

## Supporting Information

### Synthesis and Characterisation of 1

A  $\text{CHCl}_3$  solution of  $\text{I}_2$  (2.050 g; 250 mL) is slowly added to a  $\text{CHCl}_3$  solution of  $\text{Me}_2\text{dazdt}$  prepared according to ref. 5 (0.750 g; 100 mL). The solution darkens and shiny red-brown micro-crystals of **1** precipitate immediately. Well-shaped crystals of **1**, suitable for X-ray studies, are obtained from the filtrate in an almost quantitative yield by slow evaporation of the solvent, and washing with petroleum ether (40-60°). Characterisation: *Anal.* Found: C% 12.33; H% 1.76; N% 4.05; S% 9.11; Calcd. for  $\text{C}_7\text{H}_{12}\text{N}_2\text{S}_2\text{I}_4$  (695.919): C% 12.08; H% 1.74; N% 4.03; S% 9.22; *IR* ( $\text{cm}^{-1}$ ): 2930vw, 2860vw, 1530vs, 1450w, 1426vw, 1396m, 1384mw, 1351w, 1334mw, 1287mw, 1272m, 1259m, 1190vw, 1113m, 1082vw, 1019w, 967m, 824s, 739w, 682vw, 600s, 537w, 515vw, 441vw, 405w, 307w, 261w, 150vs, 114s, 95m; *Raman* ( $\text{cm}^{-1}$ ): 2986vw, 2954w, 2925mw, 1531w, 1451w, 1398w, 1286vw, 1259vw, 968vw, 876vw, 683m, 600w, 539w, 438m, 407w, 263s, 146vs; *UV-Vis* (in  $\text{CH}_3\text{CN}$ ) [ $\epsilon = \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ]: 238 (9500), 277 (13000), 300 (13000), 360 (3500), 438sh.

### Synthesis and Characterisation of 2

**2** has been prepared by stirring a THF solution of **1** (210 mg; 150 mL) with Pd-powder (12.3 mg, ACROS 99.99%) at room temperature. The colour of the solution turns from red-orange to brown with the formation of **2**. After approximately 1 h the palladium powder disappears. Well-shaped crystals of **2**, suitable for X-ray characterisation, are obtained from THF/ $\text{Et}_2\text{O}$ . Characterisation: *Anal.* Found: C% 13.81, H% 1.92, N% 4.50, S% 10.19; Calcd. for  $\text{PdC}_{14}\text{H}_{24}\text{N}_4\text{S}_4\text{I}_6$  (1244.458): C% 13.51; H% 1.94, N% 4.50, S% 10.31; *IR* ( $\text{cm}^{-1}$ ): 2920vw, 2860vw, 1518vs, 1451m, 1433mw, 1400ms, 1385s, 1352w, 1329mw, 1287ms, 1264s, 1159w, 1117s, 1105sh, 1078m, 1044mw, 1026w, 964m, 900w, 831w, 752mw, 688w, 616m, 557w, 533mw, broad band centered at 390m, 321w, 127ms; *Raman* ( $\text{cm}^{-1}$ ): 2991m, 2944m, 2936m, 2921ms, 2905m, 2856mw, 1535s, 1459mw, 1447mw, 1400m, 1357s, 1330w, 1269ms, 1218mw, 1182w, 1125mw, 1073w, 902mw, 832vw,

691w, 621mw, 535mw, 355m, 114vs; *UV-Vis* (in  $CH_3CN$ ) [ $\epsilon = dm^3 mol^{-1} cm^{-1}$ ]: 292 (112000), 357 (57500), 475sh.

## **Materials and Methods**

### ***Characterisation of Reagents and Products***

Microanalyses: Carlo Erba CHNS elemental analyser EA1108.

MIR spectra: on KBr pellets, Perkin Elemer mod. 983 spectrometer.

FIR spectra: on polyethylene pellets, Bruker EQUINOX 55 FT-spectrometer.

FT-Raman spectra: on solid sample in a capillary tube, resolution  $\pm 4 cm^{-1}$ , power 50 mW, Bruker RFS100 FT-spectrometer operating with an excitation frequency of 1064 nm, Nd:YAG laser, and an InGaAs detector.

Electronic spectra: Varian Cary 5 Spectrophotometer.

### ***Characterisation of catalysts***

Powder XRD spectra of the fresh and aged catalysts were collected on a Siemens Kristalloflex Mod. F instrument (Ni-filtered  $CuK\alpha$ ). BET surface areas were obtained from  $N_2$  adsorption isotherms at 77 K on a Micrometrics ASAP 2000 analyser.

### ***Analytical procedure for Pd determination***

The Pd content has been determined by ICP-AES Varian Liberty 200 Spectrometer, following an acid disgregation ( $HNO_3/H_2SO_4$ , 3:1 volume ratio) of the residue obtained by filtration of the solution of **2** from the catalyst and after solvent evaporation. A calibration plot has been obtained by using five standards in the 1-10 ppm range. The sample solution has been prepared diluting the disgregated solution in water containing few drops of HCl conc., to achieve a  $\sim 6$  ppm concentration.

All reagents and solvents were used as furnished by Aldrich.

## X-ray Characterization

**Data Collection and Structure Determination**<sup>1</sup>. Diffraction data were collected at room temperature on a Philips PW 1100 and on a Siemens AED diffractometers for **1** and **2** respectively. The space groups were chosen on the basis of the systematic extinctions and intensity statistics. The intensities recorded by the  $\varphi$ - $2\theta$  scan technique, were corrected for Lorentz and polarization effects. The empirical methods of Walker and Stuart<sup>1</sup> was used for the absorption correction for both compounds. The structure was solved by direct methods through Sir92<sup>2</sup> program and refined by full-matrix least-squares using SHELXL-97<sup>3</sup> program with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions and refined by use of a "riding" model correction on the corresponding carbon atoms. The refinement of **2** gave high thermal parameters for the atoms of one of I<sub>3</sub><sup>-</sup> ions when the central atom was constrained to lie on a symmetry centre. Refinement with the above cited atom off the symmetry centre and with an occupancy factor of 0.5 for the three atoms was successful. The agreement factors for the final model are:  $R_1$  0.0293 and 0.0463,  $wR_2$  0.0774 and 0.1413 [ $I > 2\sigma(I)$ ],  $R_{int}$  2.26% and 3.05% for **1** and **2** respectively. The refinement results including atomic parameters, bond distances, and angles are listed in Tables **1** and **2**.

## REFERENCES

- (1) Walker, N. and Stuart, D. *Acta Crystallogr.* 39A, 158 (1983); Ugozzoli, F., *Comput. Chem.*, 11, 109 (1987).
- (2) Altomare, A., Cascarano, C., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G., Camalli, M. *J. Appl. Crystallogr.*, 27, 435 (1994).
- (3) Sheldrick, G.M. SHELXL-97: *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

**Table S1.** Crystallographic Data of Compounds **1** and **2**

Compound	Me <sub>2</sub> dazdt·2I <sub>2</sub> ( <b>1</b> )	[Pd(Me <sub>2</sub> dazdt) <sub>2</sub> (I <sub>3</sub> ) <sub>2</sub> ] ( <b>2</b> )
Chemical formula	C <sub>7</sub> H <sub>12</sub> I <sub>4</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>24</sub> N <sub>4</sub> PdS <sub>4</sub>
Formula weight	695.92	1244.41
Crystal system	monoclinic	monoclinic
Space group	<i>P2/n</i> (No.13 )	<i>C2/c</i> (No. 15)
<i>a</i> , Å	8.680 (6)	27.354 (5)
<i>b</i> , Å	7.713 (7)	10.429 (7)
<i>c</i> , Å	12.740 (5)	10.823 (7)
<i>b</i> , deg	94.38 (2)	91.36 (2)
<i>V</i> , Å <sup>3</sup>	850.4 (1.0)	3087 (3)
<i>Z</i>	2	4
D <sub>c</sub> /Mgm <sup>-3</sup>	2.718	2.678
Wavelength, λ/Å	Mo-Kα (0.71073)	Mo-Kα (0.71073)
T/K	293 (2)	293 (2)
<i>m</i> , cm <sup>-1</sup>	75.52	68.84
Reflns collected	2561	3550
Ind. reflns	2469	3381
<i>R</i> [ <i>I</i> >2σ( <i>I</i> )] <sup>a</sup>	0.0293	0.0463
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.0774	0.1413

$${}^a R = \sum |F_o - F_c| / \sum |F_o| . \quad {}^b wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$$

<sup>1</sup> Compound **1**: Me<sub>2</sub>dazdt·2I<sub>2</sub>, Compound **2**: [Pd(Me<sub>2</sub>dazdt)<sub>2</sub>](I<sub>3</sub>)<sub>2</sub>

**Table S2.** Selected bond lengths [Å] and angles [deg] for:**a) Me<sub>2</sub>dazdt·2I<sub>2</sub> (1)**

I (1) - I (2)	2.8183 (18)	N-C (2)	1.474 (5)
I (1) - S	2.786 (2)	N-C (4)	1.463 (6)
S-C (1)	1.683 (4)	C (1) - C (1')	1.502 (7)
N-C (1)	1.315 (5)	C (2) - C (3)	1.517 (6)
S-I (1) - I (2)	175.07 (2)	N-C (1) - C (1')	116.1 (3)
C (1) - S - I (1)	104.77 (13)	N-C (1) - S	125.0 (3)
C (1) - N - C (2)	118.5 (4)	C (1') - C (1) - S	118.9 (2)
C (1) - N - C (4)	120.6 (4)	N-C (2) - C (3)	111.5 (4)
C (4) - N - C (2)	120.4 (4)	C (2') - C (3) - C (2)	113.5 (5)

Symmetry transformation used to generate equivalent atoms:

('): -x+3/2, y, -z+1/2

**b) [Pd(Me<sub>2</sub>dazdt)<sub>2</sub>](I<sub>3</sub>)<sub>2</sub> (2)**

I (1) - I (2)	2.9204 (15)	N (1) - C (5)	1.477 (12)
I (3) - I (4)	2.881 (12)	N (1) - C (6)	1.474 (14)
I (4) - I (5)	2.935 (12)	N (2) - C (2)	1.298 (13)
Pd-S (1)	2.312 (3)	N (2) - C (3)	1.456 (14)
Pd-S (2)	2.298 (3)	N (2) - C (7)	1.470 (14)
S (1) - C (1)	1.658 (11)	C (1) - C (2)	1.472 (15)
S (2) - C (2)	1.704 (12)	C (3) - C (4)	1.522 (16)
N (1) - C (1)	1.324 (12)	C (4) - C (5)	1.523 (15)
I (2) - I (1) - I (2 <sup>ii</sup> )	176.55 (6)	C (3) - N (2) - C (7)	115.0 (10)
I (3) - I (4) - I (5)	178.5 (8)	N (1) - C (1) - C (2)	118.7 (10)
S (1) - Pd - S (2 <sup>i</sup> )	89.83 (11)	N (1) - C (1) - S (1)	124.3 (8)
S (1) - Pd - S (2)	90.17 (11)	C (2) - C (1) - S (1)	117.1 (8)
C (1) - S (1) - Pd	101.0 (4)	N (2) - C (2) - C (1)	120.4 (10)
C (2) - S (2) - Pd	97.1 (4)	N (2) - C (2) - S (2)	122.0 (9)
C (1) - N (1) - C (5)	121.0 (9)	C (1) - C (2) - S (2)	117.6 (9)
C (1) - N (1) - C (6)	121.5 (10)	N (2) - C (3) - C (4)	115.3 (10)
C (5) - N (1) - C (6)	117.4 (10)	C (3) - C (4) - C (5)	109.7 (9)
C (2) - N (2) - C (3)	120.7 (10)	N (1) - C (5) - C (4)	110.7 (9)
C (2) - N (2) - C (7)	124.2 (11)		

Symmetry transformations used to generate equivalent atoms:

(i): -x+1, -y, -z+1; (ii): -x+1, y, -z+1/2

## Synthesis and Characterization of Model Three-Way Catalysts

$\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  (10 wt.%) /  $\text{Al}_2\text{O}_3$  was prepared by impregnating  $\delta\text{-Al}_2\text{O}_3$  with cerium/zirconium citrate solution. 4.72 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.99%, Aldrich) and 2.46 g of  $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.99%, Aldrich) were dissolved in 40 mL, then 30 mL of a 1.25 M water solution of  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$  (99.8%, Carlo Erba) was added. The metal cation to ligand ratio was 1 to 2.1. The resulting solution was stirred at 75 °C for 5 hrs, then at room temperature for 12 hrs, and finally concentrated to 15 mL in order to carry out an “incipient wetness” impregnation on 25.0 g of the  $\text{Al}_2\text{O}_3$  support (pore volume of 0.6 mL/g). The material was dried at 120 °C for 12 hrs, heated up to 500 °C (heating rate: 3 °C/min) and then calcined at this temperature for 5 hrs to obtain a yellow powder. Pd (0.5 – 3 wt. %) was loaded onto the support by “incipient wetness” technique using a palladium nitrate solution. A Pd-impregnated  $\delta\text{-Al}_2\text{O}_3$  was prepared as a conventional standard. After drying, the materials were calcined at 500 °C for 5 hrs (heating rate of 3 °C/min). Finally all catalysts were aged by calcination in air at 1050 °C for 200 hrs. Thus following ageing, a strong sintering of all the catalysts occurred and the total surface area decreased from 100 m<sup>2</sup>/g to below 15 m<sup>2</sup>/g, concomitantly with the transformation of  $\delta$ -alumina into  $\alpha$ -alumina. In the ceria-zirconia based catalysts, this phase transition was kinetically inhibited. Finally, the severe ageing protocol induced a phase segregation of the  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  solid solution in a  $\text{CeO}_2$  rich phase and a  $\text{ZrO}_2$  rich one. (Figure 1)

Figure 1: Powder XRD spectra of (1) 0.7% Pd/Al<sub>2</sub>O<sub>3</sub> (2) 0.7% Pd/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub>(10%)/Al<sub>2</sub>O<sub>3</sub> e (3) 2.8% Pd/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub>(10%)/Al<sub>2</sub>O<sub>3</sub> calcined at 1050°C for 200 h.

