublet), 7.65 (m, H^9, H^{10}, H^{14}), 7.45 (m, H^{11}, H^{12}, H^{13}) and 7.10 (m, H^7, H^8). The N-substituted imidazolidine-2-thiolate complexes, namely, **2**, **3**, **4**, **5** and **6**, did not show –NH proton signals and thus confirmed that the thio-ligands coordinate as monoanions after deprotonation of –NH moiety. Further, the $C^{4,5}H_2$ proton signals of these complexes appeared as a set of multiplets in the range δ 3.20–3.82 ppm at relatively upfield as compared to the free ligands (see SI). The -N-CH_2-, -CH_2-, CH_3 protons also appeared as multiplets at δ 3.20, 3.24, 1.32, 1.40 and 0.85–1.58 ppm; the azobenzene anion proton signals have pattern similar to that of complex **1**. Dinuclear complexes **7**–**14** have similar NMR pattern (see Chart 4).

The free imzSH-Me ligand shows a broad proton signal at δ 11.3 ppm due to NH protons, and its absence in complexes **16** and **19** confirmed the deprotonation of the thio-ligands. The C^4H and C^5H protons of free imzSH-Me ligand (see SI) moved to high-field at δ 2.83–4.09 ppm in its complexes. The N-methyl protons also shifted upfield at δ 1.42–1.58 ppm in complexes. Finally, the ^1H NMR spectrum of free thiazolidine-2-thione (tzdSH) ligand showed a broad signal at δ 7.61 ppm due to the NH protons and its absence in complex **17** showed deprotonation of –NH moiety. The signals due to $C^{4/5}H$ protons of free tzdSH ligand appear as a triplet centered at δ 3.57 ppm which shifted to the region, δ 3.28–4.27 ppm in its complex. Various signals due to azb⁻ and deazb⁻ anions are also listed in experimental section (Tables S2–SI). The ^1H NMR patterns of complexes **15** and **18** are similar to the trends of thio-ligands as discussed above (Chart 5).

The electronic absorption spectra of complexes **2**, **3**, and **7**–**14** have shown the absorption bands in the region 242–280 nm which are assigned to the $\pi \rightarrow \pi^*$ transitions. The electronic absorption bands in the region 308–387 nm incorporate absorption due to azobenzenes/thio-ligands involving $n \rightarrow \pi^*$ transitions from N/S donor atoms. Finally, the bands in the region 443–459 nm are attributed to LMCT/DMSO-d_6 ($^1A_{1g} \rightarrow {}^1A_{2g}$) transitions [49]. Molar absorptivity (ε) appears to vary with the nature of a thio-ligand and the type of azobenzene used (see SI; Table S1). In general the imidazolidine/imidazoline based thio-ligands and the presence of double ethoxy substitution of phenyl rings of azobenzenes lowered ε values. A rigorous correlation is not possible. Complexes **18** and **19** have less molar absorptivity as compared to that of other

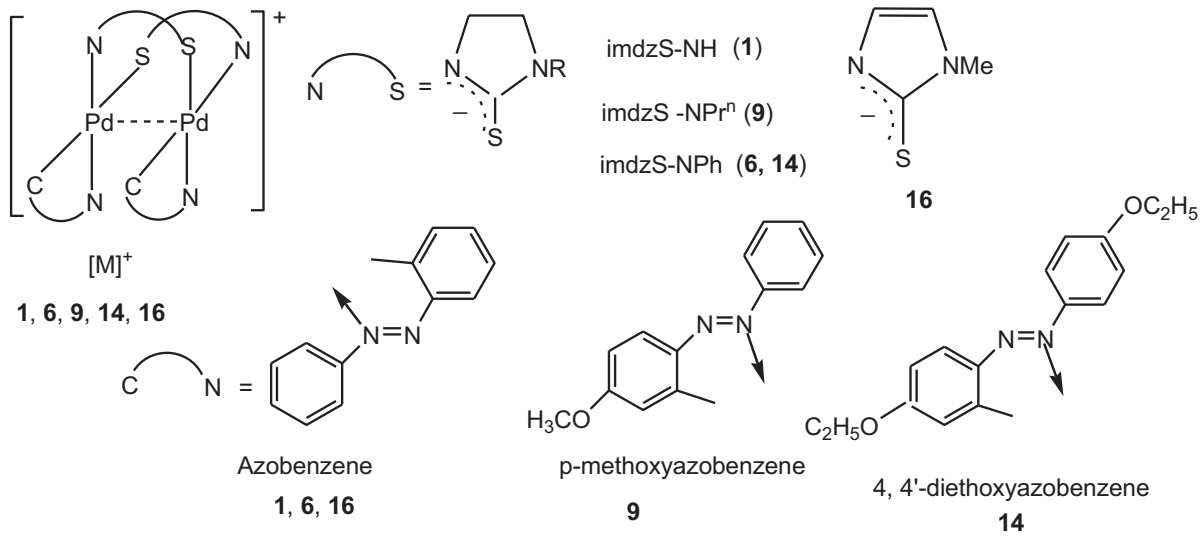

Chart 6. Molecular ion formation by complexes **1, 6, 9, 14, 16**.

homologous complexes, namely, **11**, **12**, **13** and **14,** containing substituted imidazolidines ((See SI; Fig. S5.1 to S5.7).

The fluorescence spectra of complexes **2**–**6** (Fig. 8) showed intense emission in the visible region covering a wide spectral range, 600–780 nm corresponding to the excitation in the range 270–277 nm. In literature, similar type of fluorescence behavior has been observed [18,28–32]. Complexes **3** and **15** have displayed high fluoresecence intensity among other complexes containing azobenzene as a co-ligand. Among complexes containing p-methoxyazobenzene, complex **10** has shown high fluorescence intensity. Similarly, complex **14** has shown high fluorescence intensity as compared to that of other complexes of 4, 4′-diethoxyazobenzene complexes (see SI; Fig. S6.1-6.5).

3.4. ESI-mass spectral studies

ESI-mass spectral data of complexes (**1**–**5**, **8**, **10**–**13**, **15**, **17** and **18**) have been obtained. Complexes **1**, **6, 9, 14** and **16** have shown the formation of the molecular ion species (Chart 6), $[M]^+$ {**1**: *m*/*z* obsd. 775.98, calcd. 775.98; **6**: *m*/*z* obsd. 928.04, calcd. 928.06; **9**: *m*/*z* obsd. 920.62, calcd. 920.11; **14**: *m*/*z* obsd. 1104.13, calcd. 1104.16 and **16**: *m*/*z* obsd. 799.99, calcd. 799.99} in conformity with the molecular structures solved by X-ray crystallography [50]. These complexes as well as other complexes also formed rearranged

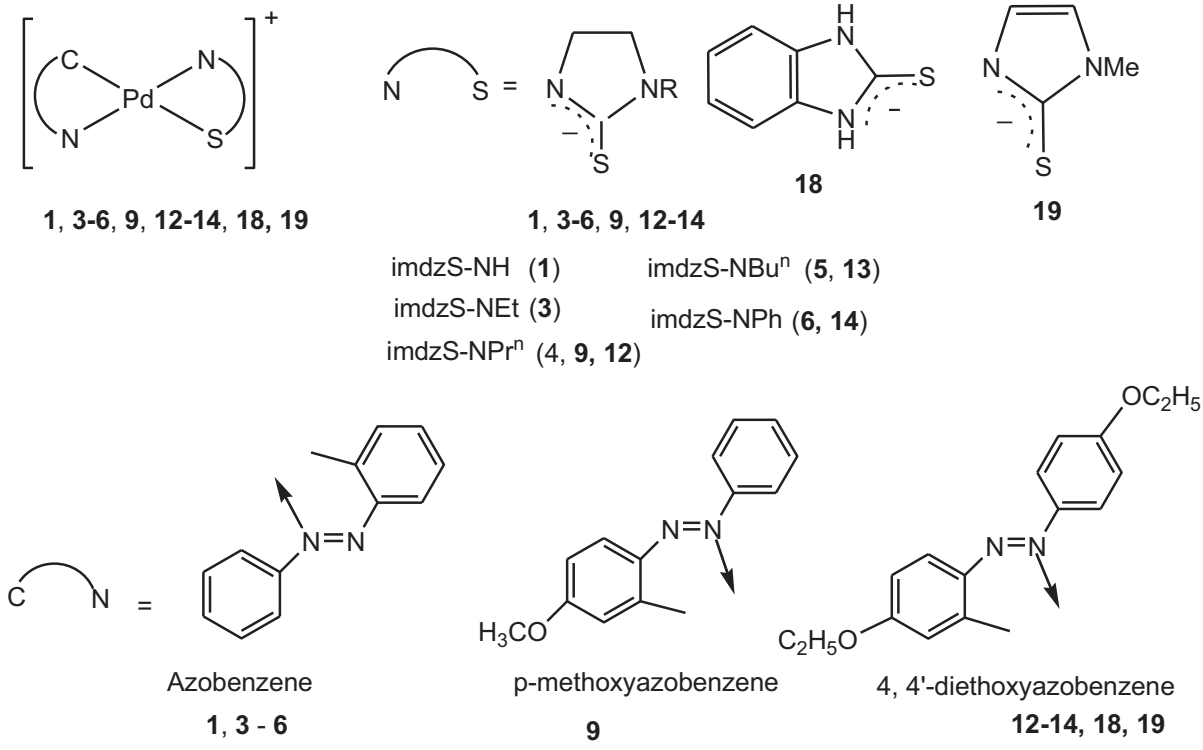

Chart 7. Formation of rearranged species of various complexes.

species as shown in Chart 7 (see SI; Fig. S7.1-S7.16).

4. Conclusion

In our previous investigation pyridine-2-thione (pySH) and pyrimidine-2-thione (pymSH) thio-ligands with cyclopalladated azobenzenes $[Pd_2(\kappa^2$:C, N- azb/mazb$)_2(\mu$-Cl$)_2]$ formed N, S-bridged dinuclear complexes, $[Pd(\kappa^2$:C, N- azb/mazb$)_2(\mu$-N, S-pyS/mpyS$)_2]$ [34]. Here functional groups, -N(H)-C(=S)- and −N(H)-C(=S)-N = were parts of six-membered rings, while in the present case the functional groups are part of the five-membered rings. However, stoichiometry of complexes, $[Pd(\kappa^2$:C, N- L′$)_2(\mu$-N, S-L$)_2]$ (L′ = azb, mazb, deazb; L = anionic N, S- thio-ligand), is similar and thio-ligands are again N, S-bridging. While azobenzenes are C, N-chelating with five-membered ring formation, same is not true of thio-ligands as N, S-chelation would have formed four-membered rings which appear strained and thus pave way for N, S-bridging over chelation. Various substituents in thio-ligands/different thio-ligands used in present investigation made small differences in bond parameters. In case of p-methoxyazobenzene {p-MeO-C_6H_4-N=N-C_6H_5}, it was p-methoxy substituted phenyl ring which was metallated, while in other cases, Ph-N=N-Ph and p-EtO-C_6H_4-N=N-C_6H_4-OEt, because rings being equivalent only one of them in each case was metallated. ESI-mass supported formation of molecular ion in some complexes, in others we could identify only rearranged ions. Fluoresecne spectra appear to be similar and are influenced by both the type of thio-ligands and the azobenzene used, but strict correlation could not be established.

Acknowledgments

Financial assistance from University Grants Commission (UGC) Major Project F. No. 34-307/2008 (SR), under UGC(BSR) scheme and the Council of Scientific and Industrial Research (CSIR), New Delhi, for Emeritus Grant [21(0904)/12-EMR-II] to Tarlok Singh Lobana, New Delhi are gratefully acknowledged.

Supplementary data

CCDC 1586210, 1586208, 1586199, 1586205, 1586206, 1586204, 1586207, 1586203, 1559369, 1559372, 1559370, 1586196, 1586197, 1586200, 1559371 and 1586209 contain the supplementary crystallographic data for compounds **1**–**5**, **7**–**9**, **11**–**13** and **15**–**19** respectively. This data can be obtained free of charge via https://www.ccdc.cam.ac.uk/services/structure_deposit/or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)1223 762911; e−mail: kamila@ccdc.cam.ac.uk). See supplementary for more details.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.02.037.

References

[1] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527–2572.
[2] I. Omae, Coord. Chem. Rev. 248 (2004) 995–1023.
[3] A.D. Ryabov, R. Van Eldik, G. Le Borgne, M. Pfeffer, Organometallics 12 (1993) 1386–1393.
[4] M. Pfeffer, J.P. Sutter, M.A. Rottvel, A. de Cian, J. Fischer, Tetrahedron 48 (1992) 2427–2440.
[5] M. Pfeffer, Recl. Trav. Chim. Pays-Bas 109 (1990) 567–576.
[6] A.D. Ryabov, Synthesis (1985) 233–252.
[7] I.P. Beletskaya, A.V. Cheprakov, J. Organomet. Chem. 689 (2004) 4055–4082.
[8] M. Albrecht, B.M. Cocks, A.L. Spek, G. van Koten, J. Organomet. Chem. 624 (2001) 271–286.
[9] J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917–1927.
[10] C. Schlenk, A.W. Kleij, H. Frey, G. van Koten, Angew. Chem. Int. Ed. 39 (2000) 3445–3447.
[11] D. Morales-Morules, R. Redon, C. Yung, C.M. Jensen, Chem. Comm. (2000) 1619–1620.
[12] R.B. Bedford, S.M. Draper, P.N. Scully, S.L. Welch, New J. Chem. 24 (2000) 745–747.
[13] A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, J. Dupont, Org. Lett. 2 (2000) 1287–1290.
[14] D.E. Bergbreiter, P.L. Osburn, Y.S. Liu, J. Am. Chem. Soc. 121 (1999) 9531–9538.
[15] M. Ohff, A. Ohff, D. Milstein, Chem. Comm. (1999) 357–358.
[16] H. Weissman, D. Milstein, Chem. Comm. (1999) 1901–1902.
[17] R.A.T.M. Abbenhuis, J. Boersma, G. van Koten, J. Org. Chem. 63 (1998) 4282–4290.
[18] M. Ghedini, I. Aiello, M. La Deda, A. Grisolia, Chem. Comm. (2003) 2198–2199.
[19] I. Aiello, M. Ghedini, M. La Deda, J. Lumin. 96 (2002) 249–259.
[20] F. Neve, A. Crispini, C. Depietro, S. Campagna, Organometallics 21 (2002) 3511–3518.
[21] I. Aiello, D. Dattilo, M. Ghedini, A. Golemme, J. Am. Chem. Soc. 123 (2001) 5598–5599.
[22] I. Aiello, D. Dattilo, M. Ghedini, A. Bruno, R. Termine, A. Golemme, Adv. Mater. 14 (2002) 1233–1236.
[23] M.J. Baena, J. Buey, P. Espinet, C.E. Garcia-Prieto, J. Organomet. Chem. 690 (2005) 998–1010.
[24] L. Diez, P. Espinet, J.A. Miguel, M. Paz Rodriguez-Medina, J. Organomet. Chem. 690 (2005) 261–268.
[25] Q.-D. Liu, W.-L. Jia, S. Wang, Inorg. Chem. 44 (2005) 1332–1343.
[26] T.-H. Kwon, H.S. Cho, M.K. Kim, J.-W. Kim, J.-J. Kim, K.-H. Lee, S.J. Park, I.-K. Shin, H. Kim, D.M. Shin, Y.K. Chung, J.-I. Hong, Organometallics 24 (2005) 1578–1585.
[27] M. Ghedini, I. Aiello, A. Crispini, M. La Deda, Dalton Trans. (2004) 1386–1392.
[28] T. Pugliese, N. Godbert, I. Aiello, M. La Deda, M. Ghedini, M. Amati, S. Belviso, F. Lelj, Dalton Trans. (2008) 6563–6572.
[29] S.-H. Li, C.-W. Yu, J.-G. Xu, Chem. Commun. (2005) 450–452.
[30] F. Neve, A. Crispini, C. Di Petrio, S. Campagna, Organometallics 21 (2002) 3511–3518.
[31] M. Juribasic, M. Curic, K. Molcanov, D.M. Calogovic, D. Babic, Dalton Trans. (2008) 6563–6572.
[32] Y. Wakatsuki, H. Yamazaki, P.A. Grutsch, M. Santhanam, C. Kutal, J. Am. Chem. Soc. 107 (1985) 8153–8159.
[33] S. Maity, R. Roy, C. Sinha, W.J. Sheen, K. Panneerselvam, T.H. Lu, J. Organomet. Chem. 650 (2002) 202–209.
[34] T.S. Lobana, A.K. Sandhu, A. Kaur, J.P. Jasinski, J. Organomet. Chem. 751 (2014) 519–524.
[35] T.S. Lobana, R. Verma, G. Hundal, A. Castineiras, Polyhedron 19 (2000) 899–906.
[36] J.A. Garcia-Vazquez, A. Sousa-Pedrares, M. Carabel, J. Romero, A. Sousa, Polyhedron 24 (2005) 2043–2054.
[37] A.C. Cope, R.W. Siekman, J. Am. Chem. Soc. 87 (1965) 3272–3273.
[38] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 26 (1993) 343–350.
[39] G.M. Sheldrick, Acta Cryst. C71 (2015) 3–8.
[40] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837–838.
[41] Bruker. SMART and SAINT. Area Detector Control and Integration Software,, Bruker Analytical X−ray Instruments Inc, Madison, Wisconsin, USA, 1997.
[42] G.M. Sheldrick, Acta Cryst. A46 (2008) 112–122.
[43] G.M. Sheldrick, SHELXL−97, in: Program for the Refinement of Crystal Structures, University of Goettingen, Germany, 1997.
[44] Oxford Diffraction, CrysAlisPro CCD and CrysAlisPro RED, Oxford Diffraction Ltd, Yarnton, England, 2009.
[45] L. Palatinus, G. Chapuis, J. Appl. Cryst. 40 (2007) 786–790.
[46] R.C. Clark, J.S. Reid, Acta Cryst. A51 (1995) 887–897.
[47] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, fourth ed., Harper Collins, New York, 1993.
[48] R.Y.C. Shin, Chun Lian Goh, Lai Yoong Goh, R.D. Webster, Yongxin Li, Eur. J. Inorg. Chem. (2009) 2282–2293.
[49] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Company, London, 1968, pp. 349–355.
[50] J. Spencer, B.Z. Chowdhry, A.I. Mallet, R.P. Rathnam, T. Adatia, A. Bashall, F. Rominger, Tetrahedron 64 (2008) 6082–6089.