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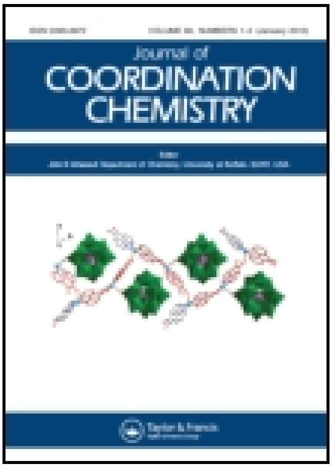

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Synthesis, characterization, and crystal structure determination of palladacycles of *para*-substituted 2-thiobenzylazobenzenes

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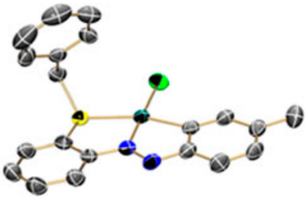

Bichelated neutral palladacycles (**1–3**), [Pd(L)Cl], were synthesized from reaction of the new potential tridentate (C,N,S) ligands, 2-thiobenzylazobenzene (**L$_1$**), 4′-methyl-2-thiobenzylazobenzene (**L$_2$**), and 4′-chloro-2-thiobenzylazobenzene (**L$_3$**) with sodium tetrachloropalladate(II), $Na_2[PdCl_4]$, in ethanol. The compounds were characterized by elemental analysis, FT-IR, ^{1}H NMR, UV–visible, and thermogravimetric analysis. The crystal structures of **L$_2$** and **1–3** were determined by single-crystal X-ray diffraction. In **1–3**, the geometry around palladium remains almost square planar, coordinated to carbon, nitrogen, and sulfur of the ligand forming a bichelated cyclopalladate complex. The C–H…Cl type intermolecular hydrogen bonds, weak $\pi \ldots \pi$, C–H…π, and van der Waals interactions are believed to be the stabilizing forces for the crystal packing of these palladacycles.

Keywords: Palladacycles; 2-Thiobenzylazobenzene; CNS-donor ligand; Thermogravimetric analysis; Crystal structure

1. Introduction

The chemistry of Pd(II) complexes [1–4] especially palladacycles (palladium complexes containing at least one metal-carbon bond intra-molecularly stabilized by at least one neutral donor) [5–8] have attracted researchers owing to their facile synthesis [9], thermal

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*Corresponding author. Email: Tirtha_07@yahoo.com stability, possibility to modulate steric and electronic properties and potential applications in organic synthesis [10], homogeneous catalysis [11], photochemistry [12], optical resolution [13], luminescence properties [14], antibacterial studies, supramolecular architecture [15], etc. Again, organic ligands containing hard (N donors) and soft (S or phosphine) donor sites [16–19] have attracted interest due to their coordination [20–23] in Pd(II) complexes and potential hemilability [18, 19].

Palladacycles have been reported to bind with bidentate [24] or tridentate donors [25] and more frequently with five-membered nitrogen-containing rings. Palladacycles are known for nearly all classes of organic ligands using different preparative methodologies [26] and mechanisms [27]. Their syntheses are facile and it is possible to modulate their electronic and steric properties simply by changing the size of the cyclic ring (3–10 member), the nature of the metallated carbon (aliphatic, aromatic, vinylic, etc.), the type of neutral donor (N, S, O containing group), and its substituent (alkyl, aryl, etc.). These factors determine its dimeric, monomeric, neutral, or cationic nature. The flexibility of the palladium binding pattern with different ligands and their consequences on structure confers a plethora of potential applications in synthetic organic and catalytic chemistry.

Synthesis of only a few tridentate (C,N,S) thioazobenzenes [28, 29] and their palladacycles [25, 30–34] has been reported. Recently palladacycles of thioazobenzenes have been mentioned in C–H bond activation and aromatic metal-oxylation (Ar–Pd → Ar–O–Pd transformation) [25, 30] reactions. For supramolecular chemistry, such palladacycles have opened up the possibility of stacking interactions in crystal packing and polymorphism [31]. The thioazobenzenes generally attain trans-π-diastereoisomeric configuration [28, 29] due to repulsive force between nucleophilic thioether and arylazo moiety which have an impact in the structures of palladacycles [32, 33].

In order to ascertain the nature of these catalytically active palladacycles, we have attempted crystallization of palladacycles to isolate them as solids and subject them to unambiguous structural elucidation. In this article, the one-pot synthesis and characterization [elemental, FT-IR, ^{1}H NMR, UV–visible, and thermogravimetric analysis (TGA)] of *p*-substituted 2-thiobenzylazobenzenes [potential tridentate (C,N,S) ligands] and their palladacycles are reported. Crystal structures of 4′-methyl-2-thiobenzylazobenzene and palladacycles have been investigated by single-crystal X-ray diffraction.

2. Experimental

2.1. *Materials and methods*

Sodium tetrachloropalladate(II) $Na_2[PdCl_4]$ was purchased from Merck. 2-Benzylsulfanyl aniline was prepared according to a literature method [35]. Nitrosobenzene, 4-methylnitrosobenzene, and 4-chloronitrosobenzene were synthesized according to the literature procedure [36]. Elemental analyses were recorded on a Perkin-Elmer Model 240C elemental analyzer. Electronic spectra were measured on a Cary 100 Bio UV–visible spectrophotometer. Infrared spectra of the ligand and complexes were recorded on an IR-affinity-I FTIR Spectrometer SHIMADZU as KBr pellets. ^{1}H NMR spectra were recorded on an Ultrasonic Bruker 300 MHz FT NMR spectrometer using TMS as internal standard and $CDCl_3$ as solvent. All other reagents and solvents used were of commercial grade and employed as received or purified by standard methods prior to use. Melting points were recorded on a Veego melting point apparatus and were uncorrected. Thermogravimetric analyses were performed on a TGA 4000 Thermal Analyzer (Perkin Elmer) with a heating rate of 10 °C min^{-1} under nitrogen.

2.2. *Synthesis*

2.2.1. Synthesis of 2-thiobenzylazobenzene (L_1). In a typical procedure, a solution of 2-benzylsulfanyl aniline (1.29 g, 6 mM) in glacial acetic acid (5 mL) was added to a solution of nitrosobenzene (0.64 g, 6 mM) in glacial acetic acid (50 mL) and stirred for 45 min. During stirring, temperature was maintained between 50 and 70 °C. Then the solution was kept overnight at room temperature. Orange crystals of 2-thiobenzylazobenzene were filtered off, washed with dilute acetic acid to remove any impurities, and dried (the purity was checked by TLC). Yield 76%; m.p. 131 °C. IR (KBr pellet, cm^{-1}): 1578(m), 769(s). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.9 (1H, d, $J = 6.3$ Hz), 7.7 (1H, d, $J = 7.5$ Hz), 7.2–7.5 (12H, m), 4.2 (2H, s). Anal. Calcd for $C_{19}H_{16}N_2S$: C, 75.00; H, 5.26; N, 9.21. Found: C, 74.92; H, 5.28; N, 9.18.

2.2.2. Synthesis of 4′-methyl-2-thiobenzylazobenzene (L_2). The preparation of $\mathbf{L_2}$ follows the same condensation procedure as that of $\mathbf{L_1}$ except that 4-methylnitrosobenzene (0.73 g, 6 mM) was used. The orange needle-like crystals of 4′-methyl-2-thiobenzylazobenzene suitable for X-ray diffraction that formed were filtered off, washed with dilute acetic acid to remove impurities, and dried (The purity was checked by TLC). Yield 85%; m.p. 111 °C. IR (KBr pellet, cm^{-1}): 1580(m), 768(s). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.0 (1H, d, $J = 7.8$ Hz), 7.7 (1H, d, $J = 7.8$ Hz), 7.0–7.4 (11H, m), 4.2 (2H, s), 2.3 (3H, s). Anal. Calcd for $C_{20}H_{18}N_2S$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.37; H, 5.65; N, 8.72.

2.2.3. Synthesis of 4′-chloro-2-thiobenzylazobenzene (L_3). The preparation of $\mathbf{L_3}$ follows the same condensation procedure as that of $\mathbf{L_1}$ except that 4-chloronitrosobenzene (0.85 g, 6 mM) was used. The reaction scheme for the synthesis of $\mathbf{L_1}$–$\mathbf{L_3}$ is given in scheme 1. Yield 81%; m.p. 134 °C. IR (KBr pellet, cm^{-1}): 1582(m), 765(s). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.8 (1H, d, $J = 8.6$ Hz), 7.6 (1H, d, $J = 8.4$), 7.1–7.4 (11H, m), 4.2 (2H, s). Anal. Calcd for $C_{19}H_{15}N_2SCl$: C, 67.35; H, 4.43; N, 8.27. Found: C, 67.28; H, 4.40; N, 8.19.

2.2.4. Synthesis of chlorido-{1-[2-(benzylsulfanyl)-phenyldiazenyl]phenyl-k^3C,N,S}-palladium(II) (1). In a typical procedure, a solution of sodium tetrachloropalladate(II) $Na_2[PdCl_4]$ (147 mg, 0.50 mM) in ethanol (20 mL) was added dropwise to a warm ethanolic solution (25 mL) of 2-thiobenzylazobenzene (136 mg, 0.45 mM). Immediately the color of the solution changed to red. The resulting solution was stirred for one hour over a water bath (90 °C) and then allowed to cool. The crystalline solid formed was filtered, washed several times with ethanol to remove impurity, and dried. The crystals of chlorido-{1-[2-(benzylsulfanyl)-phenyldiazenyl]phenyl-k^3C,N,S}-palladium(II) (**1**), suitable for single-crystal X-ray diffraction, were obtained by recrystallization from methylene chloride-hexane solvent system (10 : 1) followed by slow evaporation of the solvent (2 days). Yield 90%. IR (KBr pellet, cm^{-1}): 1569(m), 763(s). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.0 (1H, d, $J = 7.8$ Hz), 7.8 (2H, d, $J = 8.1$ Hz), 7.1–7.5 (10H, m), 4.3 (2H, s). UV–visible [Methylene chloride,

λ_{max} (nm) (ε_{max}, $M^{-1}\,cm^{-1}$)]: 341 (28,202), 415 (4977), 490 (2123). Anal. Calcd for $C_{19}H_{15}ClN_2PdS$: C, 51.24; H, 3.37; N, 6.29. Found: C, 51.20; H, 3.34; N, 6.25.

2.2.5. Synthesis of chlorido-{4-methyl-1-[2-(benzylsulfanyl)-phenyldiazenyl] phenyl-*k³C,N,S*}-palladium(II) (2). The preparation of **2** follows the same procedure as that of **1** except that 4′-methyl-2-thiobenzylazobenzene (143 mg, 0.45 mM) was used as ligand. Yield 94%. IR (KBr pellet, cm^{-1}): 1573(m), 765(s). ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.0 (1H, d, $J = 7.8$ Hz), 7.7 (1H, d, $J = 7.8$ Hz), 7.6 (1H, s), 7.4 (2H, d, $J = 7.2$ Hz), 7.1–7.2 (6H, m), 7.0 (1H, d, $J = 8.1$ Hz), 4.3 (2H, s), 2.3 (3H, s). UV–visible [Methylene chloride, λ_{max} (nm) (ε_{max}, $M^{-1}\,cm^{-1}$)]: 354 (28,977), 376 (23,390), 418 (18,310), 495 (9850). Anal. Calcd for $C_{20}H_{17}ClN_2PdS$: C, 52.29; H, 3.70; N, 6.10. Found: C, 52.25; H, 3.72; N, 6.12.

2.2.6. Synthesis of chlorido-{4-chloro-1-[2-(benzylsulfanyl)-phenyldiazenyl] phenyl-*k³C,N,S*}-palladium(II) (3). The preparation of **3** follows the same procedure as that of **1** except that 4′-chloro-2-thiobenzylazobenzene (152 mg, 0.45 mM) was used as ligand and the time required for completion of reaction was 2 h. Yield 84%. IR (KBr pellet, cm^{-1}): 1563 (m), 765(s). ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.9 (1H, d, $J = 8$ Hz), 7.7 (1H, d, $J = 8.4$ Hz), 7.6 (1H, s), 7.1–7.4 (9H, m), 4.3 (2H, s). UV–visible [Methylene chloride, λ_{max} (nm) (ε_{max}, $M^{-1}\,cm^{-1}$)]: 325 (24,423), 379 (7403), 414 (4413), 485 (3067). Anal. Calcd for $C_{19}H_{14}Cl_2N_2PdS$: C, 47.55; H, 2.92; N, 5.84. Found: C, 47.58; H, 2.88; N, 5.70.

2.3. *Crystal structure determination and refinement*

Single-crystal X-ray diffraction data for $\mathbf{L_2}$, and **1**–**3** were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromator. SMART [37] software was used for data collection and also for indexing the reflections and determining the unit cell parameters. Collected data were integrated using SAINT [37] software. Structures were solved by direct methods and refined by full-matrix least-square calculations using SHELXTL [38] software. Absorption corrections were done by multiscan method (SADABS) [37]. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The hydrogens were placed at their calculated positions and refined in the isotropic approximations. SHELXTL [38], ORTEP III [39], and Mercury [40] were used for plotting the asymmetric unit and unit cell contents. Crystal data and structure refinements are given in table 1.

3. Results and discussion

To investigate the utility of *p*-substituted 2-thiobenzylazobenzenes as potential tridentate (C, N,S) ligands, they were employed for the synthesis of palladacycles with special emphasis on synthesis, mode of coordination of palladium, and the structure motifs.

3.1. *Synthesis*

The three potential tridentate (C,N,S) ligands, $\mathbf{L_1}$–$\mathbf{L_3}$, were synthesized by condensation between equimolar quantities of 2-thiobenzylaniline and *para*-substituted nitrosobenzenes

Table 1. Crystal data and structure refinement details for $\mathbf{L_2}$ and **1**–**3**.

Compound	$\mathbf{L_2}$	**1**	**2**	**3**
CCDC entry no.	781,797	941,204	941,205	948,613
Empirical formula	$C_{20}H_{18}N_2S$	$C_{19}H_{15}Cl\ N_2PdS$	$C_{20}H_{17}ClN_2PdS$	$C_{19}H_{14}Cl_2N_2PdS$
Formula weight	318.42	445.24	459.27	479.68
T (K)	296(2)	296(2)	296(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions				
a (Å)	16.0637(15)	9.6859(2)	11.0579(3)	11.1340(1)
b (Å)	5.0183(4)	19.4386(3)	10.9588(2)	10.8880(1)
c (Å)	21.4121(18)	9.7220(1)	15.4009(3)	15.3779(2)
α (°)	90	90	90	90
β (°)	98.324(6)	108.1170(9)	100.5020(6)	100.6580(7)
γ (°)	90	90	90	90
V (Å^3)	1707.9(3)	1739.71(5)	1835.04(7)	1832.06(3)
Z	4	4	4	4
D_{Calcd} (g/cm^3)	1.238	1.700	1.662	1.739
μ (mm^{-1})	0.190	1.342	1.275	1.422
F(0 0 0)	672	888	920	952
Crystal size (mm^3)	0.23 × 0.15 × 0.13	0.33 × 0.11 × 0.03	0.41 × 0.25 × 0.16	0.27 × 0.14 × 0.09
θ Range for data collection (°)	1.92−25.99	2.10−25.50	2.10−25.00	2.09–25.00
Index ranges	$-19 \le h \le 19$ $-6 \le k \le 4$ $-23 \le l \le 26$	$-11 \le h \le 11$ $-23 \le k \le 23$ $-11 \le l \le 11$	$-13 \le h \le 12$ $-13 \le k \le 13$ $-16 \le l \le 18$	$-13 \le h \le 13$ $-12 \le k \le 12$ $-18 \le l \le 15$
Reflections collected	15,295	12,106	12,013	13,389
Independent reflections (R_{int})	3349 (0.046)	3107 (0.0756)	3229 (0.0698)	3231 (0.0522)
Completeness (%)	100	95.9	99.9	100.0
Absorption correction	none	multiscan (SADABS)	multiscan (SADABS)	multiscan (SADABS)
Max and min transmission	–	0.9583 and 0.6695	0.8181 and 0.6223	0.8875 and 0.7017
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3349/0/209	3107/0/217	3229/0/227	3231/0/226
Goodness-of-fit on F^2	1.035	1.150	1.078	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.1054$	$R_1 = 0.0595$, $wR_2 = 0.1621$	$R_1 = 0.0529$, $wR_2 = 0.1517$	$R_1 = 0.0276$, $wR_2 = 0.0720$
R indices (all data)	$R_1 = 0.1093$, $wR_2 = 0.1266$	$R_1 = 0.0751$, $wR_2 = 0.2253$	$R_1 = 0.0585$, $wR_2 = 0.1604$	$R_1 = 0.0328$, $wR_2 = 0.0770$
Largest difference in peak and hole (e Å^{-3})	0.18 and −0.17	1.32 and −1.71	1.062 and −0.842	0.270 and −0.575

in acetic acid as shown in scheme 1. One-pot condensation, simple work-up, and good yields make this method a convenient one.

The C,N,S-donor chelating nature of these *para*-substituted 2-thiobenzylazobenzenes was studied by employing them in the synthesis of three new palladacycles, chlorido-{1-[2-(benzylsulfanyl)-phenyldiazenyl] phenyl-k^3*C,N,S*}-palladium(II) (**1**), chlorido-{4-methyl-1-[2-(benzylsulfanyl)-phenyldiazenyl] phenyl-k^3*C,N,S*}-palladium(II) (**2**), and chlorido-{4-chloro-1-[2-(benzylsulfanyl)-phenyldiazenyl]phenyl-k^3*C,N,S*}-palladium(II) (**3**). $Na_2[PdCl_4]$ smoothly reacts with $\mathbf{L_1}$–$\mathbf{L_3}$ in ethanol affording the dark purple palladacycles [Pd(L)Cl] in decent yields (scheme 2).

For the chloro-substituted ligand, formation of the cyclopalladate complex required more time (2 h) for completion than the other ligands, and direct evidence of the influence of donor/acceptor groups (in the aryl ring) on the formation of the cyclopalladate complex.

Methyl groups will favor the electrophilic *ortho*-metallation during cyclization while deactivating chloride in the aryl ring will render it more difficult.

3.2. *Characterization*

$\mathbf{L_1}$–$\mathbf{L_3}$ and **1–3** were characterized by elemental analysis, FT-IR, ^{1}H NMR, UV–visible, and TGA. The structure of $\mathbf{L_2}$ and cyclopalladate complexes **1–3** were studied by single-crystal X-ray diffraction. Elemental analyses indicate that palladium(II) reacts with the tridentate (C,N,S) ligands in a 1 : 1 M ratio to afford neutral palladacycles [Pd(L)Cl]. These complexes are crystalline solids, stable in air, and soluble in some organic solvents ($CHCl_3$, CH_3CN, and DCM).

Cyclopalladate complexes **1–3** afford light brown solutions in methylene chloride and display characteristic spectra in the UV–visible region. The electronic spectral data of **1–3** are given in the Experimental section. Strong absorptions observed in the visible region are due to metal to ligand charge transfer [d(Pd) → π(azo)] transitions [41]. Bands observed in the high-energy region with high molar extinction coefficients arise from intraligand charge transfer transitions [42].

In FT-IR spectra, the ν(N=N) band of **1** shifted to lower frequency (1569 cm^{-1}) compared to ligand $\mathbf{L_1}$ (1578 cm^{-1}) indicating coordination through nitrogen of the azo moiety [43–45]. Similar ν(N=N) bands are observed for **2** and **3**. The ν(C–S) bands for **1–3** appear at 763–765 cm^{-1}.

The structures of *para*-substituted 2-thiobenzylazobenzenes $\mathbf{L_1}$–$\mathbf{L_3}$ and cyclopalladate complexes **1–3** were established by ^{1}H NMR (300 MHz) spectra recorded in $CDCl_3$. For $\mathbf{L_1}$, aromatic (Ar–H) protons appear at δ 7.2–7.9 ppm and benzylic protons ($PhCH_2$) appear as a singlet at 4.2 ppm. The methyl protons (CH_3) for $\mathbf{L_2}$ are a singlet at 2.3 ppm. Aromatic and benzylic protons for $\mathbf{L_1}$–$\mathbf{L_3}$ have a more or less similar spectral pattern. In **1–3**, the *ortho*-metallation (Pd–$C_{aromatic}$) is evident as the signal of one aromatic proton (Ar–H) is absent in the spectra. In **2**, due to Pd–$C_{aromatic}$ formation (palladacycles), the aromatic proton (Ar–H) between methyl and Pd–C moiety is a singlet at δ 7.6 ppm. For **1–3**, due to S-coordination of palladium (Pd–S), benzyl protons ($PhCH_2$) appear slightly downfield at δ 4.3 ppm (~0.2 ppm).

3.3. *X-ray crystallography*

$\mathbf{L_2}$ and palladacycles **1–3** were investigated by single-crystal X-ray diffraction. Crystals of all the complexes suitable for X-ray diffraction were obtained by slow evaporation of methylene chloride-hexane (10 : 1). Perspective views of the molecular structure of $\mathbf{L_2}$ and **1–3** are shown in figures 1–4. The crystal data and structure refinement details of **1–3** are given in table 1. $\mathbf{L_2}$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecule consists of a benzyl sulfanyl group bonded to the *ortho* position of the azo group of the 4-methylazobenzene. Due to repulsion between the nucleophilic arylazo moiety and sulfanyl S1, the molecule attains stable trans-π-diastereoisomeric configuration (figure 1) and the benzyl sulfanyl unit is moved away from the 4-methylazobenzene unit, creating the possibility of coordination of the ligand through its N, S-donor sites. The sulfanyl sulfur used sp^3 hybrid orbitals and not pure *p*-orbitals for bond formation, which is evident from the bond angle C13–S1–C14 [102.82(12)°]. The C14–S1 bond length [1.811(2) Å] is consistent with the C–S covalent bond and the S1–C13 bond length [1.762(2) Å]

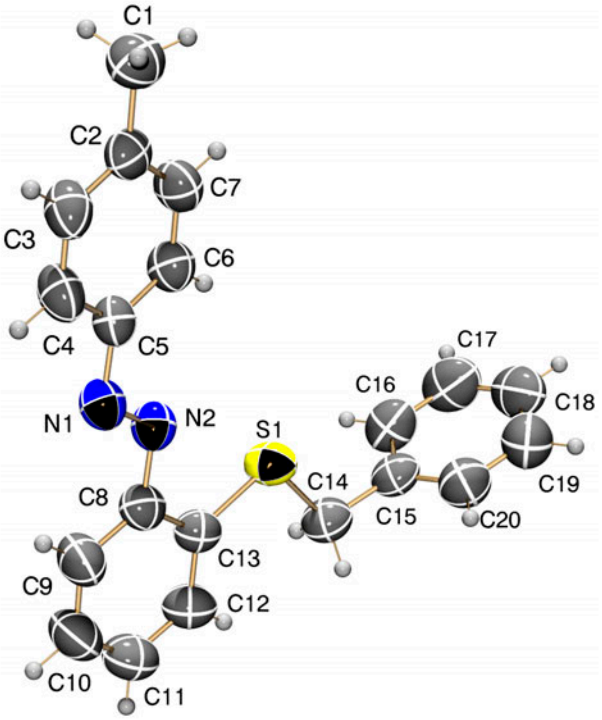


Figure 1. Molecular structure of 4′-methyl-2-thiobenzylazobenzene (**L$_2$**) shown with 50% probability ellipsoids.

is in the expected range for a sp^{2}C–sp^{3}S bond, so the d-resonance between the nucleophilic sulfur and the aromatic π-cloud is insignificant. The N1=N2 bond length of 1.253(2) Å is in the expected range for an azo N=N bond [28, 29]. The molecule is non-planar due to steric repulsion. The tolyl and benzyl rings are oriented at dihedral angles of 6.71(12)° and 89.49 (6)°, respectively, with respect to the thiophenyl ring. There are no significant intra and intermolecular hydrogen bonding interactions, and van der Waals interactions stabilize the crystal packing. The structure of **L$_1$** and **L$_3$** [28, 29] are similar to that of **L$_2$** with minor deviations of N=N bond lengths and sulfanyl (S) and azo (N) distances depending on the substituents attached to the arylazo moiety and there is no prominent heterocyclization (*ortho* azo-sulfur interaction) as found in 4′-methylazobenzene-2-sulfenyl thiocyanate (derivative of **L$_2$**) [46], which in turn favors *ortho*-metallation (Pd–C$_{\text{aromatic}}$) with Pd(II) salts.

In **1**, the palladium is coordinated to C1 of the phenyl ring, N2 of the azo moiety and S of the thioether, forming two five-membered chelate rings with bite angles of 79.7(3)° (N2−Pd−C1) and 84.93(15)° (N2−Pd−S) (table 2). The C,N,S-donor set, palladium(II) center, and chloride constitute an almost square-planar geometry. From the S−C13−C14 bond angle, it is evident that in all these palladacycles, the plane bearing the Pd(II) chelate is capped by the benzyl unit which is unique among other palladacycles reported (figure 2).

The Pd−S and Pd−Cl bond distances are in the expected range [31]. The observed N1−N2 bond distance of the coordinated azo (diazene) is longer than that of the free diazene group [29]. This may be attributed to back bonding from the filled metal orbitals to

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

Bond lengths		Bond angles	
Complex **1**			
N1−N2	1.268(7)	N2−Pd−C1	79.7(3)
Pd−N2	1.963(5)	N2−Pd−Cl	175.46(14)
Pd−S	2.390(18)	C1−Pd−Cl	97.2(2)
Pd−Cl	2.303(2)	N2−Pd−S	84.93(15)
Pd−C1	1.978(6)	C1−Pd−S	164.6(2)
		Cl−Pd−S	98.16(8)
Complex **2**			
N1−N2	1.266(6)	N2−Pd−C2	79.35(18)
Pd−N2	1.975(5)	N2−Pd−Cl	178.01(11)
Pd−S	2.3768(12)	C2−Pd−Cl	98.87(15)
Pd−Cl	2.3002(15)	N2−Pd−S	85.23(12)
Pd−C2	2.000(5)	C2−Pd−S	163.83(15)
		Cl−Pd−S	96.62(5)
Complex **3**			
N1−N2	1.271(3)	N2−Pd−C2	79.55(10)
Pd−N2	1.975(2)	N2−Pd−Cl1	177.53(6)
Pd−S	2.3691(7)	C2−Pd−Cl1	98.70(8)
Pd−Cl1	2.2975(8)	N2−Pd−S	85.25(6)
Pd−C2	1.991(2)	C2−Pd−S	163.98(8)
		Cl1−Pd−S	96.63(3)

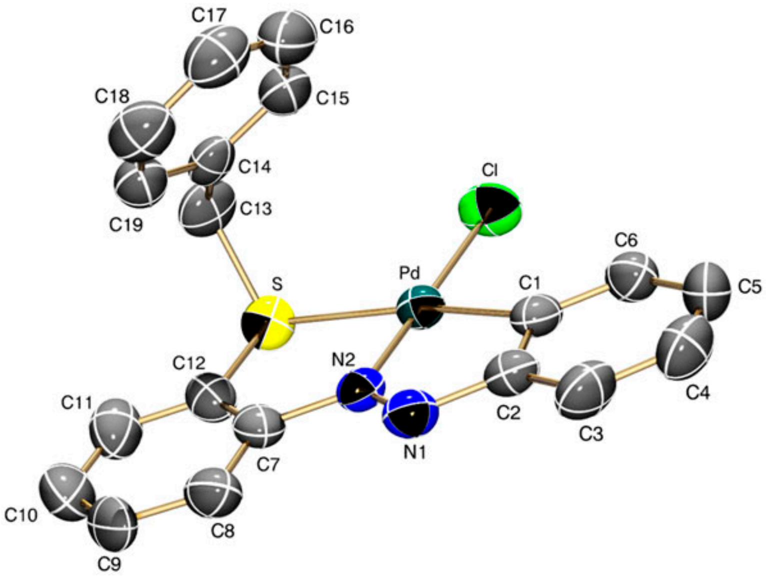


Figure 2. The molecular structure of **1** shown with 50% probability ellipsoids. Hydrogens are omitted for clarity.

the vacant π* orbital localized on the azo moiety. In **2** and **3**, the geometry around palladium(II) remains almost square planar. Selected geometric parameters are listed in table 2.

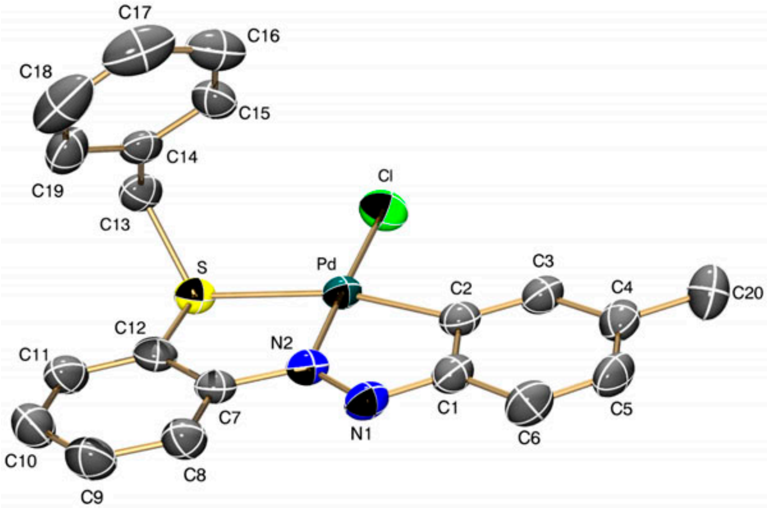


Figure 3. The molecular structure of **2** shown with 50% probability ellipsoids. Hydrogens are omitted for clarity.

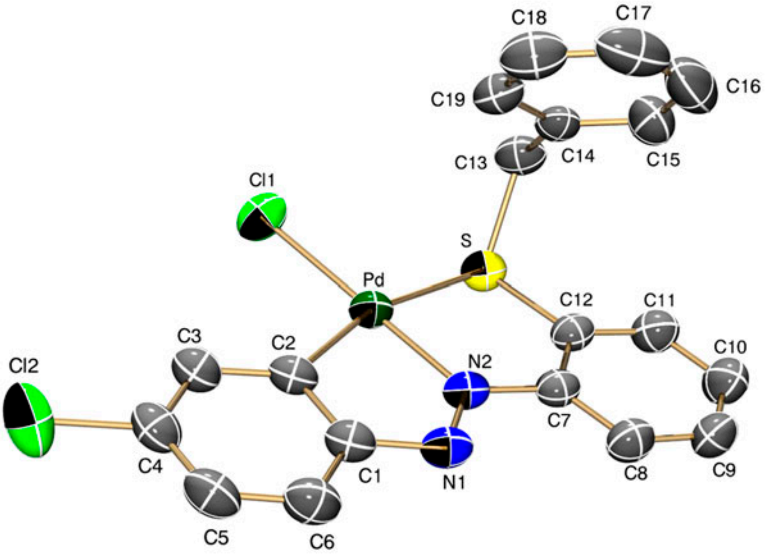


Figure 4. The molecular structure of **3** shown with 50% probability ellipsoids. Hydrogens are omitted for clarity.

In **1**, the C13-H13B…Cl intermolecular hydrogen bond between the benzylic proton H13B and Cl forms a dimer as shown in figure 5. Apart from this, weak $\pi \ldots \pi$ (3.327 Å) and C8–H8…π (3.781 Å) interactions also have an impact in the crystal architecture. In **2**, due to favorable orientation of benzyl, the intermolecular hydrogen bond is prominent between chloride, benzylic proton H13B, and between Cl and aromatic proton H11. These two C–H…Cl type hydrogen bonds form a virtual seven-membered ring structure of graph

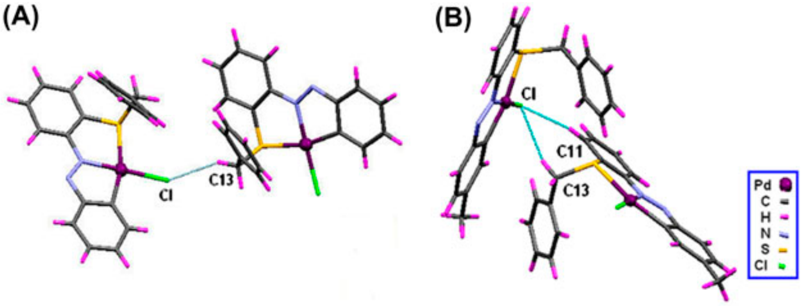


Figure 5. Perspective view of the dimeric structure formed by intermolecular hydrogen bond shown as dashed lines. (**A**) For **1**, symmetry code (i) $-1/2+x$, $3/2-y$, $-1/2+z$; (**B**) For **2**, symmetry code (i) $3/2-x$, $-1/2+y$, $1/2-z$.

set motif $R_1^2(7)$ in the dimer as shown in figure 5. The short interaction between H5 and the centroid (C14, C15, C16, C17, C18, C19) (2.979 Å) is significant while considering the packing of the crystals.

Likewise, in **3**, only one intermolecular hydrogen bond is prominent between chloride and hydrogen of the benzylic carbon. The short C–H…π (2.927 Å) interaction between aromatic proton H5 and the centroid (C14, C15, C16, C17, C18, C19) is also significant for orientation of the benzyl moiety in the formation of palladacycles. Hydrogen bond parameters for palladacycles **1–3** are given in table 3. In palladacycles **1–3** no polymorphism is found unlike chlorido-{4-chloro-1-[2-(methylsulfanyl) phenyldiazenyl] phenyl-k^3*C,N,S*}palladium(II) reported by Bagchi *et al.* [32, 33]. Again, due to the capped benzyl moiety above the square plane, the non-bonded S…S interaction (9.6 Å) is insignificant in dimer formation.

3.4. *Thermogravimetric analysis*

In order to examine the thermal stability of **1–3**, thermal analyses were carried out in nitrogen. Complexes of approximately 3.5 mg were heated from 35 to 910 °C at 10 °C min^{-1} under nitrogen (flow 90 mL min^{-1}). Complex **1** is stable up to 200 °C (figure 6), decomposing between 203 and 743 °C in a three-step process. The first step takes place between 203 and 249 °C with 18.39% weight loss (Calcd for C_6H_5, 17.29%). The second step is observed from 249 to 590 °C with 47.28% weight loss (Calcd for $C_{12}H_8N_2S$, 47.61%), and

Table 3. Hydrogen bond geometry for **1–3**.

D−H…A	d(D−H) (Å)	d(H…A) (Å)	d(D…A) (Å)	<(D−H…A) (°)
Complex **1**				
C13−H13B…Cl^i	0.97	2.71	3.601(8)	153
Complex **2**				
C11−H11…Cl^i	0.93	2.80	3.721(6)	169
C13−H13B…Cl^i	0.97	2.76	3.703(6)	163
Complex **3**				
C13–H13A…Cl1^i	0.97	2.76	3.687(2)	161

Note: Symmetry codes for **1**: $-1/2+x$, $3/2-y$, $-1/2+z$; for **2**: $3/2-x$, $-1/2+y$, $1/2-z$; for **3**: $1/2-x$, $1/2+y$, $3/2-z$.

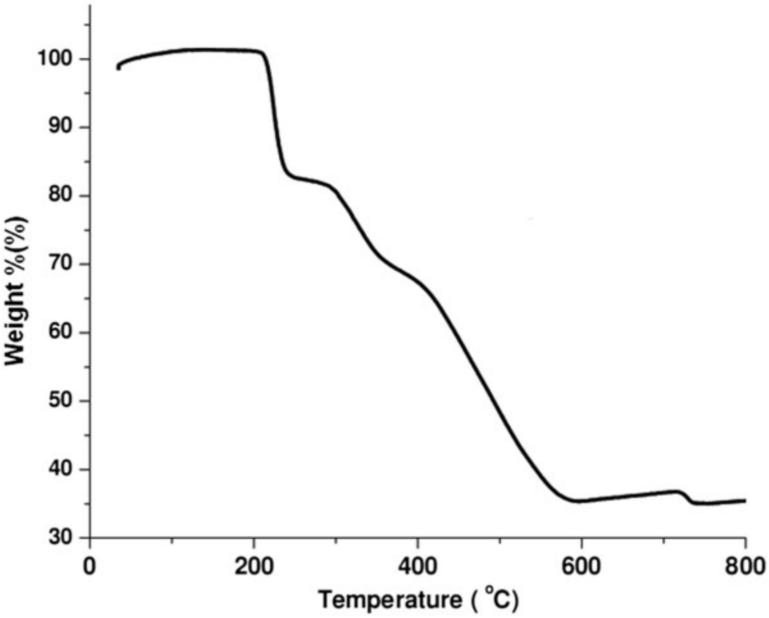
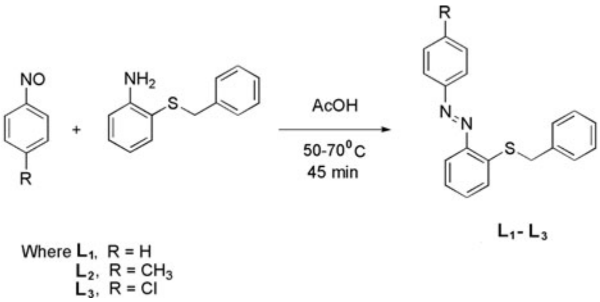
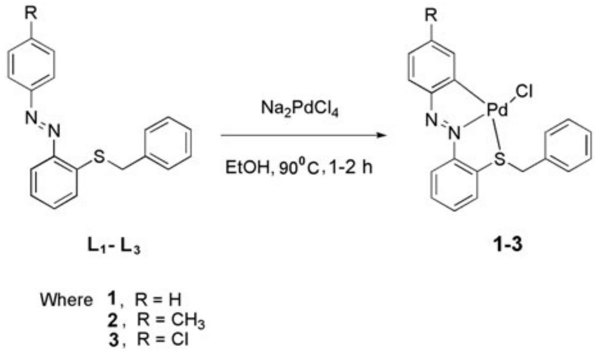


Figure 6. TG curve for **1** under nitrogen.



Scheme 1. Synthesis of *p*-substituted 2-thiobenzylazobenzenes ($\mathbf{L_1}$–$\mathbf{L_3}$).



Scheme 2. Synthesis of palladacycles (**1**–**3**).

the third step is between 590 and 743 °C with 0.36% weight loss. The total weight loss is 66.03%. These data show that the percentage of the residue is 33.97% (PdCl, 31.87%). All the complexes exhibit more or less similar weight loss patterns in the thermograms.

4. Conclusion

One-pot efficient methodology for synthesis of three tridentate (C,N,S) ligands, *para*-substituted 2-thiobenzylazobenzenes $\mathbf{L_1}$–$\mathbf{L_3}$ and their neutral palladacycles **1–3** are described. $\mathbf{L_2}$ and **1–3** are unambiguously characterized by spectroscopic methods (elemental, FT-IR, ^{1}H NMR, and UV–visible) and TGA (for complexes **1–3**). XRD study reveals that $\mathbf{L_2}$ due to repulsion between sulfanyl sulfur and azo moiety attains stable trans-π-diastereoisomeric configuration which favors the possibility of coordination with palladium ion through its N, S-donor sites. In palladacycles **1–3**, the palladium metal coordinates to sp^2 C of the phenyl ring, N of diazene, and S of thioether forming two stable five-membered chelate rings. The geometry around palladium remains almost square planar, capped by the benzyl moiety. Due to favorable orientation of the benzyl, C–H…Cl intermolecular hydrogen bonds are formed. The intermolecular hydrogen bonds along with some short interactions (C–H…π and $\pi \ldots \pi$) and van der Waals interactions are believed to be the stabilizing force for crystal packing. Thermal stability of the neutral palladacycles is established from the TG curve (first decomposition above 200 °C).

Supplementary material

CCDC 781797, 941204, 941205 and 948613 contain the supplementary crystallographic data for $\mathbf{L_2}$, **1**, **2,** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version of the article [http://dx.doi.org/10.1080/00958972.2014.922683].

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