

SUPPORTING INFORMATION

**ortho-Metallated triphenylphosphine chalcogenide complexes of platinum and palladium: synthesis and catalytic activity**

Steven H. Privér, Martin A. Bennett, Anthony C. Willis, Srinivas Pottabathula, M. Lakshmi Kantam and Suresh K. Bhargava

Table S1. Crystal and refinement data for complexes **1**, **2**, **4**, **8**, **9**, **11-14**, **16**, **17** and **20**.

	<b>1</b>	<b>2</b>	<b>4</b>	<b>8</b>
Empirical formula	C <sub>36</sub> H <sub>28</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>36</sub> H <sub>28</sub> P <sub>2</sub> PtSe <sub>2</sub> ·2(C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	C <sub>36</sub> H <sub>28</sub> P <sub>2</sub> PdSe <sub>2</sub> ·2(C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	C <sub>40</sub> H <sub>34</sub> O <sub>4</sub> P <sub>2</sub> Pd <sub>2</sub> S <sub>2</sub>
Formula weight	781.79	1073.49	984.80	917.59
Temperature (K)	200(2)	200(2)	200(2)	200(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.6154(1)	16.0935(4)	16.0798(2)	10.9570(1)
<i>b</i> (Å)	19.0693(2)	11.4059(2)	11.3798(2)	12.5765(2)
<i>c</i> (Å)	17.4036(2)	22.5098(4)	22.5745(3)	15.0107(2)
$\alpha$ (°)				102.7197(7)
$\beta$ (°)	99.0430(3)	107.2742(10)	107.2684(8)	103.9060(9)
$\gamma$ (°)				103.1252(8)
<i>V</i> (Å <sup>3</sup> )	3151.44(6)	3945.55(14)	3944.60(10)	1871.00(5)
<i>Z</i>	4	4	4	2
Colour and habit	Yellow plate	Yellow plate	Yellow block	Orange block
Crystal size (mm <sup>3</sup> )	0.36 × 0.15 × 0.09	0.35 × 0.26 × 0.04	0.43 × 0.29 × 0.23	0.31 × 0.14 × 0.14
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.648	1.807	1.658	1.629
$\mu$ (mm <sup>-1</sup> )	4.71	5.78	2.70	1.20
Number of independent reflections ( <i>R</i> <sub>int</sub> )	9227 (0.052)	4539 (0.093)	5748 (0.065)	10937 (0.032)
Number of observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	6853	3488	5747	9564
Number of parameters refined	370	260	260	515
<i>R</i> ( <i>F</i> <sup>2</sup> )	0.025	0.047	0.033	0.028
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.134	0.117	0.094	0.069
$\rho_{\text{max}}/\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.71/-1.49	2.70/-1.24	0.87/-0.71	0.49/-0.99

	<b>9</b>	<b>11</b>	<b>12</b>
Empirical formula	C <sub>23</sub> H <sub>21</sub> O <sub>2</sub> PPdS	C <sub>36</sub> H <sub>29</sub> ClP <sub>2</sub> PdS	C <sub>54</sub> H <sub>42</sub> Cl <sub>3</sub> P <sub>3</sub> Pd <sub>3</sub> S <sub>3</sub> ·CH <sub>3</sub> OH
Formula weight	498.86	697.49	1335.59
Temperature (K)	200(2)	200(2)	200(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	9.1580(2)	9.1347(1)	19.7141(2)
<i>b</i> (Å)	16.9618(3)	10.9341(2)	11.2461(1)
<i>c</i> (Å)	27.7043(6)	15.6582(3)	24.1286(2)
$\alpha$ (°)		86.7318(11)	
$\beta$ (°)	90.7247(12)	84.7318(11)	98.3879(4)
$\gamma$ (°)		76.1404(11)	
<i>V</i> (Å <sup>3</sup> )	4303.14(15)	1511.22(4)	5292.25(8)
<i>Z</i>	8	2	4
Colour and habit	Yellow needle	Pale yellow plate	Yellow block
Crystal size (mm <sup>3</sup> )	0.27 × 0.10 × 0.09	0.27 × 0.12 × 0.05	0.27 × 0.12 × 0.11
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.540	1.533	1.679
$\mu$ (mm <sup>-1</sup> )	1.05	0.90	1.41
Number of independent reflections ( <i>R</i> <sub>int</sub> )	7579 (0.079)	8844 (0.033)	15457 (0.061)
Number of observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	5327	7938	13010
Number of parameters refined	505	370	632
<i>R</i> ( <i>F</i> <sup>2</sup> )	0.038	0.029	0.031
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.086	0.070	0.077
$\rho_{\max}/\rho_{\min}$ (e Å <sup>-3</sup> )	1.28/-1.18	0.70/-0.83	1.50/-0.81

	13	14	16
Empirical formula	C <sub>36</sub> H <sub>29</sub> ClP <sub>2</sub> PdSe	C <sub>54</sub> H <sub>43</sub> Cl <sub>2</sub> P <sub>3</sub> Pd <sub>2</sub> Se ·0.376(CH <sub>3</sub> OH)	C <sub>57</sub> H <sub>49</sub> Cl <sub>2</sub> P <sub>3</sub> Pd <sub>2</sub> Se ·CH <sub>2</sub> Cl <sub>2</sub> ·CH <sub>3</sub> OH
Formula weight	744.39	1159.56	1306.58
Temperature (K)	200(2)	200(2)	200(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.0444(2)	19.3124(2)	12.3781(2)
<i>b</i> (Å)	32.6774(6)	12.3355(1)	12.4707(2)
<i>c</i> (Å)	10.7989(2)	22.5574(2)	19.1951(4)
$\alpha$ (°)			74.7759(8)
$\beta$ (°)	94.9592(8)	114.9619(4)	86.7437(11)
$\gamma$ (°)			76.0615(11)
<i>V</i> (Å <sup>3</sup> )	3179.64(11)	4871.83(8)	2776.81(9)
<i>Z</i>	4	4	2
Colour and habit	Yellow block	Yellow prism	Yellow plate
Crystal size (mm <sup>-3</sup> )	0.36 × 0.18 × 0.11	0.42 × 0.20 × 0.14	0.35 × 0.19 × 0.09
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.555	1.581	1.563
$\mu$ (mm <sup>-1</sup> )	1.94	1.73	1.62
Number of independent reflections ( <i>R</i> <sub>int</sub> )	7249 (0.072)	14243 (0.043)	12702 (0.051)
Number of observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	5460	11684	10343
Number of parameters refined	370	578	642
<i>R</i> ( <i>F</i> <sup>2</sup> )	0.024	0.028	0.038
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.093	0.061	0.100
$\rho_{\max}/\rho_{\min}$ (e Å <sup>-3</sup> )	0.55/-0.66	0.85/-0.73	1.07/-1.02

	<b>17</b>	<b>20a</b>	<b>20b</b>
Empirical formula	C <sub>32</sub> H <sub>26</sub> NO <sub>2</sub> PPdS	C <sub>31</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> PPdS	C <sub>31</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> PPdS
Formula weight	626.00	687.87	687.87
Temperature (K)	200(2)	200(2)	200(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
<i>a</i> (Å)	10.2542(2)	8.2026(2)	13.0481(2)
<i>b</i> (Å)	11.4908(2)	11.3200(3)	9.1069(2)
<i>c</i> (Å)	12.9393(3)	15.5766(4)	23.0277(3)
$\alpha$ (°)	106.1144(9)	81.6051(12)	
$\beta$ (°)	109.7145(12)	84.9680(17)	91.5870(11)
$\gamma$ (°)	96.5437(12)	71.6954(16)	
<i>V</i> (Å <sup>3</sup> )	1342.05(5)	1357.09(6)	2735.28(8)
<i>Z</i>	2	2	4
Colour and habit	Yellow block	Yellow block	Orange needle
Crystal size (mm <sup>3</sup> )	0.34 × 0.14 × 0.08	0.20 × 0.11 × 0.06	0.37 × 0.04 × 0.02
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.549	1.683	1.670
$\mu$ (mm <sup>-1</sup> )	0.86	2.12	2.10
Number of independent reflections ( <i>R</i> <sub>int</sub> )	6148 (0.038)	6216 (0.060)	5392 (0.079)
Number of observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	5466	5068	4351
Number of parameters refined	421	421	352
<i>R</i> ( <i>F</i> <sup>2</sup> )	0.027	0.031	0.031
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.067	0.068	0.067
$\rho_{\max}/\rho_{\min}$ (e Å <sup>-3</sup> )	0.47/-0.72	0.64/-0.81	0.82/-0.85