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Persistence of C–H... $\pi$ (chelate ring) interactions in the crystal structures of palladium bis(*O*-alkyldithiocarbonate)s, Pd(S<sub>2</sub>COR)<sub>2</sub>. The utility of Pd(S<sub>2</sub>COR)<sub>2</sub> as precursors for palladium sulphide materials

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#### Tables S(1)-S(12).

## Preamble:

Each of Tables S(1)-S(12) gives a molecular structure diagram, an outline of the synthesis and key characterisation data.

#### Source of materials:

All solvents were from Merck and used as supplied.  $Pd(NO_3)_2$  (Fluke). The potassium salts of the respective xanthate ligands were prepared by dissolving KOH (*ca* 0.05 mol) in excess of the respective alcohol followed by the slow addition of an equivalent amount of CS<sub>2</sub>. The precipitate which formed was filtered off, dried *in vacuo* and used without any further purification.

#### Instrumentation:

Elemental analyses were performed on a Perkin Elmer PE 2400 CHN Elemental Analyser. Melting points were determined on a Krüss KSP1N melting point meter. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub> solution on a Bruker Avance 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane. For the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the potassium salts of the xanthate ligands, D<sub>2</sub>O was the solvent and EMSURE® grade acetonitrile (Merck) was used as the internal reference. Abbreviations for NMR assignments: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; tt, triplet of triplets; tq, triplet of quartets; tsept, triplet of septets; *m*, multiplet. For the UV/vis measurements, stock solutions (10  $\mu$ M) were prepared in EMSURE® grade acetonitrile. The optical absorption spectra were measured in the range 190-1100 nm on a single-beam Agilent Cary 60 UV-Vis spectrophotometer at room temperature. IR spectra were measured on a Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer from 4000 to 400 cm<sup>-1</sup>; abbreviations: s, strong. Powder X-ray diffraction (PXRD) data were recorded with a PANalytical Empyrean XRD system with Cu-K $\alpha$ 1 radiation ( $\lambda = 1.54056$  Å) in the 20 range 5 to 50°. The comparison between experimental and calculated (from CIF's) PXRD patterns were performed with X'Pert HighScore Plus [X'Pert HighScore Plus. PANalytical B.V. Almelo, The Netherlands, 2009].

**Table S(1).** Molecular structure of bis(O-methylxanthato)palladium(II),  $[Pd(S_2COMe)_2]$  (1), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium methylxanthate (0.0125 mol, 1.8283 g) and palladium(II) nitrate (0.0063 mol, 1.4402 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (5 x 100 ml) until no colour was evident in the chloroform extract. The orange blocks formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a dichloromethane and hexane mixture (200 ml; 1:1  $\nu/\nu$ ). Orange blocks formed after 2 days. Yield: 1.76 g, 88 %. M. pt: 388.8–390.7 K. *Anal.* Calc'd for C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 14.98; H, 1.89. Found: C, 14.69; H, 1.92 %. FTIR (cm<sup>-1</sup>): 1232 (*s*)  $\nu$ (C-O), 1028 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.18 (*s*, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>:  $\delta$  234.7 (CS); 57.8 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 236 ( $\epsilon$  = 15690; n  $\rightarrow \sigma^*$ , CT); 282 ( $\epsilon$  = 35190;  $\pi \rightarrow \pi^*$ ); 379 ( $\epsilon$  = 3250; n  $\rightarrow \pi^*$ , CT); 457 ( $\epsilon$  = 110; *d-d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(2).** Molecular structure of bis(O-ethylxanthato)palladium(II),  $[Pd(S_2COEt)_2]$  (2), showing atom labelling and displacement ellipsoids at the 50% probability level.



#### Synthesis and characterisation:

Potassium ethylxanthate (0.0115 mol, 1.8382 g) and palladium(II) nitrate (0.0058 mol, 1.3213 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (5 x 100 ml) until no colour was evident in the chloroform extract. The orange plates formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a dichloromethane and hexane mixture (200 ml; 1:1  $\nu/\nu$ ). Orange plates formed after 2 days. Yield: 1.85 g, 93 %. M. pt: 413.3–414.4 K. *Anal.* Calc'd for C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 20.66; H, 2.89. Found: C, 21.02; H, 2.50 %. FTIR (cm<sup>-1</sup>): 1244 (*s*)  $\nu$ (C-O), 1015 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.70 (*q*, 2H, CH<sub>2</sub>, *J* = 7.1 Hz), 1.52 (*t*, 3H, CH<sub>3</sub>, *J* = 7.1 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>:  $\delta$  233.7 (CS), 68.3 (CH<sub>2</sub>), 13.8 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 20840; n  $\rightarrow \sigma^*$ , CT); 284 ( $\varepsilon$  = 50080;  $\pi \rightarrow \pi^*$ ); 379 ( $\varepsilon$  = 4400; n  $\rightarrow \pi^*$ , CT); 457 ( $\varepsilon$  = 150; *d*-*d*, <sup>1</sup>A<sub>1g}  $\rightarrow$ <sup>1</sup>E<sub>g</sub>).</sub>



**Table S(3).** Molecular structure of  $bis(O-n-propylxanthato)palladium(II), [Pd(S_2CO-n-Pr)_2]$  (3), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium n-propylxanthate (0.0106 mol, 1.8477 g) and palladium(II) nitrate (0.0053 mol, 1.2213 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (4 x 100 ml) until no colour was evident in the chloroform extract. The orange plates formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a dichloromethane and hexane mixture (200 ml; 1:1  $\nu/\nu$ ). Orange plates formed after 2 days. Yield: 1.67 g, 84 %. M. pt: 402.7–403.4 K. *Anal.* Calc'd for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 25.50; H, 3.74. Found: C, 25.62; H, 3.42 %. FTIR (cm<sup>-1</sup>): 1236 (*s*)  $\nu$ (C-O), 1023 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.59 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 1.91 (*tq*, 2H, CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>t</sub> = 7.0, *J*<sub>q</sub> = 7.1 Hz), 1.05 (*t*, 3H, CH<sub>3</sub>, *J* = 7.4 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>:  $\delta$  233.8 (CS), 73.6 (OCH<sub>2</sub>), 21.7 (CH<sub>2</sub>CH<sub>3</sub>), 10.3 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 18500; n  $\rightarrow \sigma^*$ , CT); 284 ( $\varepsilon$  = 45650;  $\pi \rightarrow \pi^*$ ); 380 ( $\varepsilon$  = 3920; n  $\rightarrow \pi^*$ , CT); 461 ( $\varepsilon$  = 140; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(4).** Molecular structure of bis(*O*-isopropylxanthato)palladium(II),  $[Pd(S_2CO-i-Pr)_2]$  (4), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium isopropylxanthate (0.0106 mol, 1.8477 g) and palladium(II) nitrate (0.0053 mol, 1.2213 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was extracted with further chloroform (3 x 100 ml) until no colour was evident in the chloroform extract. The orange blocks formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a dichloromethane and hexane mixture (200 ml; 1:1  $\nu/\nu$ ). Orange blocks formed after 2 days. Yield: 1.58 g, 79 %. M. pt: 416.8–417.4 K. *Anal.* Calc'd for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 25.50; H, 3.74. Found: C, 25.59; H, 3.50 %. FTIR (cm<sup>-1</sup>): 1271 (*s*)  $\nu$ (C-O), 1006 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  5.61 (*sept*, 1H, CH, *J* = 6.2 Hz), 1.49 (*d*, 6H, CH<sub>3</sub>, *J* = 6.2 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  232.7 (CS), 77.8 (CH), 21.7 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 238 ( $\varepsilon$  = 20240; n  $\rightarrow \sigma^*$ , CT); 285 ( $\varepsilon$  = 52030;  $\pi \rightarrow \pi^*$ ); 379 ( $\varepsilon$  = 4420; n  $\rightarrow \pi^*$ , CT); 461 ( $\varepsilon$  = 160; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(5).** Molecular structure of bis(O-n-butylxanthato)palladium(II),  $[Pd(S_2CO-n-Bu)_2]$  (5), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium n-butylxanthate (0.0099 mol, 1.8606 g) and palladium(II) nitrate (0.0049 mol, 1.1382 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (3 x 100 ml) until no colour was evident in the chloroform extract. The orange plates formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a dichloromethane and hexane mixture (200 ml; 1:1  $\nu/\nu$ ). Orange needles formed after 2 days. Yield: 1.82 g, 91 %. M. pt: 392.4–392.9 K. *Anal.* Calc'd for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 29.66; H, 4.48. Found: C, 29.75; H, 4.62 %. FTIR (cm<sup>-1</sup>): 1266 (*s*)  $\nu$ (C-O), 1010 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.63 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.5 Hz), 1.86 (*tt*, 2H, OCH<sub>2</sub>CH<sub>2</sub>, *J* = 6.1 Hz, *J* = 7.6 Hz), 1.49 (*tq*, 2H, CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>t</sub> = 7.5 Hz, *J*<sub>q</sub> = 7.5 Hz), 0.98 (*t*, 3H, CH<sub>3</sub>, *J* = 7.4 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.8 (CS), 72.0 (OCH<sub>2</sub>), 30.2 (OCH<sub>2</sub>CH<sub>2</sub>), 19.0 (CH<sub>2</sub>CH<sub>3</sub>), 13.6 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 18260; n  $\rightarrow \sigma^*$ , CT); 284 ( $\varepsilon$  = 45650;  $\pi \rightarrow \pi^*$ ); 380 ( $\varepsilon$  = 3840; n  $\rightarrow \pi^*$ , CT); 457 ( $\varepsilon$  = 120; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(6).** Molecular structure of  $bis(O-isobutylxanthato)palladium(II), [Pd(S_2CO-i-Bu)_2] (6), showing atom labelling and displacement ellipsoids at the 50% probability level.$ 



#### Synthesis and characterisation:

Potassium isobutylxanthate (0.0099 mol, 1.8606 g) and palladium(II) nitrate (0.0049 mol, 1.1382 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (3 x 100 ml) until no colour was evident in the chloroform extract. The orange plates formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a chloroform and acetonitrile mixture (200 ml; 3:1  $\nu/\nu$ ). Orange blocks formed after 2 days. Yield: 1.90 g, 95 %. M. pt: 439.0–439.6 K. *Anal.* Calc'd for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 29.66; H, 4.48. Found: C, 29.67; H, 4.39 %. FTIR (cm<sup>-1</sup>): 1233 (*s*)  $\nu$ (C-O), 1030 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.40 (*d*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 2.20 (*tsept*, 1H, CH, *J* = 6.7 Hz, *J* = 6.7 Hz), 1.04 (*d*, 6H, CH<sub>3</sub>, *J* = 6.7 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.8 (CS), 77.8 (OCH<sub>2</sub>), 27.7 (CH), 19.0 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 18790; n  $\rightarrow \sigma^*$ , CT); 285 ( $\varepsilon$  = 48130;  $\pi \rightarrow \pi^*$ ); 381 ( $\varepsilon$  = 3990; n  $\rightarrow \pi^*$  CT); 461 ( $\varepsilon$  = 110; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(7).** Molecular structure of  $bis(O-n-pentylxanthato)palladium(II), [Pd(S_2CO-n-Pent)_2]$ (7), showing atom labelling and displacement ellipsoids at the 50% probability level.



#### Synthesis and characterisation:

Potassium n-pentylxanthate (0.0092 mol, 1.8696 g) and palladium(II) nitrate (0.0046 mol, 1.0644 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (3 x 100 ml) until no colour was evident in the chloroform extract. The orange needles formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a chloroform and acetonitrile mixture (200 ml; 3:1  $\nu/\nu$ ). Orange needles formed after 2 days. Yield: 1.73 g, 87 %. M. pt: 364.8–365.6 K. *Anal.* Calc'd for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 33.29; H, 5.12. Found: C, 33.30; H, 5.43 %. FTIR (cm<sup>-1</sup>): 1249 (*s*)  $\nu$ (C-O), 1045 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.62 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 1.88 (*tt*, 2H, OCH<sub>2</sub>CH<sub>2</sub>, *J* = 6.4 Hz, *J* = 7.3 Hz), 1.50-1.32 (*m*, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.93 (*t*, 3H, CH<sub>3</sub>, *J* = 7.1 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.8 (CS), 72.3 (OCH<sub>2</sub>), 27.9, 27.8 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.2 (CH<sub>2</sub>CH<sub>3</sub>), 13.9 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup>L): 237 ( $\varepsilon$  = 18930; n  $\rightarrow \sigma^{*}$ , CT); 284 ( $\varepsilon$  = 45030;  $\pi \rightarrow \pi^{*}$ ); 378 ( $\varepsilon$  = 3950; n  $\rightarrow \pi^{*}$ , CT); 448 ( $\varepsilon$  = 300; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(8).** Molecular structure of  $bis(O-isopentylxanthato)palladium(II), [Pd(S_2CO-i-Pent)_2]$ (8), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium isopentylxanthate (0.0092 mol, 1.8696 g) and palladium(II) nitrate (0.0046 mol, 1.0644 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (2 x 100 ml) until no colour was evident in the chloroform extract. The orange plates formed after a few days of slow evaporation of the combined chloroform extracts. Recrystallisation was performed by dissolving the obtained crystals from a chloroform and acetonitrile mixture (200 ml; 3:1  $\nu/\nu$ ). Orange plates formed after 2 days. Yield: 1.73 g, 87 %. M. pt: 392.5–393.3 K. *Anal.* Calc'd for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 33.29; H, 5.12. Found: C, 33.42; H, 5.30 %. FTIR (cm<sup>-1</sup>): 1267 (*s*)  $\nu$ (C-O), 1018 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.66 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.5 Hz), 1.90-1.70 (*m*, 3H, CH<sub>2</sub>CH), 0.97 (*d*, 6H, CH<sub>3</sub>, *J* = 6.4 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>:  $\delta$  233.7 (CS), 70.8 (OCH<sub>2</sub>), 36.7 (CH), 24.9 (CH<sub>2</sub>CH), 23.3 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 21160; n  $\rightarrow \sigma^*$ , CT); 285 ( $\varepsilon$  = 52980;  $\pi \rightarrow \pi^*$ ); 380 ( $\varepsilon$  = 4450; n  $\rightarrow \pi^*$ , CT); 461 ( $\varepsilon$  = 180; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1E</sup>g).



**Table S(9).** Molecular structure of bis(O-neopentylxanthato)palladium(II), [Pd(S<sub>2</sub>CO-neo-Pent)<sub>2</sub>] (9), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium neopentylxanthate (0.0092 mol, 1.8696 g) and palladium(II) nitrate (0.0046 mol, 1.0644 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (2 x 100 ml) until no colour was evident in the chloroform extract. The orange plates formed after a few days of slow evaporation of the combined chloroform and acetonitrile mixture (200 ml; 3:1  $\nu/\nu$ ). Orange plates formed after 2 days. Yield: 1.49 g, 75 %. M. pt: 498.5–504.4 K. *Anal.* Calc'd for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 33.29; H, 5.12. Found C, 33.26; H, 5.20 %. FTIR (cm<sup>-1</sup>): 1247 (*s*)  $\nu$ (C-O), 1020 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.29 (*s*, 2H, OCH<sub>2</sub>), 1.05 (*s*, 9H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.9 (CS), 80.9 (OCH<sub>2</sub>), 31.8 (CH<sub>2</sub>C), 26.3 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\epsilon$  = 22080;  $n \rightarrow \sigma^*$ , CT); 285 ( $\epsilon$  = 55430;  $\pi \rightarrow \pi^*$ ); 379 ( $\epsilon$  = 4680;  $n \rightarrow \pi^*$ , CT); 451 ( $\epsilon$  = 290; *d*-*d*, <sup>1</sup>A<sub>1g</sub>  $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(10).** Molecular structure of  $bis(O-n-hexylxanthato)palladium(II), [Pd(S_2CO-n-Hex)_2]$ (10), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium n-hexylxanthate (0.0087 mol, 1.8776 g) and palladium(II) nitrate (0.0043 mol, 0.9997 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (3 times, 100 ml) until no colour was evident in the chloroform extract. The chloroform was removed by rotary-evaporation, yielding a yellow-orange powder. Recrystallisation was performed by dissolving the obtained powder from hexane (600 ml). Orange plates formed after 8 days. Yield: 1.77 g, 89 %. M. pt: 355.5–356.0 K. *Anal.* Calc'd for C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 36.47; H, 5.68. Found: C, 36.54; H, 5.89 %. FTIR (cm<sup>-1</sup>): 1251 (*s*)  $\nu$ (C-O), 1017 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.55 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 1.80 (*tt*, 2H, OCH<sub>2</sub>CH<sub>2</sub>, *J* = 7.1 Hz, *J* = 7.3 Hz), 1.46-1.14 (*m*, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.84 (*t*, 3H, CH<sub>3</sub>, *J* = 6.3 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.8 (CS), 72.3 (OCH<sub>2</sub>), 31.3 (OCH<sub>2</sub>CH<sub>2</sub>), 28.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.6 (CH<sub>2</sub>CH<sub>3</sub>), 14.0 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 21440; n  $\rightarrow \sigma^*$ , CT); 284 ( $\varepsilon$  = 55570;  $\pi \rightarrow \pi^*$ ); 379 ( $\varepsilon$  = 4550; n  $\rightarrow \pi^*$ , CT); 457 ( $\varepsilon$  = 110; *d*-*d*, <sup>1</sup>A<sub>1e</sub> $\rightarrow$ <sup>1</sup>E<sub>2</sub>).



**Table S(11).** Molecular structure of  $bis(O-isohexylxanthato)palladium(II), [Pd(S_2CO-i-Hex)_2]$ (11), showing atom labelling and displacement ellipsoids at the 50% probability level.



Synthesis and characterisation:

Potassium isohexylxanthate (0.0087 mol, 1.8776 g) and palladium(II) nitrate (0.0043 mol, 0.9997 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (2 x 100 ml) until no colour was evident in the chloroform extract. The chloroform was removed by rotary-evaporation, yielding a yellow-orange powder. Recrystallisation was performed by dissolving the obtained powder from a chloroform and acetonitrile mixture (200 ml; 3:1  $\nu/\nu$ ). Orange blocks formed after 2 days. Yield: 1.90 g, 95 %. M. pt: 361.3–361.8 K. *Anal.* Calc'd for C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 36.47; H, 5.68. Found C, 36.52; H, 5.82 %. FTIR (cm<sup>-1</sup>): 1253 (*s*)  $\nu$ (C-O), 1019 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.61 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.7 Hz), 1.87 (*tt*, 2H, OCH<sub>2</sub>CH<sub>2</sub>, *J* = 6.5 Hz, *J* = 7.9 Hz), 1.50-1.70 (*m*, 3H, CH<sub>2</sub>CH), 1.32 (*t*, 6H, CH<sub>3</sub>, *J* = 6.6 Hz) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.7 (CS), 72.6 (OCH<sub>2</sub>), 34.6 (CH), 27.7 (<u>C</u>H<sub>2</sub>CH), 26.1 (OCH<sub>2</sub><u>C</u>H<sub>2</sub>), 22.4 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\varepsilon$  = 17820; n  $\rightarrow \sigma^*$ , CT); 284 ( $\varepsilon$  = 46280;  $\pi \rightarrow \pi^*$ ); 379 ( $\varepsilon$  = 3780; n  $\rightarrow \pi^*$ , CT); 459 ( $\varepsilon$  = 90; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(12).** Molecular structure of bis(*O*-neohexylxanthato)palladium(II),  $[Pd(S_2CO-neo-Hex)_2]$  (12), showing atom labelling and displacement ellipsoids at the 50% probability level.



#### Synthesis and characterisation:

Potassium neohexylxanthate (0.0087 mol, 1.8776 g) and palladium(II) nitrate (0.0043 mol, 0.9997 g) were each dissolved in water (50 ml). The Pd(NO<sub>3</sub>)<sub>2</sub> solution was added into the ligand solution drop-wise with stirring; a brown precipitate formed immediately. The precipitate was extracted with chloroform (100 ml). The chloroform layer was filtered off and the aqueous layer was further extracted with chloroform (2 x 100 ml) until no colour was evident in the chloroform extract. The chloroform was removed by rotary-evaporation, yielding a yellow-orange powder. Recrystallisation was performed by dissolving the obtained powder from a chloroform and hexane mixture (200 ml; 1:1  $\nu/\nu$ ). Orange plates formed after 5 days. Yield: 1.49 g, 75 %. M. pt: 436.2–437.2 K. *Anal.* Calc'd for C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>PdS<sub>4</sub>: C, 36.47; H, 5.68. Found C, 36.60; H, 5.88 %. FTIR (cm<sup>-1</sup>): 1240 (*s*)  $\nu$ (C-O), 1017 (*s*)  $\nu$ (C-S). <sup>1</sup>H NMR {CDCl<sub>3</sub>}:  $\delta$  4.62 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.7 Hz), 1.74 (*t*, 2H, OCH<sub>2</sub>C<u>H</u><sub>2</sub>, *J* = 6.7 Hz), 0.92 (*s*, 9H, CH<sub>3</sub>) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR {CDCl<sub>3</sub>}:  $\delta$  233.6 (CS), 70.1 (OCH<sub>2</sub>), 41.2 (<u>C</u>CH<sub>3</sub>), 29.9 (OCH<sub>2</sub><u>C</u>H<sub>2</sub>), 29.5 (CH<sub>3</sub>) ppm. UV/vis (ACN; nm, cm<sup>-1</sup> mol<sup>-1</sup> L): 237 ( $\epsilon$  = 21270; n  $\rightarrow \sigma^*$ , CT); 285 ( $\epsilon$  = 53560;  $\pi \rightarrow \pi^*$ ); 379 ( $\epsilon$  = 4410; n  $\rightarrow \pi^*$ , CT); 455 ( $\epsilon$  = 170; *d*-*d*, <sup>1</sup>A<sub>1g</sub> $\rightarrow$ <sup>1</sup>E<sub>g</sub>).



**Table S(13).** <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR data for the potassium salts of the xanthate ligands.

 $K(S_2COMe)$ 

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.08 (*s*, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  234.0 (CS); 60.8 (CH<sub>3</sub>) ppm.

 $K(S_2COEt)$ 

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.55 (*q*, 2H, CH<sub>2</sub>, *J* = 7.1 Hz), 1.43 (*t*, 3H, CH<sub>3</sub>, *J* = 7.1 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.2 (CS), 70.7 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>) ppm.

 $K(S_2CO-n-Pr)$ 

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.47 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 1.83 (*tq*, 2H, CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>t</sub> = 7.1 Hz, *J*<sub>q</sub> = 7.1 Hz), 1.04 (*t*, 3H, CH<sub>3</sub>, *J* = 7.4 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.5 (CS), 76.5 (OCH<sub>2</sub>), 22.1 (CH<sub>2</sub>CH<sub>3</sub>), 10.3 (CH<sub>3</sub>) ppm

 $K(S_2CO-i-Pr)$ 

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  5.58 (*sept*, 1H, CH, *J* = 6.2 Hz), 1.40 (*d*, 6H, CH<sub>3</sub>, *J* = 6.2 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  232.4 (CS), 78.4 (CH), 21.3 (CH<sub>3</sub>) ppm.

 $K(S_2CO-n-Bu)$ 

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.51 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 1.81 (*tt*, 2H, OCH<sub>2</sub>C<u>H<sub>2</sub></u>, *J* = 6.8 Hz, *J* = 7.3 Hz), 1.49 (*tq*, 2H, C<u>H</u><sub>2</sub>CH<sub>3</sub>, *J*<sub>t</sub> = 7.5 Hz, *J*<sub>q</sub> = 7.4 Hz), 1.01 (*t*, 3H, CH<sub>3</sub>, *J* = 7.4 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.4 (CS), 74.7 (OCH<sub>2</sub>), 30.6 (OCH<sub>2</sub>CH<sub>2</sub>), 19.2 (CH<sub>2</sub>CH<sub>3</sub>), 13.6 (CH<sub>3</sub>) ppm.

K(S<sub>2</sub>CO-i-Bu)

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.30 (*d*, 2H, OCH<sub>2</sub>, *J* = 6.6 Hz), 2.22-2.06 (*m*, CH; overlapping with resonance due to reference ACN), 1.04 (*d*, 6H, CH<sub>3</sub>, *J* = 6.7 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.6 (CS), 81.1 (OCH<sub>2</sub>), 27.9 (CH), 18.9 (CH<sub>3</sub>) ppm.

 $K(S_2CO-n-Pent)$ 

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.50 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.7 Hz), 1.82 (*tt*, 2H, OCH<sub>2</sub>C<u>H<sub>2</sub></u>, *J* = 6.9 Hz, *J* = 6.9 Hz), 1.52-1.32 (*m*, 4H, C<u>H<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub></u>), 0.97 (*t*, 3H, CH<sub>3</sub>, *J* = 6.8 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.4 (CS), 75.0 (OCH<sub>2</sub>), 28.2, 28.0 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.2 (<u>C</u>H<sub>2</sub>CH<sub>3</sub>), 13.8 (CH<sub>3</sub>) ppm.

K(S<sub>2</sub>CO-i-Pent)

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.52 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.7 Hz), 1.88-1.56 (*m*, 3H, CH<sub>2</sub>CH), 0.97 (*d*, 6H, CH<sub>3</sub>, *J* = 6.5 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.5 (CS), 73.7 (OCH<sub>2</sub>), 37.3 (CH), 25.2 (<u>C</u>H<sub>2</sub>CH), 22.3 (CH<sub>3</sub>) ppm.

K(S<sub>2</sub>CO-neo-Pent)

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.23 (*s*, 2H, OCH<sub>2</sub>), 1.07 (*s*, 9H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.8 (CS), 84.5 (OCH<sub>2</sub>), 31.5 (CH<sub>2</sub>C), 26.3 (CH<sub>3</sub>) ppm.

# $K(S_2CO-n-Hex)$

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.51 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.7 Hz), 1.83 (*tt*, 2H, OCH<sub>2</sub>C<u>H<sub>2</sub></u>, *J* = 7.1 Hz, *J* = 7.2 Hz), 1.56-1.30 (*m*, 6H, C<u>H<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.97 (*t*, 3H, CH<sub>3</sub>, *J* = 7.0 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.4 (CS), 75.0 (OCH<sub>2</sub>), 31.4 (OCH<sub>2</sub>CH<sub>2</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.6 (CH<sub>2</sub>CH<sub>3</sub>), 14.0 (CH<sub>3</sub>) ppm.</u>

# K(S<sub>2</sub>CO-i-Hex)

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.47 (*t*, 2H, OCH<sub>2</sub>, *J* = 6.7 Hz), 1.80 (*tt*, 2H, OCH<sub>2</sub>C<u>H<sub>2</sub></u>, *J* = 7.0 Hz, *J* = 7.8 Hz), 1.63 (*tsept*, 1H, CH, *J<sub>t</sub>* = 6.7 Hz, *J<sub>sept</sub>* = 6.7 Hz), 1.33 (*dt*, 3H, C<u>H</u><sub>2</sub>CH, *J<sub>d</sub>* = 8.0 Hz, *J<sub>t</sub>* = 6.3 Hz), 0.94 (*d*, 6H, CH<sub>3</sub>, *J* = 6.6 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.5 (CS), 75.3 (OCH<sub>2</sub>), 35.0 (CH), 27.6, 26.5 (OCH<sub>2</sub>CH<sub>2</sub>CH), 22.4 (CH<sub>3</sub>) ppm.

# K(S<sub>2</sub>CO-neo-Hex)

<sup>1</sup>H NMR {D<sub>2</sub>O}:  $\delta$  4.56 (*t*, 2H, OCH<sub>2</sub>, *J* = 7.2 Hz), 1.74 (*t*, 2H, OCH<sub>2</sub>CH<sub>2</sub>, *J* = 7.7 Hz), 1.00 (*s*, 9H, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR {D<sub>2</sub>O}:  $\delta$  233.3 (CS), 72.9 (OCH<sub>2</sub>), 41.7 (<u>C</u>CH<sub>3</sub>), 29.5 (OCH<sub>2</sub><u>C</u>H<sub>2</sub>), 29.5 (CH<sub>3</sub>) ppm.

Parameter	1	<b>2</b> <sup>a,i</sup>	3	<b>4</b> a,i	<b>5</b> <sup>a,i</sup>	<b>6</b> <sup>a,ii</sup>	<b>7</b> <sup>a,i</sup>	<b>8</b> a,i	<b>9</b> a,i	<b>10</b> a,iii	<b>11</b> a,iv	<b>12</b> <sup>a,i</sup>
Pd–S1	2.3233(15)	2.3387(5)	2.3253(9)	2.3229(6)	2.3233(6)	2.3243(7)	2.3322(13)	2.3318(7)	2.3210(6)	2.3249(7)	2.3256(4)	2.3368(12)
Pd–S2	2.3376(15)	2.3341(6)	2.3414(9)	2.3366(6)	2.3398(5)	2.3333(7)	2.3397(13)	2.3332(6)	2.3283(5)	2.3354(6)	2.3370(4)	2.3202(12)
Pd-S3	2.3320(15)	2.3387(5)	2.3386(9)	2.3229(6)	2.3233(6)	2.3243(7)	2.3322(13)	2.3318(7)	2.3210(6)	2.3249(7)	2.3256(4)	2.3368(12)
Pd–S4	2.3432(15)	2.3341(6)	2.3371(9)	2.3366(6)	2.3398(5)	2.3333(7)	2.3397(13)	2.3332(6)	2.3283(5)	2.3354(6)	2.3370(4)	2.3202(12)
C1-S1	1.702(6)	1.705(3)	1.700(3)	1.706(3)	1.698(2)	1.700(3)	1.693(6)	1.706(3)	1.696(2)	1.700(2)	1.6968(15)	1.704(5)
C1-S2	1.698(6)	1.695(2)	1.697(3)	1.697(3)	1.702(2)	1.701(3)	1.694(6)	1.698(3)	1.696(2)	1.697(3)	1.7028(15)	1.705(5)
C-S3	1.698(5)	1.705(3)	1.700(3)	1.706(3)	1.698(2)	1.700(3)	1.693(6)	1.706(3)	1.696(2)	1.700(2)	1.6968(15)	1.704(5)
C-S4	1.693(5)	1.695(2)	1.702(3)	1.697(3)	1.702(2)	1.701(3)	1.694(6)	1.698(3)	1.696(2)	1.697(3)	1.7028(15)	1.705(5)
C1O1	1.304(6)	1.311(3)	1.304(4)	1.300(3)	1.301(3)	1.306(4)	1.309(7)	1.302(3)	1.304(2)	1.298(3)	1.3025(17)	1.296(6)
С-О2	1.307(6)	1.311(3)	1.304(4)	1.300(3)	1.301(3)	1.306(4)	1.309(7)	1.302(3)	1.304(2)	1.298(3)	1.3025(17)	1.296(6)
S1-Pd-S2	75.66(5)	75.50(2)	75.51(3)	75.39(2)	75.57(2)	75.83(3)	75.50(5)	75.62(2)	75.624(19)	75.60(2)	75.647(13)	75.60(4)
S1-Pd-S3	177.93(5)	180	177.62(3)	180	180	180	180	180	180	180	180	180
S1-Pd-S4	103.99(5)	104.50(2)	103.84(3)	104.61(2)	104.43(2)	104.17(2)	104.50(5)	104.38(2)	104.376(19)	104.40(2)	104.353(13)	104.40(4)
S2-Pd-S3	104.80(5)	104.50(2)	104.97(3)	104.61(2)	104.43(2)	104.17(2)	104.50(5)	104.38(2)	104.376(19)	104.40(2)	104.353(13)	104.40(4)
S2-Pd-S4	176.91(4)	180	176.34(3)	180	180	180	180	180	180	180	180	180
S3-Pd-S4	75.44(5)	75.50(2)	75.53(3)	75.39(2)	75.57(2)	75.83(3)	75.50(5)	75.62(2)	75.624(19)	75.60(2)	75.647(13)	75.60(4)
Pd-S1-C1	85.13(19)	84.79(8)	85.20(11)	85.60(9)	85.35(8)	84.94(10)	84.7(2)	84.89(9)	85.10(7)	85.06(9)	85.16(5)	85.08(17)
Pd-S2-C1	84.76(19)	85.14(10)	84.76(12)	85.34(9)	84.73(8)	84.63(10)	84.5(2)	85.02(9)	84.87(7)	84.79(8)	84.67(5)	85.59(17)
Pd-S3-C	84.89(19)	84.79(8)	84.91(12)	85.60(9)	85.35(8)	84.94(10)	84.7(2)	84.89(9)	85.10(7)	85.06(9)	85.16(5)	85.08(17)
Pd-S4-C	84.65(19)	85.14(10)	84.91(12)	85.34(9)	84.73(8)	84.63(10)	84.5(2)	85.02(9)	84.87(7)	84.79(8)	84.67(5)	85.59(17)
S1C1O1	119.2(4)	119.66(17)	119.2(2)	118.86(19)	119.29(17)	119.2(2)	119.5(4)	119.5(2)	118.77(16)	119.58(18)	119.55(11)	120.8(4)
S2C1O1	126.3(4)	125.8(2)	126.3(3)	127.46(19)	126.35(17)	126.2(2)	125.2(4)	126.2(2)	126.86(16)	125.91(18)	125.95(11)	125.4(4)
S3-C-O2	118.5(4)	119.66(17)	119.8(2)	118.86(19)	119.29(17)	119.2(2)	119.5(4)	119.5(2)	118.77(16)	119.58(18)	119.55(11)	120.8(4)
S4-C-O2	126.5(4)	125.8(2)	125.6(3)	127.46(19)	126.35(17)	126.2(2)	125.2(4)	126.2(2)	126.86(16)	125.91(18)	125.95(11)	125.4(4)

# Table S(14). Selected bond lengths and angles (Å, $^{\circ}$ ) for 1–12.

a The Pd atom is located at a centre of inversion, with symmetry operations: i 1-x, 1-y, 1-z; ii -x, 1-y, 1-z; iii 1-x, -y, 1-z; iv 2-x, 1-y, 1-z.

## Table S(15). Thermogravimetric data for 1–12.

#### Compound

## 1

Degradation to PdS:	two steps between 95 and 308 °C, with weight loss of 55.4 % cf. calcd. 56.9%
Degradation to Pd:	two steps between 308 and 602 °C left a residue 33.3 % cf. calcd. 33.2 %.

#### 2

Degradation to PdS:	two steps between 151 and 385 °C, with weight loss of 58.2 % cf. calcd. 60.4%
Degradation to Pd:	two steps between 385 and 562 °C, left a residue 31.1 % cf. calcd. 30.5 %

#### 3

Degradation to PdS:	two steps between 100 and 427 °C, with weight loss of 62.9 % cf. calcd. 63.3 %
Degradation to Pd:	one step between 427 and 804 °C, left a residue 29.5 % cf. calcd. 28.2 %

#### PdiPrX, 4

Degradation to PdS:three steps between 144 and 480 °C, with weight loss of 66.2 % *cf.* calcd. 63.3 %Degradation to Pd:one step between 480 and 579 °C, left a residue 29.3 % *cf.* calcd. 28.2 %

#### 5

Degradation to PdS: two steps between 154 and 400 °C, with weight loss of 64.0 % *cf.* calcd. 65.9 % Degradation to Pd: one step between 400 and 505 °C, left a residue 27.7 % *cf.* calcd. 26.3 %

#### 6

Degradation to PdS:three steps between 175 and 394 °C, with weight loss of 64.8 % *cf.* calcd. 65.9 %Degradation to Pd:one step between 394 and 508 °C, left a residue 27.2 % *cf.* calcd. 26.3 %

Degradation to PdS:two steps between 154 and 370 °C, with weight loss of 67.1 % *cf.* calcd. 68.1 %Degradation to Pd:two steps between 370 and 679 °C, left a residue 24.2 % *cf.* calcd. 24.6 %

# 

Degradation to PdS:	two steps between 162 and 357 °C, with weight loss of 66.6 % cf. calcd. 68.1 %
Degradation to Pd:	two fsteps between 357 and 502 °C, left a residue 24.6 % cf. calcd. 24.6 %

#### 

Degradation to PdS:	one step between 212 and 316 °C, with weight loss of 68.1 % cf. calcd. 68.1 %
Degradation to Pd:	one step between 316 and 464 °C, left a residue 24.7 % cf. calcd. 24.6 %.

# 

Degradation to PdS:	two steps between 159 and 355 °C, with weight loss of 69.9 % cf. calcd. 70.0 %
Degradation to Pd:	one step between 355 and 573 °C, left a residue 22.7 % cf. calcd. 23.1 %

# 

Degradation to PdS:	two steps between 167 and 372 °C, with weight loss of 68.1 % cf. calcd. 70.0 %
Degradation to Pd:	one step between 372 and 498 °C, left a residue 24.4 % cf. calcd. 23.1 %

# PdneoHxX, 12

Degradation to PdS:	two steps between 179 and 357 °C, with weight loss of 68.7 % cf. calcd. 70.0 %
Degradation to Pd:	one step between 357 and 820 °C, left a residue 24.7 % cf. calcd. 23.1 %

**Figure S(1).** Overlay diagram of the experimental (red image) and calculated (blue) molecular structures for bis(O-n-propylxanthato)palladium(II),  $[Pd(S_2COPr)_2]$  (**3**), overlapped so that one chelate ring was coincident. (b) Calculated UV/visible spectrum.



**Figure S(2).** Views of the unit cell contents for bis(*O*-methylxanthato)palladium(II),  $[Pd(S_2COMe)_2]$  (1) in projection down the (a) *c*-axis, and (b) *a*-axis. No directional interactions are noted other than the Pd...S1<sup>i</sup> interactions [3.3165(13) Å; black dashed lines] leading to dimeric aggregates; symmetry operation *i*: 1-*x*, 2-*y*, 1-*z*. In (a), the orange dotted lines indicate S1...S2<sup>ii</sup> interactions of 3.6206(18) Å, which are just beyond the sum of the van der Waals radii; *ii*: -1+*x*, *y*, *z*.



(a)



**Figure S(3).** Views of the unit cell contents for bis(*O*-n-propylxanthato)palladium(II),  $[Pd(S_2COPr)_2]$  (**3**): in projection down the (a) *b*-axis, and (b) *a*-axis. Chains are separated by hydrophobic interactions. The Pd…S, C–H… $\pi$ (PdS<sub>2</sub>C) and Pd…H interactions are shown as black, purple and blue dashed lines, respectively.



(a)





**Figure S(4).** View of the unit cell contents for bis(O-ethylxanthato)palladium(II), [Pd(S<sub>2</sub>COEt)<sub>2</sub>] (2): in projection down the (a)*b*-axis. Layers are separated by hydrophobic interactions.



**Figure S(5).** View of the unit cell contents for bis(O-isopropylxanthato)palladium(II), [Pd(S<sub>2</sub>CO-i-Pr)<sub>2</sub>] (4): in projection down the*b*-axis. Layers parallel to (-1 0 1), sustained by weak C-H. S hydrogen bonds shown as orange dashed lines, are separated by hydrophobic interactions.



**Figure S(6).** View of the unit cell contents for bis(*O*-neopentylxanthato)palladium(II),  $[Pd(S_2CO\text{-neo-Pent})_2]$  (9): in projection down the *b*-axis. Rows of molecules, along the *b*-axis and connected by C-H… $\pi$ (PdS<sub>2</sub>C) interactions are separated by hydrophobic interactions.



**Figure S(7).** View of the unit cell contents for bis(*O*-n-butylxanthato)palladium(II),  $[Pd(S_2CO-n-Bu)_2]$  (5): in projection down the *b*-axis. Rows of molecules, along the *b*-axis and connected by C-H··· $\pi$ (PdS<sub>2</sub>C) interactions, are linked by weak C-H···S hydrogen bonds, shown as orange dashed lines, to form layers that are separated by hydrophobic interactions.



**Figure S(8).** Views of the crystal packing in bis(*O*-n-pentylxanthato)palladium(II),  $[Pd(S_2CO-n-Pent)_2]$  (7): (a) supramolecular chain aligned along the *b*-axis, being connected by C–H··· $\pi$ (PdS<sub>2</sub>C) interactions; and (b) the unit cell contents in projection down the *b*-axis. Chains of molecules do not form specific interactions in the crystal packing.



(a)





**Figure S(9).** Views of the crystal packing in bis(*O*-n-hexylxanthato)palladium(II),  $[Pd(S_2CO-n-Hex)_2]$  (10): (a) supramolecular chain aligned along the *b*-axis, being connected by C-H··· $\pi$ (PdS<sub>2</sub>C) interactions; and (b) the unit cell contents in projection down the *b*-axis. Chains of molecules do not form specific interactions in the crystal packing.



(a)



(b)

**Figure S(10).** Views of the crystal packing in bis(*O*-isohexylxanthato)palladium(II),  $[Pd(S_2CO-i-Hex)_2]$  (11): (a) supramolecular chain aligned along the *b*-axis, being connected by C-H $\cdots\pi(PdS_2C)$  interactions; and (b) the unit cell contents in projection down the *b*-axis. Chains of molecules do not form specific interactions in the crystal packing.



(a)



![](_page_26_Figure_4.jpeg)

**Figure S(11).** View of the crystal packing in bis(*O*-isopentylxanthato)palladium(II),  $[Pd(S_2CO-i-Pent)_2]$  (8): the unit cell contents in projection down the *b*-axis. Chains of molecules do not form specific interactions in the crystal packing.

![](_page_27_Figure_1.jpeg)

**Figure S(12).** View of the crystal packing in bis(*O*-isobutylxanthato)palladium(II),  $[Pd(S_2CO-i-Bu)_2]$  (6): the unit cell contents in projection down the *a*-axis. Chains of molecules do not form specific interactions in the crystal packing.

![](_page_27_Figure_3.jpeg)

**Figure S(13).** View of the crystal packing in bis(*O*-neohexylxanthato)palladium(II),  $[Pd(S_2CO-neo-Hex)_2]$  (12): the unit cell contents in projection down the *b*-axis. Chains of molecules do not form specific interactions in the crystal packing.

![](_page_27_Figure_5.jpeg)

Figure S(14). Thermogravimetric traces for 1–12.

![](_page_28_Figure_1.jpeg)

![](_page_29_Figure_0.jpeg)

![](_page_29_Figure_1.jpeg)

![](_page_29_Figure_2.jpeg)

![](_page_29_Figure_3.jpeg)

![](_page_30_Figure_0.jpeg)

![](_page_30_Figure_1.jpeg)

![](_page_30_Figure_2.jpeg)

![](_page_30_Figure_3.jpeg)

![](_page_30_Figure_4.jpeg)

![](_page_31_Figure_0.jpeg)

![](_page_31_Figure_1.jpeg)

![](_page_31_Figure_2.jpeg)

![](_page_31_Figure_3.jpeg)

![](_page_31_Figure_4.jpeg)