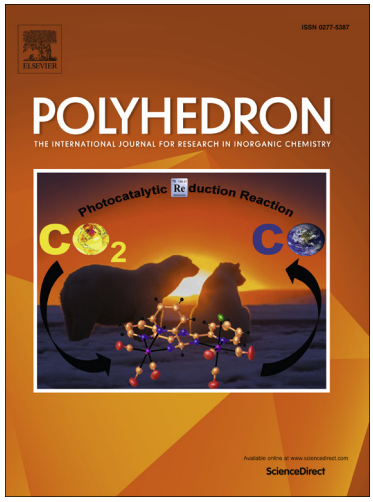

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Palladium(II) complexes bearing bidentate pyridyl-sulfonamide ligands: Synthesis and catalytic applications

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Abstract

New palladium(II) complexes ([Pd(**1-5**)$_2$], **6-10**, (**1-5** = bidentate pyridyl-sulfonamide ligands)) were obtained from the reaction between Pd(OAc)$_2$ and bidentate pyridyl-sulfonamide ligands. The synthesized compounds were characterized by elemental analysis, TG, NMR, IR and X-ray diffraction. The Pd(II) complexes **6-10** were investigated as catalysts for the oxidation of benzyl alcohol to benzaldehyde in the presence of periodic acid as the oxidant and acetonitrile as the solvent under reflux. All the complexes were moderately active catalysts for the catalytic reaction (the oxidation of benzyl alcohol to benzaldehyde), with good yields under mild conditions.

Keywords: Sulfonamides, Pd(II) complexes, pyridines, oxidation, benzyl alcohol, benzaldehyde

1. INTRODUCTION

Sulfonamides are well-documented compounds of synthetic importance which have been widely used in chemistry, biology and medicine fields. The sulfonamides may be synthesized by different techniques, such as the reaction of sulfonyl chlorides with excess ammonia in the presence of a basic media or N-sulfonylation of amines in the presence of homogeneous and heterogeneous catalytic systems [1-6].

The catalytic oxidation of alcohols to aldehydes is a fundamentally important process both in the laboratory and on an industrial scale [7-8]. Especially, benzaldehyde is a significant fine chemical, finding extensive uses in pharmaceuticals, dyestuff etc., and it is currently produced by the liquid phase hydrolysis of benzyl chloride or by the selective oxidation of toluene; however, the hazardous chemicals, complicated processes, Cl-contamination and low yields for products are severe drawbacks for environmental effects and low cost manufacturing steps. For these reasons, there is big research interest for innovative synthesis routes, mostly based on the selective oxidation of benzyl alcohol [9-11].

Recently, palladium catalysts were synthesized and tested for the solvent-free selective aerobic oxidation of toluene to obtain benzaldehyde [12]. With another method, a $Pd(OAc)_2$/pyridine/K_2CO_3 system selectively converted terpenic alcohols to aldehydes under dioxygen [13]. More recently, Pd(II) complexes bearing sulfonamide ligands were reported for the catalytic oxidation of benzyl alcohol to benzaldehyde in the presence of H_5IO_6 [14]. Another example for the oxidation of benzyl alcohol to benzaldehyde in heterogeneous catalytic systems was reported by Hou and co-workers [15].

Herein, we report a simple synthesis and the structural characterization of Pd(II) complexes bearing sulfonamido ligands by spectroscopic analyses. These Pd(II) complexes were examined as catalysts for the oxidation of benzyl alcohol to benzaldehyde.

2. EXPERIMENTAL

2.1. Materials and methods

All chemicals were purchased from commercial suppliers and used as received. NMR spectra were recorded at 297 K on a Bruker 400 NMR spectrometer at 400 MHz (^{1}H) and 100.56 MHz (^{13}C). The C, H and N analyses were performed using a Truspec MICRO (LECO) instrument. FT-IR spectra were measured with a Perkin-Elmer Spectrum 400 FTIR system and recorded using a universal ATR sampling accessory within the range 550-4000 cm^{-1}. The

DTA and TG curves were obtained with a TG-DTA Perkin Elmer Diamond system apparatus. The measurements were performed using a dynamic nitrogen atmosphere at a flow rate of 200 mL min^{-1} up to 1000 ºC. The heating rate was 10 °C min^{-1} and the sample sizes ranged in mass from 8 to 10 mg, contained in a platinum crucible. A Younglin Acme 6100 GC instrument for catalytic experiments was used with an FID and Optima 5MS capillary column.

2.2. Synthesis of the compounds

2.2.1. General procedure for the synthesis of the ligands

1, **2** [16] and **5** [17] were synthesized according to the literature. For characterization data of these compounds, please see supplementary materials. The other ligands were synthesized as follows:

A THF solution (15 ml) of triethylamine (20 mmol) and 2-picoylamine (10 mmol) was slowly added to another THF solution (10 ml) of the arylsulfonyl chlorides (10 mmol) and stirred for 24 h. At the end of this time, the mixture was filtered and the volatiles were removed *in vacuo*. The residue was washed with H_2O (3 x 20 ml) and recrystallized from CH_2Cl_2 (5 ml)/diethyl ether (20 ml) (Scheme 1).

2.2.1.1. Data for 4-n-propyl-butyl-N-(pyridine-2-ylmethyl)benzenesulfonamide, **3**

^{1}H NMR ($CDCl_3$, δ ppm): 8.44 (1H, d, J = 8 Hz, -H_1), 7.74 (2H, d, J = 8.0 Hz, -H_a), 7.61 (1H, t, J = 8.0 Hz, -H_3), 7.22 (2H, d, J = 8.0 Hz, -H_b), 7.20 (1H, d, J = 4.0 Hz, -H_4), 7.15 (1H, t, J = 8.0 Hz, -H_2), 6.32 (1H, t, J = 4 Hz, -*NH*-), 4.26 (2H, d, J =8 Hz, -H_5), 2.60 (2H, t, J = 8.0 Hz, -$CH_2CH_2CH_3$), 1.63 (2H, m, -$CH_2CH_2CH_3$), 0.92 (3H, t, J = 8.0 Hz, -$CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm): 155.0 (-C_{i1}), 148.7 (-C_1), 147.9 (-C_c), 137.1 (-C_{i2}), 136.9 (-C_3), 129.0 (-C_b), 127.2 (-C_a), 122.7 (-C_4), 122.2 (-C_2), 47.4 (-CH_2), 37.8 (-$CH_2CH_2CH_3$), 24.2 (-$CH_2CH_2CH_3$), 13.7 (-$CH_2CH_2CH_3$). IR (cm^{-1}): 3057 (-*NH*), 2959, 2929, 2861, 2807, 1596, 1570, 1483, 1462, 1438, 1409, 1310 (ν_{as}-SO_2), 1187, 1160 (ν_s-SO_2), 1147, 1093, 1070, 1053, 1018, 1006, 971, 905, 852, 829, 798, 767, 713, 672, 634, 617, 574, 559, 524, 498, 462. Anal. Calcd. For [$C_{16}H_{20}N_2O_2S$]: C 62.04, H 6.25, N 9.65, O 11.02, S 11.04. Found: C 62.93, H 6.07, N 9.92, S: 11.32%.

2.2.1.2. Data for 4-methoxy-butyl-N-(pyridine-2-ylmethyl)benzenesulfonamide, **4**

^{1}H NMR ($CDCl_3$, δ ppm): 8.45 (1H, d, J = 8.0 Hz, -H_1), 7.78 (2H, d, J = 8.0 Hz, -H_a), 7.68 (1H, t, J = 8.0 Hz, -H_3), 7.23 (1H, d, J = 4.0 Hz, -H_4), 7.19 (1H, t, J = 8.0 Hz, -H_2), 6.90 (2H,

d, J = 8.0 Hz, -H_b), 6.23 (1H, t, J = 4.0 Hz, -*NH*-), 4.25 (2H, d, J = 8.0 Hz, -H_5), 3.83 (3H, s, -OCH_3). ^{13}C NMR ($CDCl_3$, ppm): 162.8 (-C_c), 155.0 (-C_{i1}), 148.5 (-C_1), 137.3 (-C_3), 131.2 (-C_{i2}), 129.3 (-C_a), 122.8 (-C_4), 122.3 (-C_2), 114.2 (-C_b), 55.6 (-OCH_3), 47.3 (-CH_2). IR (cm^{-1}): 3270 (-*NH*), 3098, 3073, 3020, 2978, 2951, 1593, 1574, 1495, 1476, 1455, 1434, 1321 (ν_{as}-SO_2), 1300, 1260, 1143 (ν_s-SO_2), 1111, 1091, 1072, 1016, 997, 860, 833, 801, 771, 751, 716, 667, 627, 603, 563, 538, 502, 463. Anal. Calcd. For [$C_{13}H_{14}N_2O_3S$]: C 56.10, H 5.07, N 10.06, O 17.25, S 11.52. Found: C 57.02, H 4.92, N 9.88, S 11.81%.

2.2.2. General procedure for the synthesis of Pd(II) complexes, **6-10**

A mixture of $Pd(OAc)_2$ (0.25 mmol) and the *N*-(pyridine-2-ylmethyl)benzenesulfonamides (0.50 mmol) in DMSO (5 ml) was heated at 70 ^{o}C for 72 hours. The solution was allowed to cool to ambient temperature, then the solvent was removed under reduced pressure. The residues were washed with diethyl ether (10 ml) and dried *in vacuo* (Scheme 1).

2.2.2.1. Data for bis-[N-(pyridine-2-ylmethyl)-2,4,6-tri-methyl-benzenesulfonamido]palladium(II), **6**

^{1}H NMR ($CDCl_3$, δ ppm): 8.38-7.17 (8H, m, -H_{1-4}), 6.95 (4H, s, -H_b), 4.07 (4H, d, J = 8.0 Hz, -H_5), 2.52 (12H, s, -2,6-(CH_3)), 2.22 (6H, s, -4-(CH_3)). ^{13}C NMR (d_6-DMSO, ppm): 157.8 (-C_{i1}), 149.1 (-C_1), 141.9 (-C_c), 138.7 (-C_a), 136.9 (-C_3), 135.1 (-C_{i2}), 132.0 (-C_b), 122.7 (-C_4), 121.9 (-C_2), 47.7 (-CH_2), 23.1 (-2,6-(CH_3)), 20.8 (-4-(CH_3)). IR (cm^{-1}): 3032, 2967, 2934, 2910, 2840, 1606, 1563, 1470, 1454, 1445, 1402, 1376, 1339 (ν_{as}-SO_2), 1277, 1246, 1217, 1184, 1159, 1128 (ν_s-SO_2), 1116, 1056, 992, 977, 898, 862, 844, 830, 785, 770, 718, 666. Anal. Calcd. For [$C_{28}H_{30}N_4O_4PdS_2$]: C 51.18, H 4.60, N 8.53, S 9.76. Found: C 51.04, H 4.71, N 8.48, S 9.91%.

2.2.2.2. Data for bis-[N-(pyridine-2-ylmethyl)-4-tert-butyl-benzenesulfonamido]palladium(II), **7**

^{1}H NMR ($CDCl_3$, δ ppm): 8.69-7.00 (16H, m, Ar.*H*), 4.61 (4H, d, J = 8.0 Hz, -H_5), 1.21 (18H, s, -C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): 165.7 (-C_c), 154.2 (-C_{i1}), 152.8 (-C_1), 139.7 (-C_{i2}), 138.3 (-C_3), 127.4 (-C_a), 125.2 (-C_b), 121.9 (-C_4), 119.7 (-C_2), 58.1 (-CH_2), 34.8 (-C(CH_3)$_3$), 31.09 (-C(CH_3)$_3$). IR (cm^{-1}): 2963, 2929, 2903, 2870, 1609, 1594, 1473, 1438, 1399, 1363, 1335, 1300 (ν_{as}-SO_2), 1283, 1251, 1208, 1185, 1143 (ν_s-SO_2), 1104, 1083, 1050, 999, 894, 852, 831, 806, 776, 754, 733, 722, 652, 599, 564, 552, 525, 468. Anal. Calcd. For

$[C_{30}H_{34}N_4O_4PdS_2]$: C 52.59, H 5.00, N 8.18, S 9.36. Found: C 52.71, H 5.11, N 8.03, S 9.17%.

2.2.2.3. Data for bis-[N-(pyridine-2-ylmethyl)-4-n-propyl-butyl-benzenesulfonamido]palladium(II), **8**

^{1}H NMR ($CDCl_3$, δ ppm): 7.00-8.83 (16H, m, Ar.-*H*), 4.42 (4H, d, *J* = 8.0 Hz, -H_5), 2.56 (4H, t, *J* = 8.0 Hz, -$CH_2CH_2CH_3$), 1.59 (4H, m, -$CH_2CH_2CH_3$), 0.90 (6H, t, *J* = 8.0 Hz, -$CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm): 150.5 (-C_{i1}), 138.9 (-C_1), 129.0 (-C_c), 128.6 (-C_{i2}), 127.4 (-C_3), 126.7 (-C_b), 126.4 (-C_a), 122.7 (-C_4), 120.1 (-C_2), 41.1 (-CH_2), 37.8 (-$CH_2CH_2CH_3$), 24.3 (-$CH_2CH_2CH_3$), 13.7 (-$CH_2CH_2CH_3$). IR (cm^{-1}): 2955, 2926, 2863, 1606, 1598, 1569, 1472, 1435, 1403, 1335, 1313 (ν_{as}-SO_2), 1267, 1251, 1207, 1135, 1112 (ν_s-SO_2), 1083, 1051, 997, 971, 953, 892, 841, 792, 773, 740, 719, 686, 639, 629, 617, 578, 546, 513, 465. Anal. Calcd. For $[C_{28}H_{30}N_4O_4PdS_2]$: C 51.18, H 4.60, N 8.53, S 9.76. Found: C 51.29, H 4.49, N 8.43, S 9.67%.

2.2.2.4. Data for bis-[N-(pyridine-2-ylmethyl)-4-methoxy-butyl-benzenesulfonamido]palladium(II), **9**

^{1}H NMR ($CDCl_3$, δ ppm): 8.84-6.60 (16H, m, Ar.*H*), 4.55 (4H, d, *J* = 8 Hz, -H_5), 3.81 (6H, s, -OCH_3). ^{13}C-NMR ($CDCl_3$, ppm): 150.4 (-C_c), 138.6 (-C_{i1}), 129.6 (-C_1), 128.7 (-C_3), 123.7 (-C_{i2}), 120.1 (-C_a), 114.1 (-C_4), 113.6 (-C_2), 113.4 (-C_b), 55.6 (-OCH_3), 41.0 (-CH_2). IR (cm^{-1}): 3038, 2955, 2929, 2836, 1595, 1576, 1495, 1474, 1439, 1336, 1307 (ν_{as}-SO_2), 1282, 1255, 1210, 1192, 1171, 1135 (ν_s-SO_2), 1108, 1085, 1052, 1030, 999, 975, 893, 853, 828, 808, 797, 775, 723, 675, 635, 610, 564, 539, 486. Anal. Calcd. For $[C_{24}H_{22}N_4O_6PdS_2]$: C 45.54, H 3.50, N 8.85, S 10.13. Found: C 45.32, H 3.29, N 8.9, S 10.13%.

2.2.2.5. Data for bis-[N-(pyridine-2-ylmethyl)benzenesulfonamido]palladium(II), **10**

^{1}H NMR (DMSO, δ ppm): 8.68-7.23 (18H, m, Ar.*H*). 4.16 (d, 2H, *J* = 8.0 Hz, -H_5). ^{13}C NMR (DMSO, ppm): 155.5 (-C_{i1}), 149.8 (-C_1), 143.5 (-C_{i2}), 139.5 (-C_3), 133.0 (-C_c), 129.7 (-C_b), 126.9 (-C_a), 123.7 (-C_4), 123.2 (-C_2), 47.3 (-CH_2). IR (cm^{-1}): 3104, 3057, 3028, 2954, 2902, 1608, 1573, 1481, 1447, 1418, 1356, 1316 (ν_{as}-SO_2), 1283, 1255, 1228, 1167, 1148 (ν_s-SO_2), 1118, 1087, 1073, 1061, 1038, 1001, 987, 959, 937, 896, 885, 860, 825, 802, 767, 750, 716, 691, 661, 635, 580, 531, 455, 419. Anal. Calcd. For $[C_{22}H_{18}N_4O_4PdS_2]$: C 46.12, H 3.17, N 9.78, S 11.19. Found: C 46.30, H 3.02, N 9.59, S 11.30%.

2.3. Oxidation of benzyl alcohol

A test tube was filled with benzyl alcohol as the substrate, H_5IO_6 (periodic acid) as the oxidant, Pd(II) complex as the catalyst and CH_3CN (5 ml) as the solvent in a typical reaction. This tube was heated under reflux conditions for the appropriate time. After this time, the sample was treated with diethyl ether (10 ml) and filtered. The reactions were monitored by gas chromatography.

2.4. X-ray analysis

Diffraction data of **6** were collected on a STOE IPDS II diffractometer at room temperature (296 K) using graphite-monochromated Mo Kα radiation (λ=0.71073 Å) by applying the ω-scan method. The structure was solved by direct methods using SHELXS-97 [18] and refined with full-matrix least-squares calculations on F^2 using SHELXL-97 [18] implemented in the WinGX [19] program suite. All H atoms were placed geometrically and treated using a riding model, fixing the bond lengths at 0.93, 0.97 and 0.96 Å for CH, CH_2 and CH_3 atoms, respectively. The displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for methyl) of their parent atoms. Data collection: X-AREA [20], cell refinement: X-AREA, data reduction: X-RED32 [20]. Crystal data, data collection and structure refinement details are summarized in Table 1. The general-purpose crystallographic tool PLATON [21] was used for the structure analysis and presentation of the results. Molecular graphics were generated using ORTEP-3 [22].

Table 1. Crystal data and structure refinement parameters for **6**.

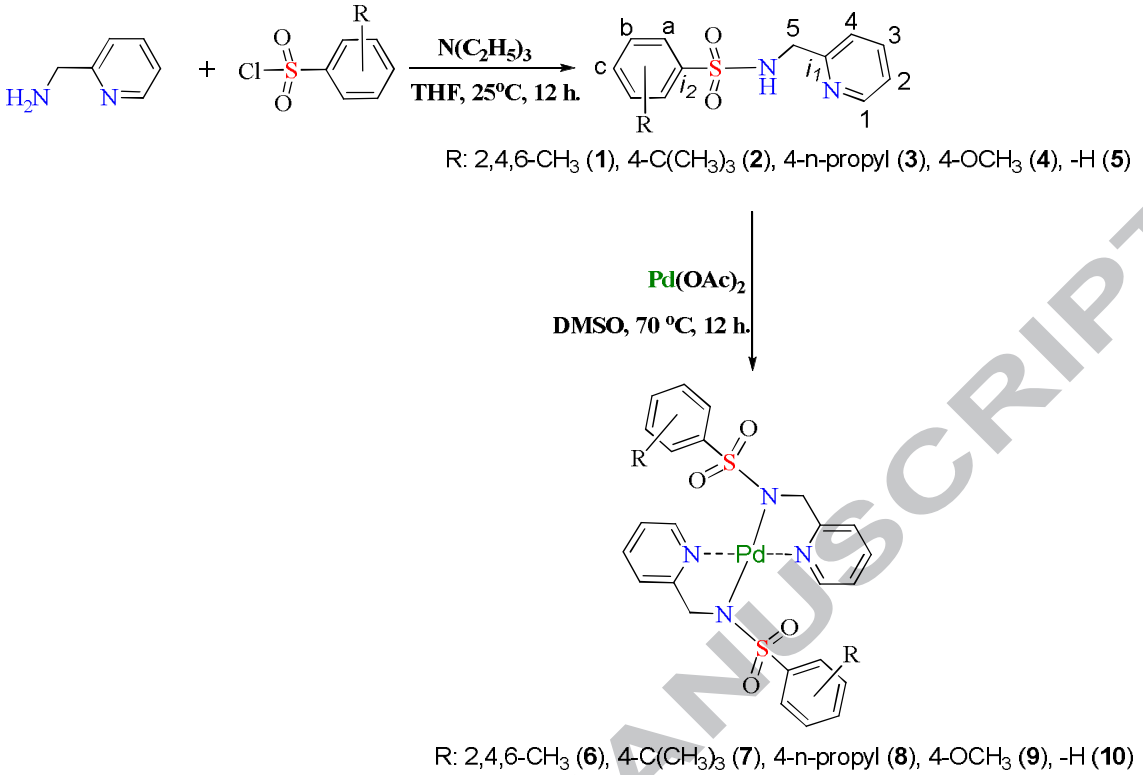
CCDC depository	929522
Color/shape	Colorless/prism
Chemical formula	$[Pd(C_{15}H_{34}N_2O_2S)_2]$
Formula weight	685.13
Temperature (K)	296
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a, b, c (Å)	15.4276(8), 8.8284(5), 11.2048(5)
α, β, γ (°)	90, 108.053(4), 90
Volume (Å^3)	1450.98(13)
Z	2
D_{calc} (g/cm^3)	1.568
μ (mm^{-1})	0.827
Absorption correction	Integration
T_{min}, T_{max}	0.8834, 0.9607

F_{000}	704
Crystal size (mm^3)	0.19 × 0.12 × 0.05
Diffractometer/measurement method	STOE IPDS II/rotation (ω scan)
Index ranges	$-18 \leq h \leq 18, -10 \leq k \leq 10, -13 \leq l \leq 13$
θ range for data collection (°)	$2.69 \leq \theta \leq 25.00$
Reflections collected	12817
Independent/observed reflections	2550/2075
R_{int}	0.093
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2550/0/190
Goodness-of-fit on F^2	1.07
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0525$, $wR_2 = 0.1127$
R indices (all data)	$R_1 = 0.0715$, $wR_2 = 0.1211$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e/Å^3$)	0.74, −1.36

3. RESULT AND DISCUSSION

3.1. Synthesis

The synthesis of the *N*-(pyridine-2-ylmethyl)benzenesulfonamides (**1-4**) was performed with a conventional method, by the reaction of 2-picoylamine and the commercially available arylsulfonyl chlorides [16]. Additionally, the palladium(II) complexes (**6-10**) were also synthesized from the reaction of $Pd(OAc)_2$ and the appropriate ligands (**1-5**) (Scheme 1). All the complex precursors and palladium complexes have been characterized by ^1H and ^{13}C NMR, FT-IR, elemental and TG/DTA analyses. Furthermore, a single crystal-X-ray diffraction study for **6** has been achieved.



Scheme 1 Synthesis and numbering scheme for the ligands (**1-5**) and Pd(II) complexes (**6-10**)

In the ^{1}H NMR spectra of the *N*-(pyridine-2-ylmethyl)benzenesulfonamides (**1-5**), the -H_5 proton was located between 4.06 and 4.31 ppm as a doublet. The -4-(CH_3) (**x**), -2,6-(CH_3) (**y**), -C(CH_3)$_3$ (**z**), -$CH_2CH_2CH_3$ (**t, q, p**) and -OCH_3 (**k**) protons could be assigned as a singlet for (**x, y, z** and **k**), triplet for (**t** and **p**), multiplet for (**q**) at δ 2.21 for (**x**), 2.52 for (**y**), 1.31 for (**z**), 2.60 for (**t**), 1.63 for (**q**), 0.92 for (**p**) and 3.83 for (**k**). Alike, in the ^{13}C NMR spectra for **1-4**, the -CH_2 carbon peak was assigned at around 47.0-48.4 ppm. The peaks of -4-(CH_3) (**x**), -2,6-(CH_3) (**y**), -C(CH_3)$_3$ (**z, v**), -$CH_2CH_2CH_3$ (**t, q, p**) and -OCH_3 (**k**) carbons were observed at 20.4 for (**x**), 22.5 for (**y**), 35.1 for (**z**), 31.0 for (**v**), 37.8 for (**t**), 24.2 for (**q**), 13.7 for (**p**), 55.6 for (**k**). The peaks in the region 3270 to 3057 cm^{-1} are assigned to -*NH* vibrations in the FT-IR spectra for the ligands (**1-5**).

While reviewing the ^{1}H-NMR spectra of the Pd(II) complexes (**6-10**), the -H_5 protons were assigned between 4.07 and 4.61 ppm as an apparent doublet. In a similar way to the ^{1}H NMR spectra of the ligands, the -4-(CH_3) (**x**), -2,6-(CH_3) (**y**), -C(CH_3)$_3$ (**z**), -$CH_2CH_2CH_3$ (**t, q, p**) and -OCH_3 (**k**) protons were observed at δ 2.22 for (**x**), 2.52 for (**y**), 1.21 for (**z**), 2.56 for (**t**), 1.59 for (**q**), 0.90 for (**p**) and 3.83 for (**k**), and in the ^{13}C NMR spectra for **6-10**, the -CH_2 was

identified as being between 41.0 and 58.1 ppm. Additionally, N-H stretching frequency peaks belonging to sulfonamide groups were not observed.

3.2. Description of the crystal structure of ***6***

The solid-state structure of **6** has been unambiguously confirmed by X-ray crystallography. A perspective ORTEP-3 view of the complex with the atomic numbering scheme are depicted in Fig. 1, while selected bond lengths and angles are given in Table 2. The complex crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell.

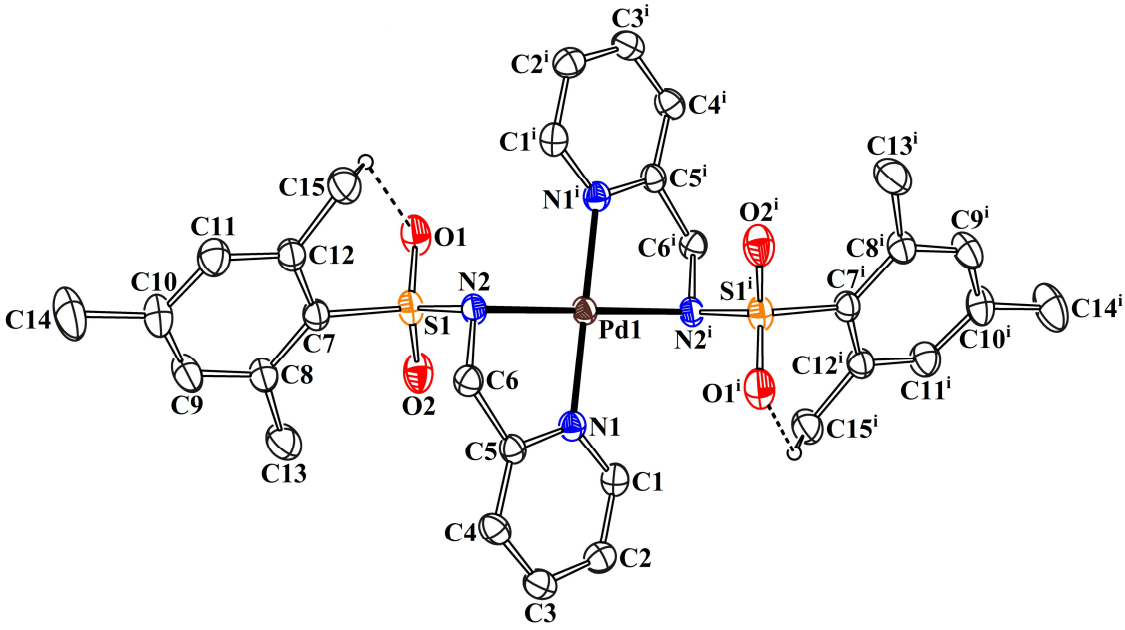


Figure 1. A view of **6** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed lines represent the intramolecular interactions and only H atoms involved in the interactions are shown as small spheres of arbitrary radii.

Table 2. Selected geometric parameters for **6**.

Bond lengths (Å)			
Pd1—N1	2.015(4)	S1—C7	1.792(5)
Pd1—N2	2.070(4)	N1—C5	1.346(6)
S1—O1	1.429(4)	N1—C1	1.359(6)
S1—O2	1.452(4)	N2—C6	1.472(6)
S1—N2	1.618(4)	C5—C6	1.509(7)
Bond angles (°)			
N1—Pd1—N1^{i}	180.0	O2—S1—N2	112.3(2)
N1—Pd1—N2^{i}	98.28(16)	O1—S1—C7	107.8(3)
N1^{i}—Pd1—N2^{i}	81.72(16)	O2—S1—C7	107.1(2)
N1—Pd1—N2	81.72(16)	N2—S1—C7	105.4(2)
N1^{i}—Pd1—N2	98.28(16)	C5—N1—C1	119.4(4)
N2^{i}—Pd1—N2	180.000(1)	C6—N2—S1	113.2(3)

O1—S1—O2	116.4(3)	N2—C6—C5	111.9(4)
O1—S1—N2	107.2(2)		
Torsion angles (°)			
O1—S1—N2—C6	172.0(3)	O1—S1—C7—C12	−54.0(5)
O2—S1—N2—C6	−58.9(4)	O2—S1—C7—C12	−180.0(4)
C7—S1—N2—C6	57.3(4)	O1—S1—C7—C8	122.7(5)
S1—N2—C6—C5	84.1(4)	O2—S1—C7—C8	−3.3(5)
N1—C5—C6—N2	27.5(5)	N2—S1—C7—C12	60.2(4)
C4—C5—C6—N2	−153.0(4)	N2—S1—C7—C8	−123.0(5)

Symmetry code: [i] $-x + 1, -y + 1, -z + 1$.

The molecule of **6** is composed of two 2,4,6-trimethyl-*N*-(pyridine-2-ylmethyl)benzenesulfonamide ligands with a Pd(II) metal centre. The Pd(II) cation resides on a crystallographic inversion center and the two benzenesulfonamide ligands are coordinated to the palladium(II) center in a square-planar fashion *via* the pyridine and amine nitrogen atoms. The Pd—N bond distances are slightly different, the Pd—N_{amine} bond length [2.070(4) Å] is longer than the Pd—$N_{pyridine}$ bond [2.015(4) Å] by 0.55 Å. The difference can be attributed to the different hybridization of the Nsp^2 and Nsp^3 atoms. As can be seen from the *cis* angles, which vary from 81.72(16) to 98.28(16)°, the coordination around the Pd(II) ion is rather deformed. The square plane makes dihedral angles of 15.40(22) and 37.72(18)° with the planes of the pyridine and trimethylbenzene rings, while the dihedral angle between the pyridine and trimethylbenzene rings is 34.97(20)°. The pyridine and amine N-donor atoms form a five-membered metallacycle (containing atoms Pd1/N1/C5/C6/N2), which has an envelope conformation, with the atom N2 atom displaced from the Pd1—N1—C5—C6 mean plane by 0.566(2) Å [puckering parameters: Q = 0.368(4) Å and φ = 323.11(15)°] [23]. In the benzenesulfonamide ligand, the N2—C6 bond length of 1.472(6) Å confirms the single bond character, and the S1—O1 and S1—O2 distances of 1.429(4) and 1.452(4) Å are consistent with S=O double bonding. The atom S1 has a distorted tetrahedral configuration, which is evident from the angles changing from 105.4(2) to 112.3(2)°.

In the molecular structure of the complex, there is an intramolecular interaction, C—H···O, forming a six-membered ring with the graph-set descriptor $S(6)$ [24]. In the crystal structure, the molecules are packed into columns running along the *b* axis. The molecules in each column are connected to one another *via* C—H···O hydrogen bonds and π—π stacking interactions. In these C—H···O interactions, the pyridine carbon atom C3 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atom H3, to the sulfonyl atom O1 in the molecule at (x, $y + 1$, z). At the same time, the pyridine rings of the molecules at (x, y, z) and (x, $y + 1$, z) are mutually parallel, with a distance of 3.619(4) Å between the ring centroids, and a

perpendicular distance of 3.371(5) Å between the rings. Together, these result in the formation of molecular chains along the *b* axis (Fig. 2). Finally, the 2_1-screw symmetry-related columns are connected to each other by means of other C—H···O interactions, in which the pyridine carbon atom C2 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* atom H3, to the other sulfonyl atom O2 in the molecule at (−*x* + 1, *y* + 1/2, −*z* + 3/2). Full details of the hydrogen-bonding geometries are given in Table 3.

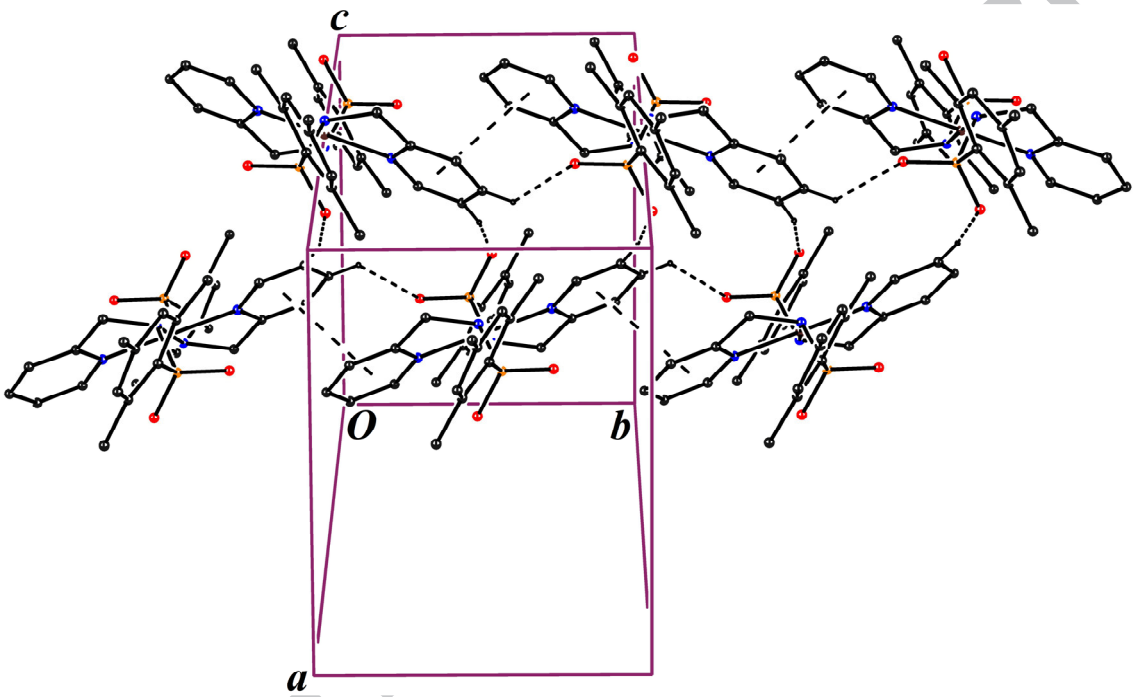


Figure 2. A partial cell packing diagram for **6** showing the C—H···O and π—π interactions (dashed lines). For clarity, only H atoms involved in hydrogen bonding have been included.

Table 3. Hydrogen bonding geometry for **6**.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
C15—H15A···O1	0.96	2.44	3.072(8)	123
C2—H2···O2^{ii}	0.93	2.39	3.242(7)	152
C3—H3···O1^{iii}	0.93	2.48	3.147(7)	128

Symmetry codes: ^{ii} −*x* + 1, *y* + 1/2, −*z* + 3/2; ^{iii} *x*, *y* + 1, *z*.

*3.3. Thermal behavior of the Pd(II) complexes **6-10***

The palladium(II) complexes (**6-10**) were thermally studied from ambient temperature to up to 900 ºC under a nitrogen atmosphere. Typical thermal curves for **6-10** are reported in the Supplementary Materials (Fig. S1). The thermal decomposition results of the complexes, including initial and final temperatures and total mass loss for each decomposition step, are summarized Table 4.

Table 4. TGA data of the synthesized complexes

Comp.	First degradation temp. °C				Second degradation temp. °C				Char at 900 °C %	Loss of absorbed solvent %
	T_{on}	T_{max}	T_{end}	Percentage of weight loss	T_{on}	T_{max}	T_{end}	Percentage of weight loss		
6	267	271	1000	81.5	-	-	-	-	17	1.5
7	205	277	900	75.5	-	-	-	-	23	1.5
8	209	293	900	79.5	-	-	-	-	18	2.5
9	209	276	900	85	-	-	-	-	13	2
10	202	286	308	20	308	342	900	51	27	2

***** T_{on} – thermal degradation onset temperature, T_{max} – maximum weight loss temperature, T_{end} – final thermal degradation temperature

The thermal curves of the Pd(II) complexes are similar, except for **10**. The results show that the samples decompose in one stage for complexes **6-9**. On the other hand, for **10**, two decomposition stages are observed. From Table 4, the thermal stabilities of the Pd(II) complexes increase as follows: **10 < 7 < 9 = 8 < 6**.

3.4. Catalysis

In this study, we also investigated the synthesized Pd(II) complexes as catalysts for the oxidation reaction of benzyl alcohol to benzaldehyde. For this purpose, identical conditions of a published work [14] were chosen to allow a direct comparison of the results. In a typical reaction, a test tube filled with an acetonitrile (5 ml) solution of benzyl alcohol (1 mmol), H_5IO_6 (1mmol) and the Pd(II) complex (0.01 mmol) was heated at reflux under open air. Under these conditions, benzaldehyde was formed as the only product, according to GC and TLC results. As a result, the synthesized complexes are good catalysts for the oxidation of benzyl alcohol to benzaldehyde (Table 5). The catalytic efficiency is easily affected by ligand substitution. Electron donating groups increase the oxidation of benzyl alcohol to benzaldehyde under the studied conditions. Moreover, a sterically hindered group (2,4,6-trimethyl) decreases the catalytic activity of the catalyst.

Table 5. The oxidation of benzyl alcohol to benzaldehyde using the Pd(II) complexes as catalysts

Entry	Catalyst	Yield[d] [%]			TOF[e] (h^{-1})
		a	b	C	
1	**6**	73	79	87	146[a]
2	**7**	78	86	93	156[a]
3	**8**	75	82	88	150[a]
4	**9**	83	95	100	166[a]
5	**10**	65	76	81	130[a]
6	Absence of catalyst	<3[b]			n.c.[b]

[a] : 30 minutes, [b] : 60 minutes, [c] : 120 minutes, [d] : GC yields, yields are based on benzaldehyde, [e]: TOF= moles of product/(moles of catalyst) x (hour), n.c.= not calculated.

Reaction conditions: 1.0 mmol of benzyl alcohol, 1.0 mmol of H_5IO_6, 0.01 mmol of Pd(II) complexes, CH_3CN (5 mL), under reflux conditions.

4. CONCLUSION

In this work, we have synthesized a series of Pd(II) complexes bearing pyridyl-sulfonamide ligands, and we have characterized them by different techniques. Also, the thermal behaviour of the Pd(II) complexes was investigated. Thermal curves showed that these complexes are thermally stable up to ca. 200 °C. Moreover, their catalytic efficiency was tested for the oxidation reaction of benzyl alcohol to benzaldehyde. Catalytic experiments showed the Pd(II) complexes **6**-**10** are good catalysts for the oxidation of benzyl alcohol to benzaldehyde. The results indicate that their catalytic efficiency depends significantly on the ligand properties. Electron donating groups increase the catalytic efficiency of the Pd(II) complexes towards the oxidation of benzyl alcohol to benzaldehyde under the studied conditions.

Supplementary Information

CCDC 929522 contains the supplementary crystallographic data (excluding structure factors) for compound **6** reported in this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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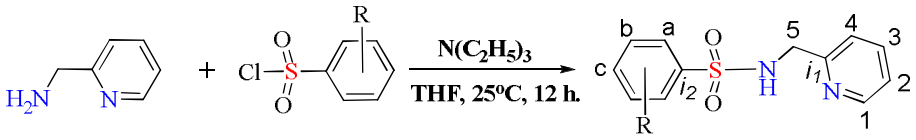
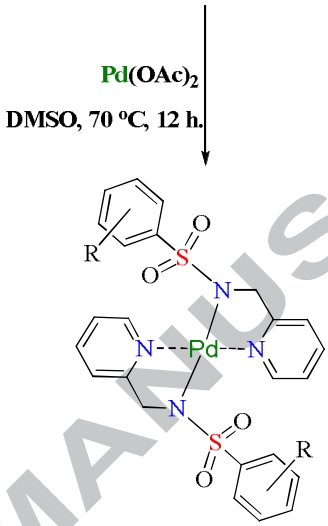
Scheme 1

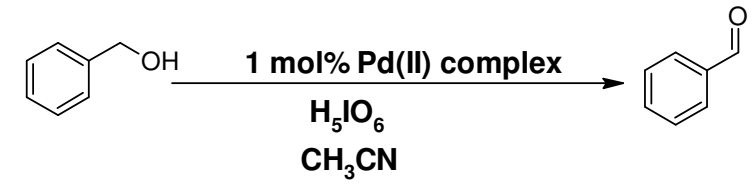


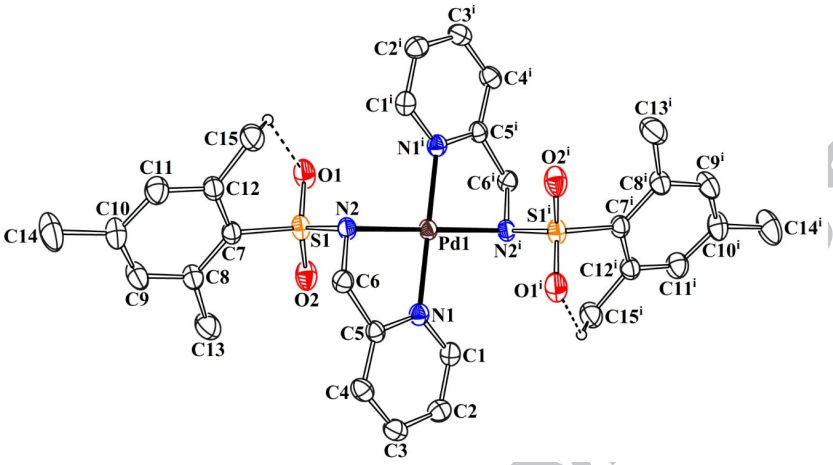
R: 2,4,6-CH_3 (**1**), 4-$C(CH_3)_3$ (**2**), 4-n-propyl (**3**), 4-OCH_3 (**4**), -H (**5**)



R: 2,4,6-CH_3 (**6**), 4-$C(CH_3)_3$ (**7**), 4-n-propyl (**8**), 4-OCH_3 (**9**), -H (**10**)

Graphical Abstract





Graphical abstract

New palladium(II) complexes have been synthesized from $Pd(OAc)_2$ and bidentate pyridinyl-sulfonamide ligands. The compounds were characterized by elemental analysis, TG, NMR, IR and X-ray diffraction. Additionally, the synthesized Pd(II) complexes were tested as catalysts for the oxidation of benzyl alcohol to benzaldehyde.