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Synthesis, characterization and catalytic properties of novel palladium(II) complexes containing aromatic sulfonamides: effective catalysts for the oxidation of benzyl alcohol

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In this article, *N*-(2-aminophenyl)arylsulfonamides (1–5) were successfully synthesized by the reaction of *o*-phenylenediamine and various benzenesulfonyl chlorides. The Schiff base derivatives (1a–f; 4e) of those compounds were obtained using different aldehydes. Then, a series of neutral-four coordinate Pd(II) complexes (6–10) were prepared from the reaction of $Pd(OAc)_2$ and 1–5. On the other hand, when we tried to synthesize Pd(II) complexes containing Schiff base/sulfonamide ligands, two different situations were observed. Generally, when an electron-donating group was attached to the imine fragment (1a–d) except for 1f, the Schiff base hydrolyzed and 6 was isolated. When an electron-withdrawing group was attached to the imine fragment (1e, 4e), neutral four-coordinate Pd(II) complexes (11–13) bearing Schiff base/sulfonamide ligands were isolated. The synthesized compounds were characterized by FT-IR, elemental analysis and NMR spectroscopy. The complexes were used as a catalyst in the oxidation reaction of benzyl alcohol to benzaldehyde in the presence of H_5IO_6 in acetonitrile. All complexes showed satisfactory catalytic activity. The highest catalytic activity was obtained with 9. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: oxidation reaction; Pd(II) complexes; catalyst; aromatic sulfonamides; Schiff base

Introduction

In general, sulfonamides are obtained from the reaction of sulfonyl chloride with primary or secondary amines in alkaline.[1] Sulfonamides and their derivatives have attracted the interest of many researchers' owing to their importance in the development of coordination chemistry, and their application in medicinal chemistry, catalytic fields, etc.[2–18] For example, metal complexes containing sulfonamide ligands have been used as catalysts in various organic reactions.[19–32]

The catalytic oxidation of simple alcohols to aldehydes is a fundamentally important laboratory and commercial procedure.[33] There are many methods in the oxidation of alcohols, but most of them are not preferred due to environmental contamination and provide a by-product. Palladium-catalyzed oxidation of alcohols has been attracting because of both environmental contamination and the formation of a little by-product.[34] Moreover, the palladium-catalyzed oxidation reaction was found dominated by high activity and high selectivity under mild conditions.[35–39]

In recent times, high-activity ultra-fine Pd catalyst was synthesized and used in solvent-free selective aerobic oxidation of toluene.[40] A $Pd(OAc)_2$/pyridine/K_2CO_3 system selectively converted terpenic alcohols to respective aldehydes in the presence of dioxygen.[41] A series of oligomeric methylsiloxane compounds functionalized with pyridyl groups was synthesized and used as ligands in the aerobic $Pd(OAc)_2$-catalyzed oxidation of benzyl alcohol to benzaldehyde at 80°C.[42] The immobilization of palladium complexes or nanoparticles in *N*-heterocyclic carbene (NHC)-modified mesoporous SBA-15 materials was carried out by a post-grafting route. The catalytic properties of these materials were investigated for the aerobic oxidation of benzyl alcohol.[43]

Herein, a series of Pd(II) complexes containing sulfonamide ligands was synthesized and characterized by various spectroscopic techniques. The synthesized complexes (**6–13**) were used as catalysts in the oxidation of benzyl alcohol to benzaldehyde.

Experimental

Materials and Methods

All reagents and solvents were obtained from commercial suppliers and used without any additional purification. 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 NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet signal. The C, H, and N analyses were performed using a Truspec MICRO (LECO) instrument. Infrared spectra were measured with a PerkinElmer Spectrum 400 FT-IR system and recorded using a universal ATR

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(attenuated total reflectance) sampling accessory within the range 550–4000 cm^{-1}. Melting points were determined in open capillary tubes on a digital Electrothermal 9100 melting point apparatus. Gas chromatographic measurements for catalytic experiments were performed using a Younglin Acme 6100 gas chromatograph with a flame ionization detector and an Optima 5MS capillary column (The gas chromatographic parameters were as follows: oven 80°C (isothermal); carrier gas H_2 (split ratio 15:1); flow rate: 4 ml min^{-1}; injector port temperature 220°C; detector temperature 280°C; injection volume 6.0 μl).

General Procedure for the Synthesis of Compounds 1–5

N-(2-Aminophenyl)arylsulfonamides (**1–5**) were prepared by modifying of the published procedure.[44]

A solution of arylsulfonyl chlorides (10 mmol) in THF (10 ml) was added dropwise to a solution of triethylamine (20 mmol) in THF (5 ml) in a Schlenk tube. After a few minutes, a THF (5 ml) solution of *o*-phenylenediamine (10 mmol) was added slowly at room temperature because the reaction is an exothermic reaction, and the reaction continued for a period of 12 h. The reaction mixture was then stirred and heated at 70°C for 1 h (in order to obtain a high yield), after which it was cooled and filtered. The volatiles were removed under reduced pressure. The product was recrystallized from chloroform–diethyl ether (15 ml, 1:3, v/v).

Data for Compounds 1–5

Color light-brown; yield 92%; m.p. 170–172°C. ^{1}H NMR ($CDCl_3$, δ ppm): 4.18 (br., 2 H, -NH_2), 6.48 (d, 1H, J = 8 Hz, -H_1), 6.56 (t, 2H, J = 8 Hz, -H_3), 6.80 (d, 1H, J =8 Hz, -H_4), 7.06 (t, 1H, J = 8 Hz, -H_2), 7.48 (t, 2H, J = 8 Hz, -H_b), 7.59 (t, 1H, J = 8 Hz, -H_c), 7.77 (d, 2H, J = 8 Hz, -H_a). ^{13}C NMR ($CDCl_3$, ppm): 117.6 (arom. -*C*H), 119.2 (arom. -*C*H), 121.4 (arom. -*C*H), 127.6 (arom. -*C*H), 128.6 (arom. -*C*H), 129.0 (arom. -*C*H), 129.1 (arom. -*C*H), 132.1 (arom. -*C*H), 138.8 (arom. -*C*H), 143.6 (arom. -*C*H). IR (cm^{-1}): 3479, 3390, 3204, 3071, 2863, 2791, 2720, 1621, 1584, 1498, 1464, 1449, 1406, 1313, 1295, 1262, 1214, 1181, 1146, 1091, 1030, 1000, 971, 941, 911, 853, 754, 732, 716, 687, 666, 608, 558, 535, 477.

Compound 2

Color yellow; yield 75%; m.p. 180–182°C. ^{1}H NMR ($CDCl_3$, δ ppm): 4.03 (br., 2H, -NH_2), 6.46–7.10 (m, 4H, -H_{1-4}), 7.95 (d, 2H, J = 8 Hz, -H_a), 8.32 (d, 2H, J = 8 Hz, -H_b), ^{13}C NMR ($CDCl_3$, ppm): 117.4 (arom. -*C*H), 118.8 (arom. -*C*H), 124.2 (arom. -*C*H), 124.3 (arom. -*C*H), 128.5 (arom. -*C*H), 129.0 (arom. -*C*H), 129.6 (arom. -*C*H), 130.5 (arom. -*C*H), 144.7 (arom. -*C*H), 170.9 (arom. -*C*H). IR (cm^{-1}): 3469, 3380, 3240, 3122, 3105, 3036, 3859, 1615, 1517, 1498, 1475, 1463, 1399, 1378, 1369, 1348, 1332, 1310, 1253, 1207, 1162, 1107, 1087, 1030, 1009, 975, 960, 948, 934, 904, 853, 846, 817, 790, 739, 678.

Compound 3

Color yellow; yield 85%; m.p. 180–182°C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.33 (s, 9H, -C(CH_3)$_3$), 3.69 (br., 2H, -NH_2), 6.51–7.05 (m, 4H, -H_{1-4}), 7.47 (d, 2H, J = 8 Hz, -H_b); 7.68 (d, 2H, J = 8 Hz, -H_a).^{13}C NMR ($CDCl_3$, ppm): 31.1 (-C(CH_3)$_3$), 35.2 (-*C*(CH$_3$)$_3$), 117.1 (arom. -*C*H), 118.6 (arom. -*C*H), 121.2 (arom. -*C*H), 126.0 (arom. -*C*H), 127.4 (arom. -*C*H), 128.5 (arom. -*C*H), 128.9 (arom. -*C*H), 135.9 (arom. -*C*H), 144.4 (arom. -*C*H), 156.9 (arom. -*C*H). IR (cm^{-1}): 3465, 3386, 3066, 3039, 2960, 2908, 2868, 2792, 1623, 1596, 1500, 1463, 1405, 1368, 1362, 1322, 1293, 1267, 1258, 1215, 1197, 1153, 1111, 1087, 1030, 1015, 943, 915, 852, 831, 755, 734, 661, 624, 572, 547, 517, 472.

Compound 4

Color light brown; yield 82%; m.p. 175–178°C. ^{1}H NMR ($CDCl_3$, δ ppm): 3.77 (br., 2H, -NH_2), 3.86 (s, 3H, -OCH_3), 6.54–7.05 (m, 4H, -H_{1-4}), 6.92 (d, 2H, J = 8 Hz, -H_b), 7.68 (d, 2H, J = 8 Hz, -H_a). ^{13}C NMR ($CDCl_3$, ppm); 55.6 (-O*C*H$_3$), 114.1 (arom. -*C*H), 117.2 (arom. -*C*H), 118.7 (arom. -*C*H), 121.3 (arom. -*C*H), 128.7 (arom. -*C*H), 128.9 (arom. -*C*H), 129.7 (arom. -*C*H), 130.4 (arom. -*C*H), 144.4 (arom. -*C*H), 163.2 (arom. -*C*H). IR (cm^{-1}): 3465, 3369, 3239, 3075, 2979, 2947, 2846, 1615, 1593, 1576, 1496, 1462, 1439, 1415, 1383, 1323, 1302, 1259, 1214, 1193, 1183, 1153, 1112, 1090, 1008, 928, 897, 828, 801, 743, 727, 717, 684, 667, 643, 629, 605, 578, 555, 534.

Compound 5

Color light-brown; yield 74%; m.p. 178–180°C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.94 (t, 3H, J = 8 Hz, -$CH_2CH_2CH_3$), 1.66 (m, 2H, -$CH_2CH_2CH_3$), 2.65 (t, 2H, J = 8 Hz, -$CH_2CH_2CH_3$), 3.84 (br., 2H, -NH_2), 6.47–7.67 (m, 8H, -H_{1-4} and -H_{a-b}).^{13}C NMR ($CDCl_3$, ppm); 13.9 (-$CH_2CH_2CH_3$), 24.4 $CH_2CH_2CH_3$), 38.1 (-$CH_2CH_2CH_3$), 117.4 (arom. -*C*H), 118.9 (arom. -*C*H), 121.5 (arom. -*C*H), 127.8 (arom. -*C*H), 128.8 (arom. -*C*H), 129.1 (arom. -*C*H), 129.3 (arom. -*C*H), 136.3 (arom. -*C*H), 144.6 (arom. -*C*H), 148.8 (arom. -*C*H). IR (cm^{-1}): 3445, 3364, 3235, 3036, 2961, 2928, 2867, 1622, 1597, 1505, 1495, 1465, 1409, 1376, 1325, 1313, 1250, 1213, 1184, 1159, 1116, 1089, 1033, 1019, 929, 902, 876, 843, 817, 804, 743, 733, 692, 666, 611, 593, 559, 533, 501.

General Procedure for the Synthesis of Compounds 1a–f and 4e

A solution of *N*-(2-aminophenyl)arylsulfonamides (10 mmol) in methanol (10 ml) was added to solutions of aromatic aldehydes (10 mmol) in methanol (5 ml) in a Schlenk tube. The reaction mixture was stirred at room temperature for a period of 24 h. The volatiles were removed under reduced pressure. The residue was recrystallized from chloroform (5 ml)–diethyl ether (10 ml).

Data for Compounds 1a–f and 4e

Compound 1a

Color light-brown; yield 86%; m.p. 120–123°C. ^{1}H NMR ($CDCl_3$, δ ppm): 7.01–7.73 (m, 14H, -H_{1-4}, -H_{a-c} and -H_{x-z}), 7.82 (s, 1H, -N*H*-), 8.21 (s, 1H, -N *CH*-). ^{13}C NMR ($CDCl_3$, ppm): 117.0 (arom. -*C*H), 121.2 (arom. -*C*H), 125.5 (arom. -*C*H), 127.1 (arom. -*C*H), 127.5 (arom. -*C*H), 127.7 (arom. -*C*H), 128.5 (arom. -*C*H), 128.7 (arom. -*C*H), 128.9 (arom. -*C*H), 129.0 (arom. -*C*H), 132.1 (arom. -*C*H), 132.8 (arom. -*C*H), 135.5 (arom. -*C*H), 140.9 (arom. -*C*H), 159.7 (-N *CH*-). IR (cm^{-1}): 3227, 3057, 3030, 2964, 2886, 1619, 1596, 1577, 1498, 1483, 1448, 1406, 1383, 1371, 1336, 1323, 1313, 1292, 1273, 1211, 1169, 1158, 1091, 1072, 1047, 1027, 999, 989, 967, 940, 918, 880, 856, 846, 835, 812, 757, 729, 685.

Compound 1b

Color light-yellow; yield 80%; m.p. 145–146°C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.47 (s, 3H, -CH_3), 7.01–7.73 (m, 13H, -H_{1-4}, -H_{a-c} and -H_{x-y}), 7.82 (s, 1H, -N*H*-), 8.16 (s, 1H, -N *CH*-). ^{13}C NMR ($CDCl_3$, ppm): 21.7 (-CH_3), 117.0 (arom. -*C*H), 125.4 (arom. -*C*H), 127.1 (arom. -*C*H), 127.5 (arom. -*C*H), 128.7 (arom. -*C*H), 129.1 (arom. -*C*H), 129.7 (arom. -*C*H), 129.7 (arom. -*C*H), 129.9 (arom. -*C*H), 132.0 (arom. -*C*H), 132.7 (arom. -*C*H), 139.1 (arom. -*C*H), 159.6 (-N *CH*-). IR (cm^{-1}): 3230, 3072, 3060, 3029, 2887, 1620, 1606, 1588, 1567,

1511, 1484, 1446, 1390, 1332, 1310, 1291, 1280, 1214, 1168, 1094, 1042, 970, 921, 881, 842, 815, 771, 754, 726, 691, 665.

Compound 1c

Color light-yellow; yield 85%; m.p. 130–132°C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.41 (s, 3H, -(CH_3)$_p$), 2.50 (s, 3H, -(CH_3)$_o$), 6.99–7.79 (m, 12H, H_{1-4}, -H_{a-c}, and -H_{x-y}), 7.84 (s, 1H, -N*H*-), 8.45 (s, 1H, -N C*H*-). ^{13}C NMR ($CDCl_3$, ppm): 19.6 (- (CH_3)$_p$), 21.6 (- (CH_3)$_o$), 117.0 (arom. -*C*H), 121.0 (arom. -*C*H), 125.4 (arom. -*C*H), 127.1 (arom. -*C*H), 127.2 (arom. -*C*H), 127.4 (arom. -*C*H), 127.4 (arom. -*C*H), 127.6 (arom. -*C*H), 128.5 (arom. -*C*H), 128.7 (arom. -*C*H), 129.0 (arom. -*C*H), 132.0 (arom. -*C*H), 132.7 (arom. -*C*H), 138.9 (arom. -*C*H), 158.5 (-N *C*H-). IR (cm^{-1}): 3225, 3066, 3002, 2921, 1623, 1606, 1583, 1498, 1482, 1463, 1446, 1405, 1395, 1372, 1322, 1313, 1295, 1274, 1251, 1230, 1213, 1170, 1150, 1113, 1089, 1037, 1000, 938, 912, 871, 847, 825, 801, 753, 729, 686, 672.

Compound 1d

Color light yellow; yield 92%; m.p. 145–148°C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.35 (s, 3H, -(CH_3)$_p$), 2.50 (s, 6H, - (CH_3)$_{o,m}$), 6.96 (s, 2H, -H_y) 7.02–7.76 (m, 9H, -H_{1-4} and -H_{a-c}), 7.84 (s, 1H, -N*H*-), 8.71 (s, 1H, -N C*H*-). ^{13}C NMR ($CDCl_3$, ppm): 21.3 (- (CH_3)$_p$), 21.7 (- (CH_3)$_o$), 116.6 (arom. -*C*H), 119.9 (arom. -*C*H), 125.1 (arom. -*C*H), 127.1 (arom. -*C*H), 127.4 (arom. -*C*H), 127.7 (arom. -*C*H), 128.8 (arom. -*C*H), 129.1 (arom. -*C*H), 129.4 (arom. -*C*H), 130.3 (arom. -*C*H), 132.1 (arom. -*C*H), 132.8 (arom. -*C*H), 139.3 (arom. -*C*H), 141.0 (arom. -*C*H), 160.1 (-N *C*H-). IR (cm^{-1}): 3254, 3065, 2970, 2952, 2910, 2848, 1621, 1607, 1586, 1562, 1488, 1461, 1449, 1433, 1404, 1390, 1379, 1329, 1312, 1278, 1210, 1165, 1152, 1090, 1074, 1037, 1027, 998, 979, 9441, 914, 853, 829, 755, 743, 718, 687, 667, 654, 603, 580, 566, 551, 540, 519, 500, 473, 458.

Compound 1e

Color yellow; yield 72%; m.p. 225–227°. ^{1}H NMR ($CDCl_3$, δ ppm): 7.10–7.79 (m, 9H, -H_{1-4} and -H_{a-c}), 7.81 (s, 1H, -N*H*-), 7.97 (d, 2H, J = 8 Hz, -H_x), 8.35 (d, 2H, J = 8 Hz, -H_y), 8.36 (s, 1H, -N C*H*-). ^{13}C NMR ($CDCl_3$, ppm): 116.8 (arom. -*C*H), 121.4 (arom. -*C*H), 124.2 (arom. -*C*H), 125.5 (arom. -*C*H), 127.1 (arom. -*C*H), 127.2 (arom. -*C*H), 127.4 (arom. -*C*H), 127.7 (arom. -*C*H), 128.8 (arom. -*C*H), 128.9 (arom. -*C*H), 129.0 (arom. -*C*H), 129.6 (arom. -*C*H), 132.9 (arom. -*C*H), 133.2 (arom. -*C*H), 156.7 (-N *C*H-). IR (cm^{-1}): 3287, 3103, 3077, 3055, 2841, 1623, 1590, 1507, 1494, 1484, 1462, 1447, 1378, 1338, 1313, 1288, 1277, 1209, 1182, 1154, 1104, 1090, 1076, 1047, 1025, 1014, 1000, 977, 956, 923, 885, 850, 825, 757, 728, 716, 693, 685, 626, 583, 559, 534, 512, 501, 460.

Compound 1f

Color light-yellow; yield 88%; m.p. 120–123°C. ^{1}H NMR ($CDCl_3$, δ ppm): 3.92 (s, 3H, -OCH_3), 7.73 (s, 1H, -N*H*-), 7.00–7.80 (m, 13H, H_{1-4}, -H_{a-c} and -H_{x-y}), 8.10 (s, 1H, -N C*H*-). ^{13}C NMR ($CDCl_3$, ppm): 55.5 (-OCH_3); 114.4 (arom. -*C*H), 117.0 (arom. -*C*H), 121.5 (arom. -*C*H), 125.5 (arom. -*C*H), 127.1 (arom. -*C*H), 127.3 (arom. -*C*H), 127.6 (arom. -*C*H), 128.5 (arom. -*C*H), 128.7 (arom. -*C*H), 129.0 (arom. -*C*H), 131.1 (arom. -*C*H), 131.9 (arom. -*C*H), 132.7 (arom. -*C*H), 139.2 (arom. -*C*H), 159.2 (-N *C*H-). IR (cm^{-1}): 3208, 3065, 2997, 2961, 2836, 1619, 1608, 1591, 1572, 1511, 1499, 1485, 1464, 1448, 1424, 1406, 1386, 1314, 1295, 1276, 1246, 1214, 1149, 1111, 1092, 1034, 1000, 974, 943, 914, 883, 831, 803, 756, 733, 688, 666.

Compound 4e

Color light-yellow; yield 79%; m.p. 183–185°C. ^{1}H NMR ($CDCl_3$, δ ppm): 3.75 (s, 3H, -OCH_3), 6.75 (d, 2H, J = 8 Hz, -H_b), 7.65 (s, 1H, -N*H*-), 7.98 (d, 2H, J = 8 Hz, -H_a); 7.12–8.35 (m, 8H, H_{1-4} and -H_{x-y}), 8.37 (s, 1H, -N C*H*-).^{13}C NMR ($CDCl_3$, ppm); 55.5 (-OCH_3), 114.0 (arom. -*C*H), 116.9 (arom. -*C*H), 121.4 (arom. -*C*H), 124.2 (arom. -*C*H), 125.3 (arom. -*C*H), 127.4 (arom. -*C*H), 129.0 (arom. -*C*H), 129.3 (arom. -*C*H), 129.6 (arom. -*C*H), 130.7 (arom. -*C*H), 132.9 (arom. -*C*H), 139.7 (arom. -*C*H), 140.7 (arom. -*C*H), 149.5 (arom. -*C*H), 156.5 (-N *C*H-). IR (cm^{-1}): 3219, 3070, 3001, 2944, 2894, 2838, 1628, 1593, 1575, 1520, 1495, 1484, 1464, 1454, 1437, 1415, 1392, 1341, 1331, 1304, 1278, 1258, 1214, 1161, 1157, 1105, 1092, 1026, 1010, 986, 969, 950, 916, 886, 869, 855, 838, 800, 764, 752, 738, 722, 710, 688, 680, 648, 623, 612, 587, 571, 553, 538, 505, 490, 467.

General Procedure for the Synthesis of Compounds 6–10

A solution of **1–5** (0.50 mmol) in DMSO (2 ml) was added to a solution of $Pd(OAc)_2$ (0.25 mmol) in DMSO(2 ml) in a Schlenk tube. The reaction mixture was stirred and heated at 70°C for 12 h, and then cooled. The volatiles were removed under reduced pressure. The residue was washed with diethyl ether (20 ml) and dried under vacuum.

Data for Compounds 6–10

Compound 6

Color brown; yield 73%; m.p. 300–301°C (dec.). ^{1}H NMR (DMSO-d_6, δ ppm): 6.55 (s, 4H, -NH_2), 6.68–6.74 (m, 2H, -$H_{1,3}$), 6.90 (t, 2H, J = 8 Hz, -H_2), 7.03 (d, 2H, J = 8 Hz, -H_4), 7.41–7.96 (m, 10H, -H_{x-z}), ^{13}C NMR (DMSO-d_6, ppm): 115.2 (arom. -*C*H), 121.5 (arom. -*C*H), 127.2 (arom. -*C*H), 129.2 (arom. -*C*H), 129.5 (arom. -*C*H), 130.0 (arom. -*C*H), 130.2 (arom. -*C*H), 133.1 (arom. -*C*H), 135.7 (arom. -*C*H), 143.5 (arom. -*C*H). IR (cm^{-1}): 3228, 3217, 2987, 2906, 2838, 2799, 1616, 1575, 1488, 1455, 1445, 1429, 1414, 1399, 1299, 1264, 1242, 1165, 1155, 1121, 1107, 1080, 1039, 1023, 948, 926, 893, 866, 847, 817, 775, 753, 718, 688, 652, 624, 584, 556.

Compound 7

Color brown; yield 68%; m.p. >350°C (dec.). ^{1}H NMR (DMSO-d_6, δ ppm): 6.53 (s, 4H, -NH_2), 6.78–7.59 (m, 8H, -H_{1-4}), 8,14 (d, 4H, J = 12 Hz, -H_b), 8,33 (d, 4H, J = 8 Hz, -H_a). ^{13}C NMR (DMSO-d_6, ppm): 121.8 (arom. -*C*H), 122.5 (arom. -*C*H), 124.6 (arom. -*C*H), 126.5 (arom. -*C*H), 127.1 (arom. -*C*H), 128.4 (arom. -*C*H), 136.7 (arom. -*C*H), 146.9 (arom. -*C*H), 149.3 (arom. -*C*H), 149.4 (arom. -*C*H). IR (cm^{-1}): 3253, 3184, 3099, 3074, 3034, 3867, 2795, 1605, 1581, 1522, 1489, 1452, 1430, 1400, 1349, 1312, 1297, 1280, 1258, 1243, 1196, 1151, 1122, 1109, 1085, 1030, 1015, 966, 950, 931, 846, 824, 790, 752, 744, 733, 702, 686, 648, 631, 622, 599, 561, 536, 493, 461.

Compound 8

Color brown; yield 70%; m.p. 315–316°C (dec.). ^{1}H NMR (DMSO-d_6, δ ppm): 1.27 (s, 18H, -C(CH_3)$_3$), 6.63 (s, 4H, -NH_2), 6.72–6.78 (m, 4, -$H_{1,3}$), 6.94 (t, 2H, J = 8 Hz, -H_2), 7.08 (d, 2H, J = 8 Hz, -H_4), 7.50 (d, 4H, J = 8 Hz, -H_b), 7.94 (d, 2H, J = 8 Hz, -H_a). ^{13}C NMR (DMSO-d_6, ppm): 29.1 (-C(CH_3)$_3$), 31.3 (-C(CH_3)$_3$), 116.1 (arom. -*C*H), 118.5 (arom. -*C*H), 122.7 (arom. -*C*H), 126.0 (arom. -*C*H), 127.2 (arom. -*C*H), 128.1 (arom. -*C*H), 129.0 (arom. -*C*H), 135.5 (arom. -*C*H), 143.8 (arom. -*C*H), 154.6 (arom. -*C*H). IR (cm^{-1}): 3241, 3188, 3158, 3111, 2969, 2958, 2869, 1611, 1595, 1573, 1516, 1486, 1463, 1452, 1396, 1361, 1301, 1284, 1262, 1238, 1192, 1161, 1138, 1107, 1097, 1080, 1035, 1015, 979, 954, 849, 828, 813, 774, 750, 735, 704, 652, 633, 615, 573, 566, 552, 537.

Compound 9

Color brown; yield 74%; m.p. 270–272°C (dec.). ^{1}H NMR (DMSO-d$_6$, δ ppm): 3.79 (s, 6H, -OCH_3), 6.58 (s, 4H, -NH_2), 7.45 (d, 4H, J = 8 Hz, -H_b), 7.91 (d, 4H, J = 8 Hz, -H_a), 6.71–7.06 (m, 8H, -H_{1-4}).^{13}C NMR (DMSO-d$_6$, ppm): 56.0 (-OCH_3), 114.3 (arom. -CH), 121.2 (arom. -CH), 121.4 (arom. -CH), 126.2 (arom. -CH), 127.0 (arom. -CH), 129.2 (arom. -CH), 135.4 (arom. -CH), 135.7 (arom. -CH), 147.8 (arom. -CH), 161.9 (arom. -CH). IR (cm^{-1}): 3247, 3228, 3196, 3155, 3129, 2975, 2947, 2846, 1616, 1592, 1574, 1496, 1484, 1448, 1410, 1308, 1284, 1259, 1237, 1197, 1185, 1176, 1155, 1137, 1112, 1101, 1081, 1034, 1020, 946, 869, 838, 810, 800, 770, 718, 670, 649, 628, 617, 571, 554, 538, 520, 486, 457.

Compound 10

Color brown; yield 81%; m.p. 275–277°C (dec.). ^{1}H NMR ($CDCl_3$, δ ppm): 0.87 (t, 6H, J = 8 Hz, -$CH_2CH_2CH_3$), 1.58 (m, 4H, -$CH_2CH_2CH_3$), 2.59 (t, 4H, J = 8 Hz, -$CH_2CH_2CH_3$), 6.59 (s, 4H, -NH_2), 6.69–7.97 (m, 16H, -H_{1-4} and -H_{a-b}).^{13}C NMR ($CDCl_3$, ppm): 13.7 (-$CH_2CH_2CH_3$), 23.7 (-$CH_2CH_2CH_3$), 37.0 (-$CH_2CH_2CH_3$), 120.6 (arom. -CH), 120.9 (arom. -CH), 125.7 (arom. -CH), 126.6 (arom. -CH), 126.8 (arom. -CH), 128.6 (arom. -CH), 135.1 (arom. -CH), 140.5 (arom. -CH), 145.8 (arom. -CH), 147.3 (arom. -CH). IR (cm^{-1}): 3244, 3183, 3150, 3095, 2954, 2927, 2867, 1610, 1596, 1573, 1488, 1454, 1406, 1379, 1302, 1288, 1261, 1239, 1207, 1140, 1105, 1080, 1037, 1017, 977, 950, 861, 849, 799, 772, 745, 705, 679, 647, 624, 583, 558, 516.

General Procedure for the Synthesis of Compounds 11–13

A solution of **1a–f** and **4e** (0.50 mmol) in DMSO (2 ml) was added to a solution of Pd(OAc)$_2$ (0.25 mmol) in DMSO (2 ml) in a reaction flask. The reaction mixtures were stirred and heated at 70°C for 72 h and then cooled. The volatiles were removed under reduced pressure. The residues were washed with diethyl ether (30 ml) and dried under vacuum.

Data for Compounds 11–13

Compound 11

Color dark-red; yield 72%; m.p. 281–282°C (dec.). ^{1}H NMR ($CDCl_3$, δ ppm): 6.64–7.71 (m, 18H, H_{1-4} and -H_{a-c}), 7.70 (d, 4H, J = 8 Hz, -H_x), 7.90 (d, 4H, J = 8 Hz, -Hy), 8.78 (s, 2H, -N CH-). ^{13}C NMR ($CDCl_3$, ppm): 118.1 (arom. -CH), 121.7 (arom. -CH), 123.3 (arom. -CH), 126.2 (arom. -CH), 127.1 (arom. -CH), 127.4 (arom. -CH), 127.6 (arom. -CH), 128.1 (arom. -CH), 129.5 (arom. -CH), 129.7 (arom. -CH), 131.7 (arom. -CH), 132.0 (arom. -CH), 133.5 (arom. -CH), 137.6 (arom. -CH), 165.6 (-N CH-). IR (cm^{-1}): 3093, 3065, 1621, 1595, 1571, 1509, 1489, 1477, 1445, 1334, 1306, 1287, 1266, 1236, 1218, 1157, 1118, 1080, 1048, 999, 954, 918, 872, 851, 827, 809, 749, 730, 719, 702, 686, 641, 629, 586, 567, 556, 547, 516, 475.

Compound 12

Color dark-red; yield 78%; m.p. 275–277°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 3.90 (s, 6H, -OCH_3), 7.00–7.95 (m, 26H, H_{1-4}, -H_{a-c} and -$H_{x,y}$), 9.89 (s, 2H, -N CH-). ^{13}C NMR ($CDCl_3$, ppm): 55.6 (-OCH_3), 114.3 (arom. -CH), 126.1 (arom. -CH), 126.7 (arom. -CH), 127.1 (arom. -CH), 127.3 (arom. -CH), 128.4 (arom. -CH), 128.9 (arom. -CH), 129.2 (arom. -CH), 130.0 (arom. -CH), 130.3 (arom. -CH), 131.8 (arom. -CH), 132.0 (arom. -CH), 132.7 (arom. -CH), 137.1 (arom. -CH), 164.9 (-N CH-). IR (cm^{-1}): 3054, 2996, 2935, 2909, 2834, 1578, 1539, 1509, 1468, 1444, 1430, 1330, 1307, 1265, 1231, 1155, 1121, 1108, 1080, 1015, 949, 926, 848, 751, 718, 687, 652, 624, 610, 583, 555, 478.

Compound 13

Color dark-red; yield 68%; m.p. 265–266°C (dec.). ^{1}H NMR ($CDCl_3$, δ ppm): 3.74 (s, 6H, -OCH_3), 6.85 (d, 4H, J = 8 Hz, -H_b); 7.83 (d, 4H, J = 8 Hz, -H_a), 7.09–8.92 (m, 16H, -H_{1-4} and -H_{x-y}), 8.48 (s, 2H, -N CH-).^{13}C NMR ($CDCl_3$, ppm); 55.6 (-OCH_3), 113.3 (arom. -CH), 117.9 (arom. -CH), 121.2 (arom. -CH), 124.7 (arom. -CH), 125.7 (arom. -CH), 127.5 (arom. -CH), 128.3 (arom. -CH), 129.6 (arom. -CH), 129.8 (arom. -CH), 131.1 (arom. -CH), 134.2 (arom. -CH), 141.1 (arom. -CH), 141.6 (arom. -CH), 150.5 (arom. -CH), 159.8 (-N CH-). IR (cm^{-1}): 3070, 3011, 2970, 2912, 2837, 1593, 1578, 1516, 1495, 1454, 1339, 1304, 1249, 1152, 1119, 1087, 1020, 1001, 949, 853, 829, 801, 745, 715, 681, 667, 629, 551, 489, 477, 452.

Catalytic Experiments

In a typical oxidation reaction, a Schlenk tube was charged with a solvent solution of alcohol, oxidant and complex. This mixture was stirred at 70°C for an appropriate time. After completion of the reaction, the mixture was cooled to room temperature and the products extracted with diethyl ether (10 ml); they were then filtered through a pad of silica gel with copious washing and the removed volatiles were concentrated. Reactions were monitored by gas chromatography (GC) and thin-layer chromatography.

Results and Discussion

N-(2-Aminophenyl)arylsulfonamides, their Schiff base derivatives and novel Pd(II) complexes were successfully synthesized (Fig. 1). The synthesized compounds were characterized by elemental analysis, ^{1}H-NMR, ^{13}C NMR and IR spectroscopy.

Compounds **1–5** were obtained by the reaction of *o*-phenylenediamine with *R*-arylsulfonyl chloride in the presence of triethylamine in THF. Benzensulfonyl chloride, *p*-nitrobenzenesulfonyl chloride, *p*-isobutyl-benzenesulfonyl chloride, *p*-methoxybenzenesulfonyl chloride and 4-*n*-propylbenzenesulfonyl chloride compounds were used as *R*-arylsulfonyl chloride. Then, the novel Pd(II) complexes (**6–10**) were synthesized by the reaction of **1–5** with Pd(OAc)$_2$ in DMSO.

On the other hand, **1a–f** and **4e** were synthesized by the reaction of *R*′-benzaldehyde with appropriate *N*-(2-aminophenyl) arylsulfonamides in methanol. Benzaldehyde, 4-methylbenzaldehyde, 2,4-dimethylbenzaldehyde, 2,4,6-trimethylbenzaldehyde, 4-nitrobenzaldehyde and 4-methoxybenzaldehyde were used as *R*′-benzaldehyde. Then, we studied to synthesis of Pd(II) complexes of those ligands (**1a–f, 4e**). Two different situations occurred from the reaction of **1a-f** and **4e** with Pd(OAc)$_2$. In the first, when **1a–d** were used as ligands, they were hydrolyzed and the Pd(II) complex (**6**) of *N*-(2-aminophenyl)benzenesulfonamide was obtained. This situation is considered to be caused by water molecules from the solvent.[45a,b] In the second, when **1e–f**, **4e** were used as ligands, the Pd(II) complexes (**11–13**) containing Schiff base ligands were obtained. The formation of these two different situations is related to the electronic parameters.

Satisfactory elemental analysis was obtained for all compounds (Table 1). The structure of all the compounds was determined on the basis of FT-IR and NMR spectroscopy. From the ^{1}H NMR spectra, the formation of compounds (**1–13**) could clearly be seen.

In the ^{1}H NMR spectra, the -H_a, -H_b and -H_c protons were observed as doublets, triplets and triplets, respectively, in a 2:2:1 ratio around δ 7.43–7.81 ppm in *N*-(2-aminophenyl)benzenesulfonamide (**1**). Similarly, other *N*-(2-aminophenyl)arylsulfonamide

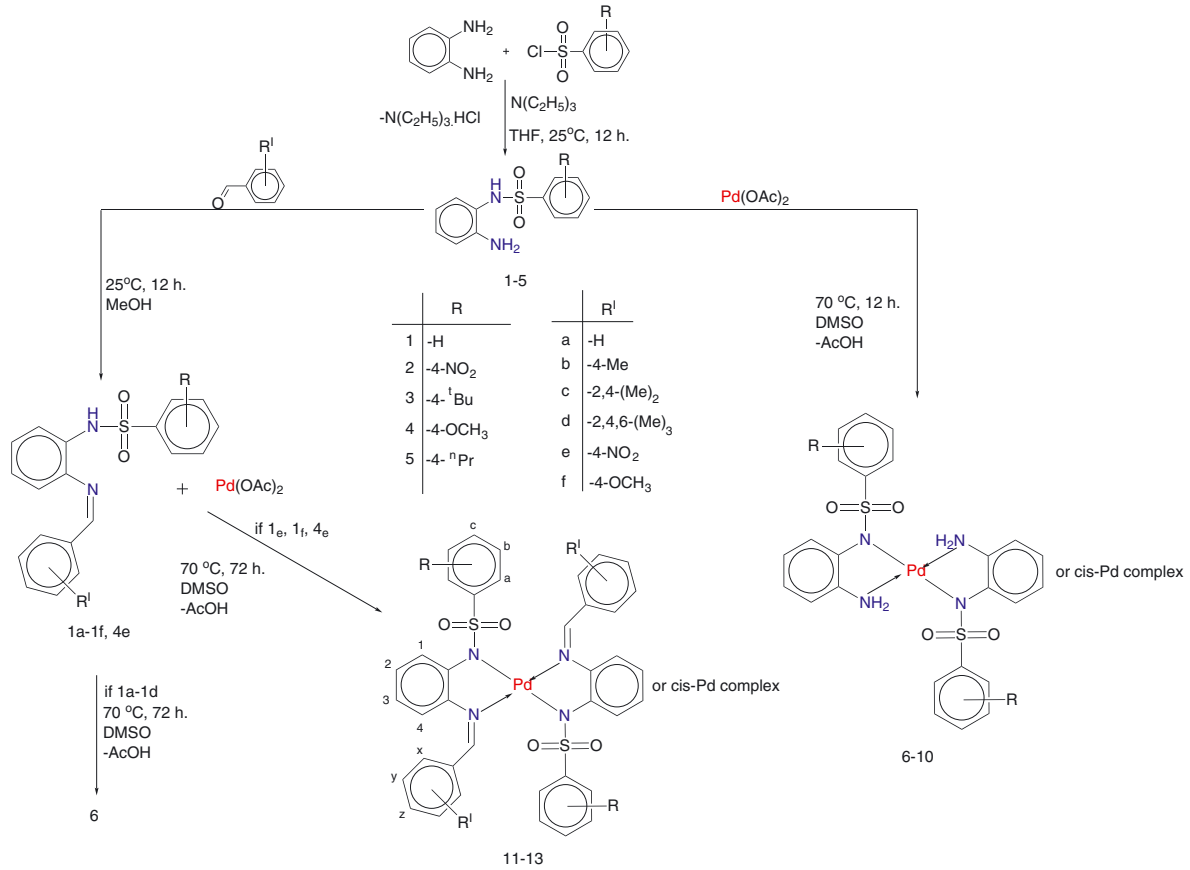


Figure 1. Synthesis of the compounds together with NMR numbering scheme.

Table 1. Analytical data for the synthesized compounds

Compound	No.	C (%)		H (%)		N (%)		S (%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$(C_{12}H_{12}N_2O_2S)$	**1**	58.05	57.13	4.87	4.91	11.28	11.25	12.91	12.90
$(C_{12}H_{11}N_3O_4S)$	**2**	49.14	49.20	3.78	3.72	14.33	14.30	10.93	10.95
$(C_{16}H_{20}N_2O_2S)$	**3**	63.13	63.15	6.62	6.59	9.20	9.24	10.53	10.48
$(C_{13}H_{14}N_2O_3S)$	**4**	56.10	56.13	5.07	5.11	10.06	10.05	11.52	11.57
$(C_{15}H_{18}N_2O_2S)$	**5**	62.04	62.07	6.25	6.22	9.65	9.64	11.04	11.06
$(C_{19}H_{16}N_2O_2S)$	**1a**	67.84	67.90	4.79	4.85	8.33	8.30	9.53	9.55
$(C_{20}H_{18}N_2O_2S)$	**1b**	68.55	68.53	5.18	5.20	7.99	7.98	9.15	9.17
$(C_{21}H_{20}N_2O_2S)$	**1c**	69.20	69.22	5.53	5.50	7.69	7.72	8.80	8.84
$(C_{22}H_{22}N_2O_2S)$	**1d**	69.81	69.84	5.86	5.90	7.40	7.41	8.47	8.50
$(C_{19}H_{15}N_3O_4S)$	**1e**	59.83	59.80	3.96	4.01	11.02	11.03	8.41	8.45
$(C_{20}H_{18}N_2O_3S)$	**1f**	65.55	65.40	4.95	4.85	7.64	7.70	8.75	8.81
$(C_{20}H_{17}N_3O_5S)$	**4e**	58.38	58.43	4.16	4.18	10.21	10.20	7.79	7.82
$Pd[C_{12}H_{11}N_2O_2S]_2$	**6**	47.96	48.02	3.69	3.76	9.32	9.38	10.67	10.74
$Pd[C_{12}H_{10}N_3O_4S]_2$	**7**	41.72	41.81	2.92	3.00	12.16	12.20	9.28	9.28
$Pd[C_{16}H_{19}N_2O_2S]_2$	**8**	53.89	53.83	5.37	5.43	7.86	7.90	8.99	8.93
$Pd[C_{13}H_{13}N_2O_3S]_2$	**9**	47.24	47.31	3.96	3.92	8.48	8.50	9.70	9.73
$Pd[C_{15}H_{17}N_2O_2S]_2$	**10**	52.59	52.50	5.00	4.92	8.18	8.16	9.36	9.40
$Pd[C_{19}H_{14}N_3O_4S]_2$	**11**	52.63	52.70	3.25	3.28	9.69	9.70	7.39	7.44
$Pd[C_{20}H_{17}N_2O_3S]_2$	**12**	57.38	57.45	4.09	4.12	6.69	6.75	7.66	7.62
$Pd[C_{20}H_{16}N_3O_5S]_2$	**13**	51.81	51.85	3.48	3.50	9.06	9.10	6.92	6.85

ligands (**2–5**), the *-H*$_a$ and *-H*$_b$ protons were observed as doublets in a 2:2 ratio around δ 6.92–8.32 ppm. *-NH*$_2$ protons were found at around δ 3.69–4.18 ppm in compounds **1–5**. In (**c**) position, the *-p-*C(*CH*$_3$)$_3$, *-p-*O*CH*$_3$ and *-CH*$_2$*CH*$_2$*CH*$_3$ protons were observed as singlet in 9 proton eq. at δ 1.33 ppm for compound **3**, singlet in 3 proton eq. at δ 3.86 ppm for compound **4**, triplet, and

multiplet and quartet in a 2:2:3 ratio at round δ 0.94–2.65 ppm for compound **5**, respectively. In the ^{13}C NMR spectra for **3–5**, the -C$(CH_3)_3$, -OCH_3 and -$CH_2CH_2CH_3$ carbons were found at 35.2, 31.1, 55.6, 38.1, 24.4 and 13.9 ppm, respectively. In the ^{1}H NMR spectra for **6–10**, the ^{1}H NMR signals shifted to lower field for the -NH_2 protons compared with free ligands (**1–5**) and were found around δ 6.53–6.63 ppm.

In the ^{1}H NMR spectra for the Schiff base ligands (**1a–f** and **4e**); the -*NH*- protons were observed around δ 7.65–7.84 ppm. Similarly, -N*CH*- proton peaks appeared around δ 8.10–8.71 ppm. In the ^{13}C NMR spectra for the Schiff base ligands (**1a–f** and **4e**), the -N*C*H- carbons were observed around 156.5–160.1 ppm. In the ^{1}H NMR spectra of Pd(II) complexes (**11–13**) bearing Schiff base ligands, the -N*H*- protons belonging to the sulfonamide groups disappeared. ^{1}H NMR signals shifted to lower fields for the -N*CH*- protons compared with **1e–f** and **4e** and were observed around δ 8.48–9.89 ppm in **11–13**. These observations show that **1e–f** and **4e** coordinate to the Pd(II) through the imine nitrogen atom and the deprotonated nitrogen of the sulfonamide group. In the ^{13}C NMR spectra of **11–13**, the signals for the -N*C*H- carbons shifted to lower fields compared with **1e–f** and **4e** and appeared around δ 159.8–165.6 ppm.

In the IR spectra for **1–5**, N-H stretching frequency peaks appeared around 3204–3240 cm^{-1} and NH_2 stretching frequency peaks were observed around 3479–3364 cm^{-1}. In the Pd(II) complexes (**6–10**), the NH_2 stretching frequency peaks appeared around 3247–3150 cm^{-1}. These bands are shifted approximately 200 cm^{-1} to a lower wavenumber which supports the participation of the -NH_2 group of these ligands in binding to the Pd (II). Also, in **1a–f** and **4e**, N-H stretching frequency peaks appeared around 3219–3208 cm^{-1} and -N CH- frequency peaks were observed around 1619–1628 cm^{-1}. In the Pd(II) complexes (**11–13**), N-H stretching frequency peaks belonging to sulfonamide groups were not observed and -N CH- frequency peaks were observed around 1621–1576 cm^{-1}. -N CH- frequency peaks are shifted 2–50 cm^{-1} to a lower wavenumber which supports the participation of the -N CH- group of these ligands in binding to Pd(II). In addition, in all the compounds (**1–13**) SO_2 stretch peaks were observed at around 1339–1105 cm^{-1}. All the measurements and interpretations are compatible with the proposed structure of ligands. The NMR data are consistent with a transoid or cisoid type of complex because they the same symmetry elements which would give the same degree of magnetic equivalence in the NMR. Therefore, the transoid or cisoid structures of the complexes have not been determined since single crystals have not been obtained. The representative IR and NMR spectra are shown in Figs S1 and S2 as supporting information.

Catalytic Studies

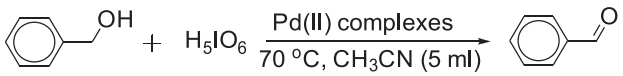
In recent times, oxidation reactions have been studied in a wide range of new ligands and their transition metal complexes as catalysts.[46–53]

In this study, we described the synthesis of a series of novel Pd(II) complexes containing sulfonamide ligands (**6–13**) which were employed as catalysts for the oxidation reaction of benzyl alcohol to benzaldehyde. The rate of oxidation is dependent on a variety of parameters such as temperature, solvent, oxidant and catalyst loading.

For the choice of oxidant, we examined H_2O_2, H_5IO_6 and O_2 of air. Experiments were also carried out in the absence of catalyst. To find the optimum conditions, a series of experiments was performed. Finally, we found that the use of 0.01 mmol novel Pd(II) complexes containing aromatic sulfonamide ligands, 1 mmol benzyl alcohol and 1 mmol H_5IO_6 in acetonitrile (5 ml) at 70°C led to the best conversions at 120 min. Under these conditions, benzaldehyde was observed as a single product. The reactions were performed under identical conditions to allow comparison of results. All the complexes showed good activity as catalysts.

The catalytic experiments showed that complex **9** was a more active catalyst than **6–8** or **10**. This situation was observed to be associated with electron-donating properties of the *R*-group. At the same time, complex **7** bearing a nitro group was observed to be more active compared to complex **6**: **9** > **8** > **10** > **7** > **6**. On the other hand, complex **11**, containing nitro group (electron-withdrawing) at the 4- position of -N CH-R′, showed better activity compared to complex **12**. Therefore, Schiff base deriva-

Table 2. Catalytic activity for the oxidation reaction of benzyl alcohol to benzaldehyde in using Pd(II) complexes



Entry	Catalyst	Yield[a] (%)	Time	Oxidant	TON[b]	TOF[c] (h^{-1})
1	**6**	32	90 min	H_5IO_6	32	21
2	**7**	46			46	31
3	**8**	84			84	56
4	**9**	93			93	62
5	**10**	76			76	51
6	**11**	91			91	61
7	**12**	49			49	33
8	**13**	42			42	28
9	**6**	71	120 min		71	35.5
10	**7**	100			100	50
11	**10**	100			100	50
12	**12**	100			100	50
13	**13**	57			57	38
14	Absence of catalyst	Trace			—	—
15	**9**	Trace[d]		H_2O_2	—	—
16	**9**	Trace[d]		O_2 of air	—	—

[a]GC yields; yields are based on benzaldehyde.
[b]TON, moles of product/moles of catalyst.
[c]TOF, moles of product/(moles of the catalyst) × (hour).
[d]H_2O_2 or O_2 of air used as oxidant.
Reaction conditions: 1.0 mmol $C_6H_5CH_2OH$, 1.0 mmol H_5IO_6, 0.01 mmol Pd(II) complexes, CH_3CN (5 ml); all reactions were monitored by TLC and GC; temperature 70°C.

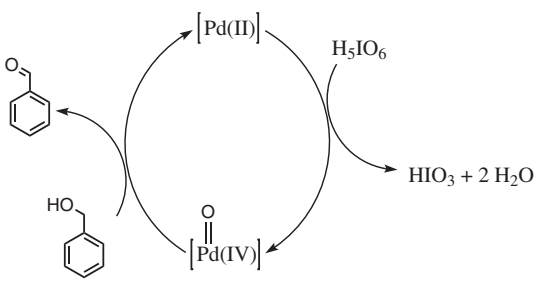


Figure 2. Proposed mechanism for oxidation of benzyl alcohol to benzaldehyde-catalyzed palladium complexes in the presence of H_5IO_6.

tive **4e** was synthesized using **4** and 4-nitrobenzaldehyde. Pd(II) complexes of **4e** were then synthesized (**13**). In this way, we hoped to synthesize the best catalyst. However, compound **13** as not as good a catalyst as expected. The results are summarized in Table 2.

All the experiments were carried out in an air atmosphere since there was no change in conversion if the reaction is carried out under argon. This indicates that air is not involved in the oxidation process and palladium complexes are air-stable. A plausible mechanism has been proposed for the above described results (Fig. 2). The mechanistic studies suggest that an initial carbonyl-bound palladium(IV) species is generated upon reaction with H_5IO_6 and concomitant loss of water molecules. The loaded catalysts then regenerate and initiate a second catalytic cycle.[54,55]

Conclusion

We reported the synthesis and characterization of a series of the Pd(II) complexes bearing aromatic sulfonamides, and their catalytic activities for the oxidation reaction of benzyl alcohol to benzaldehyde using H_5IO_6 in acetonitrile.

Catalytic experiments showed that the novel Pd(II) synthesized complexes **6–13** showed good activity as catalysts. The catalytic activity increased in the order **13** < **6** < **7** < **12** < **10** < **8** < **11** < **9** for a 90 min period. However, the catalytic experiments indicate that Pd complexes containing imine hydrolyzed or unhydrolyzed sulfonamide ligands such as **9** and **11** have similar catalytic activity. These observations could be explained by the sulfonamide groups being an active site in the catalytic cycle.

Acknowledgments

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