New Sterically-hindered o-Quinones Annelated with Metal-dithiolate: Regiospecificity in Oxidative Addition Reactions of Bifacial Ligand to the Pd and Pt Complexes

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X-ray crystallography

The X-ray diffraction data were collected on a Bruker D8 Quest (for 2a, 2b) and Agilent Xcalibur E (for 3) diffractometers (Mo Kα radiation, ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by SAINT\cite{1} (for 2a, 2b) and CrysAlisPro\cite{2} (for 3) programs. SADABS\cite{3} for 2a, 2b and SCALE3 ABSPACK\cite{4} for 3 were used to perform area-detector scaling and absorption corrections. The structures were solved by dual-space\cite{5} method and were refined on F^2 using all reflections with the SHELXTL package\cite{6}. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and refined in the “riding model”. The details of crystallographic, collection and refinement data for 2a, 2b and 3 are presented in Table SI1. CCDC-1446632 (2a), 1446633 (2b), 1446634 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure SI1. An ORTEP plot of 2b. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted and phenyl rings are marked “Ph” for clarity.

Figure SI2. An ORTEP plot of 3, illustrating slightly distorted square planar surrounding of metal center and strong distortion in quinone ring. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms, tBu groups are omitted and phenyl rings are marked “Ph” for clarity.
Table SI1. Selected bond lengths, angles and torsions for 2 (M=Pd) and 3 (M=Pt)

<table>
<thead>
<tr>
<th></th>
<th>2a</th>
<th>2b</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1) – P(1), Å</td>
<td>2.3411(5)</td>
<td>2.307(1)</td>
<td>2.3190(7)</td>
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<tr>
<td>M(1) – P(2), Å</td>
<td>2.3230(5)</td>
<td>2.322(1)</td>
<td>2.3078(7)</td>
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<tr>
<td>M(1) – S(1), Å</td>
<td>2.2707(5)</td>
<td>2.271(1)</td>
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<tr>
<td>M(1) – S(2), Å</td>
<td>2.2707(6)</td>
<td>2.287(1) [S(2)], 2.30(1) [S(2)']*</td>
<td>2.2971(7)</td>
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<tr>
<td>S(1) – M(1) – S(2), °</td>
<td>85.03(2)</td>
<td>85.58(4) [S(2)], 82.3(3) [S(2)']*</td>
<td>85.58(2)</td>
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<tr>
<td>P(1) – M(1) – P(2), °</td>
<td>98.71(2)</td>
<td>97.17(4)</td>
<td>97.93(2)</td>
</tr>
<tr>
<td>O(1)-C(5), Å</td>
<td>1.229(3) [O(1)], 1.289(8) [O(1')]*</td>
<td>1.229(5)</td>
<td>1.228(4)</td>
</tr>
<tr>
<td>O(2)-C(4), Å</td>
<td>1.224(3)</td>
<td>1.233(5)</td>
<td>1.231(4)</td>
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<tr>
<td>C(1)-C(6), Å</td>
<td>1.379(3)</td>
<td>1.368(6)</td>
<td>1.384(4)</td>
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<tr>
<td>C(1)-C(2), Å</td>
<td>1.493(3)</td>
<td>1.496(5)</td>
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<tr>
<td>C(2)-C(3), Å</td>
<td>1.370(3)</td>
<td>1.370(6)</td>
<td>1.384(4)</td>
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<tr>
<td>C(3)-C(4), Å</td>
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<td>1.459(6)</td>
<td>1.455(4)</td>
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<tr>
<td>C(4)-C(5), Å</td>
<td>1.504(3)</td>
<td>1.527(6)</td>
<td>1.518(4)</td>
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<tr>
<td>C(5)-C(6), Å</td>
<td>1.454(3)</td>
<td>1.455(5)</td>
<td>1.467(4)</td>
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<tr>
<td>φ[O(1)-C(5)-C(4)-O(2)], °</td>
<td>39.6(3) [O(1)], 14.0(8) [O(1')]*</td>
<td>29.9(5)</td>
<td>37.3(4)</td>
</tr>
</tbody>
</table>

* Two values are given owing to structural disordering on oxygen (2a) and sulfur (2b) atom

Table SI2. Crystallographic data and refinement parameters for 2 and 3.

<table>
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<tr>
<th></th>
<th>2a</th>
<th>2b</th>
<th>3</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C₅₀H₄₈O₂P₂PdS₂</td>
<td>C₅₂H₅₂O₂.₅P₂PdS₂</td>
<td>C₅₀H₄₈O₂P₂PtS₂</td>
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<tr>
<td>MW</td>
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<td>949.39</td>
<td>1002.03</td>
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<tr>
<td>Crystal system</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P₂₁/c</td>
<td>P-1</td>
<td>P₂₁/c</td>
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<tr>
<td>a, Å</td>
<td>9.7933(8)</td>
<td>10.760(2)</td>
<td>9.82880(10)</td>
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<tr>
<td>b, Å</td>
<td>27.530(2)</td>
<td>12.877(3)</td>
<td>27.6805(3)</td>
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<tr>
<td>c, Å</td>
<td>15.9433(13)</td>
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<td>90</td>
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<td>β, °</td>
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<td>99.297(3)</td>
<td>98.0410(10)</td>
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<td>γ, °</td>
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<td>90</td>
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<td>V, Å³</td>
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<td>2355.1(9)</td>
<td>4330.68(8)</td>
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<td>Z</td>
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<td>4</td>
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<td>ρcalcd., g·cm⁻³</td>
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<td>1.339</td>
<td>1.537</td>
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<td>μ, mm⁻¹</td>
<td>0.650</td>
<td>0.591</td>
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<td>F(000)</td>
<td>1888</td>
<td>984</td>
<td>2016</td>
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<td>Crystal dimension, mm</td>
<td>0.280 · 0.260 · 0.050</td>
<td>0.520 · 0.170 · 0.110</td>
<td>0.250 · 0.200 · 0.100</td>
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<tr>
<td>2θ range, °</td>
<td>2.424 – 26.000</td>
<td>3.031 – 27.000</td>
<td>3.042 – 25.999</td>
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<td>Reflections measured</td>
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<td>Reflections with I&gt;2σ(I)</td>
<td>7448</td>
<td>7872</td>
<td>7896</td>
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<td>R₁ (all data)</td>
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<td>R₁ with I&gt;2σ(I)</td>
<td>0.0280</td>
<td>0.0563</td>
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<td>wR₂ (all data)</td>
<td>0.0663</td>
<td>0.1448</td>
<td>0.0519</td>
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<td>wR₂ with I&gt;2σ(I)</td>
<td>0.0646</td>
<td>0.1361</td>
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<td>Goodness-of-fit on F²</td>
<td>1.061</td>
<td>1.050</td>
<td>1.121</td>
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<td>Highest residue, e·Å⁻³</td>
<td>0.534</td>
<td>1.525</td>
<td>1.104</td>
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<td>Lowest residue, e·Å⁻³</td>
<td>-0.332</td>
<td>-1.078</td>
<td>-1.152</td>
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</table>
Figure SI3. UV/Vis spectrum of 2 in THF, c = 4.11 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}, 1.0 \text{ cm quartz cell}; 
\epsilon = 520 \text{ M}^{-1}\text{cm}^{-1} (\lambda_{\text{max}} = 588 \text{ nm}), \epsilon = 19800 \text{ M}^{-1}\text{cm}^{-1} (\lambda_{\text{max}} = 422 \text{ nm}), \epsilon = 20200 \text{ M}^{-1}\text{cm}^{-1} (\lambda_{\text{max}} = 398 \text{ nm})

Figure SI4. UV/Vis spectrum of 3 in THF, c = 2.5 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}, 1.0 \text{ cm quartz cell}; 
\epsilon = 580 \text{ M}^{-1}\text{cm}^{-1} (\lambda_{\text{max}} = 611 \text{ nm}), \epsilon = 19900 \text{ M}^{-1}\text{cm}^{-1} (\lambda_{\text{max}} = 424 \text{ nm})
Figure SI5. $^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$, 25°C)

Figure SI6. $^1$H NMR spectrum of 3 (400 MHz, CDCl$_3$, 25°C)
Figure SI9. $^{31}$P NMR spectrum of 2 (161.97 MHz, CDCl$_3$, 25°C)

Figure SI10. $^{31}$P NMR spectrum of 3 (161.97 MHz, CDCl$_3$, 25°C)
Cyclic voltammograms

Figure SI11. Cyclic voltammogram of parent $\alpha$-quinone 1 (DMF, vs Ag/AgCl)

Figure SI12. Cyclic voltammogram of complex 2 (DMF, vs Ag/AgCl)

Figure SI13. Cyclic voltammogram of complex 3 (DMF, vs Ag/AgCl)
Figure SI14. IR spectrum of 2 in nujol
\[ \nu = 1624 \text{ s (C=O)}, 1435, 1307, 1216, 1189, 1159, 1091, 1026, 997, 914, 840, 813, 754, 692 \text{ cm}^{-1} \]

Figure SI15. IR spectrum of 3 in nujol
\[ \nu = 1624 \text{ s (C=O)}, 1438, 1313, 1217, 1163, 1096, 1067, 1029, 996, 912, 841, 816, 754, 741, 691 \text{ cm}^{-1} \]
Scheme SI1. Synthesis of dithiolate complexes 10 and 13 from 2 and 3

Figure SI16. Experimental (top) and simulated (bottom) X-band EPR spectra of 10 in THF, 298K.

Figure SI17. Experimental (top) and simulated (bottom) X-band EPR spectra of 13 in THF, 298K.
Figure SI18. Experimental (top) and simulated (bottom) X-band EPR spectra of 15 in THF, 298K.
Literature


