

## Electronic Supplementary Information: Gossage *et al.*

### General X-ray Data for Complexes 1, 2 and 6 (J. W. Quail: U. Saskatchewan).

Data was collected at -100°C on a Nonius Kappa CCD diffractometer, using the COLLECT program (Nonius, 1998). Cell refinement and data reductions used the programs DENZO and SCALEPACK (Otwinowski & Minor, 1997). SHELXS97 (Sheldrick, 1990) was used to solve the structure and SHELXL97 (Sheldrick, 1997) was used to refine the structure. Ortep-3 for Windows (Farrugia, 1997) was used for molecular graphics and PLATON (Spek, 2001) was used to prepare material for publication. H atoms were placed in calculated positions with  $U_{iso}$  constrained to be 1.2 times  $U_{eq}$  of the carrier atom for aromatic protons and 1.5 times  $U_{eq}$  of the carrier atoms for methyl hydrogen atoms. Further details on the crystallographic evaluation of complexes **1**, **2** and **6** can be found in the appropriate cif files.

Farrugia, L.J. (1997). *J. Appl. Cryst.* 30, 565.

Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C.W. Carter & R.M. Sweet, pp. 307-326. London: Academic Press.

Sheldrick, G.M. (1990). *Acta Cryst.* A46, 467-473.

Sheldrick, G.M. (1997). SHELXL97. University of Göttingen. Germany.

Spek, A.L. (2001). PLATON. University of Utrecht, The Netherlands.

## **General X-ray experimental: complex 4 (A. Decken: U. New Brunswick).**

Single crystals were coated with Paratone-N oil, mounted using a 20 micron cryo-loop and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using  $\omega$  and  $\theta$  scans with a scan width of  $0.3^\circ$  and 30 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)<sup>1</sup> and corrected for absorption (SADABS).<sup>2</sup> The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ (SHELXTL)<sup>3</sup>. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model. Further details on the crystallographic evaluation of complex **4** can be found in the appropriate cif file.

NOTE: Thermal ellipsoid plots are at the 50% probability level. JPEGs are drawn at the 50% probability level.

- (1) SAINT 7.23A, 2006, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (2) SADABS 2004, George Sheldrick, 2004, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (3) SHELXTL 6.14, George Sheldrick, 2000, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (4) GEMINI 1.0, 1999, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (5) RLATT 2.72, 1999, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (6) SMART 5.054, 1999, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (7) CELL\_NOW, 2005 George Sheldrick, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (8) ROTAX, 2001, S. Parsons and R.O. Gould, 2001, Oxford University, UK.

## **General X-ray experimental: complex 7 (R.C. Jones & M. G. Gardiner: U. Tasmania).**

Further details on the crystallographic evaluation of complex **7** can be found in the appropriate cif file.

Data were collected at 100(2) K for crystals of **7** mounted on a Hampton Scientific cryoloop at the PX1 beamline of the Australian Synchrotron ( $\lambda = 0.77487 \text{ \AA}$ ) using Blue Ice<sup>1</sup> software. The structure was solved by direct methods with SHELXS-97, refined using full-matrix least squares routines against *F*<sup>2</sup> with SHELXL-97,<sup>2</sup> and visualised using X-SEED.<sup>3</sup> All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C-H distances of 0.95 Å (*sp*<sup>2</sup>CH<sub>2</sub>), 0.98 Å (CH<sub>3</sub>), and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  (*sp*<sup>2</sup>), and 1.5 $U_{\text{eq}}(\text{C})$  (*sp*<sup>3</sup>) except for amide and hydroxy protons which were found in difference maps and subsequently refined in *x*, *y*, *z*.

A summary of crystallographic data and views of the structure are given below. *Crystal data*: PdC<sub>26</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>, *M* = 560.88, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.005(4), *b* = 18.8040(14), *c* = 19.2330(14)Å,  $\beta = 92.225(2)^\circ$ , *V* = 4338.4(14)Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.717 gcm<sup>-3</sup>, specimen: orange needle, 0.05 x 0.02 x 0.02 mm, 47831 measured reflections, *R*<sub>int</sub> = 0.0575, *R* = 0.0350 for 5687 observed data (*I* > 2σ(*I*)), *wR* = 0.0945, and GOOF = 1.070 for all data (6240).

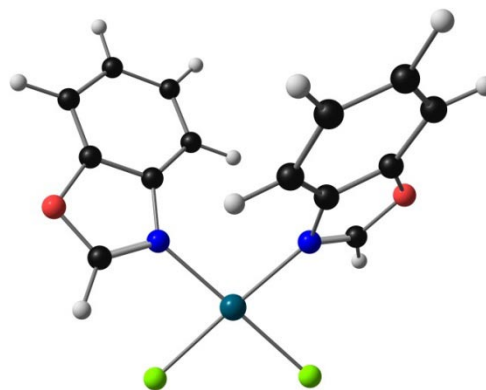
1. T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and P. Kuhn, *J. Synchrotron Rad.*, 2002, **9**, 401.
2. G. M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis; Universität Göttingen: Germany, 1998.
3. L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**,189.

## DFT calculated structures

### Atomic Coordinates

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C	3.072131000	-1.390443000	0.225627000
C	1.902898000	-0.915121000	-0.375404000
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C	2.068556000	-2.674478000	-1.965578000
C	3.238701000	-3.141484000	-1.336371000
C	3.773551000	-2.501662000	-0.217202000
C	2.394039000	0.370940000	1.281872000
H	0.486680000	-1.188164000	-1.992048000
H	1.696562000	-3.199154000	-2.840297000
H	3.742291000	-4.016534000	-1.735589000
H	4.679003000	-2.842011000	0.272542000
H	2.440102000	1.169978000	2.005493000
H	-0.370475000	-1.228931000	1.991947000
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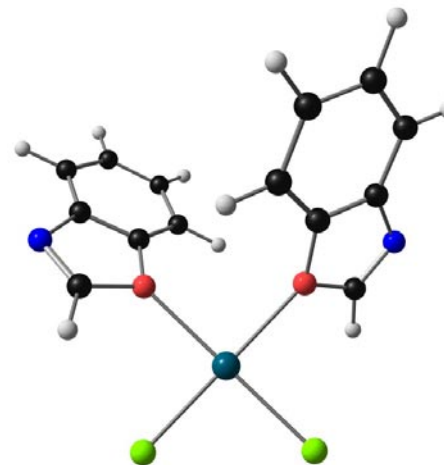


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C	-2.418485000	0.139737000	-1.282150000
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O	3.368843000	-0.557855000	1.285919000

Cis-PdCl<sub>2</sub>(box)<sub>2</sub> -O-bound

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C	3.274971000	1.075075000	-0.324600000
C	3.622972000	2.721654000	1.361961000
H	2.126035000	2.830842000	2.911411000
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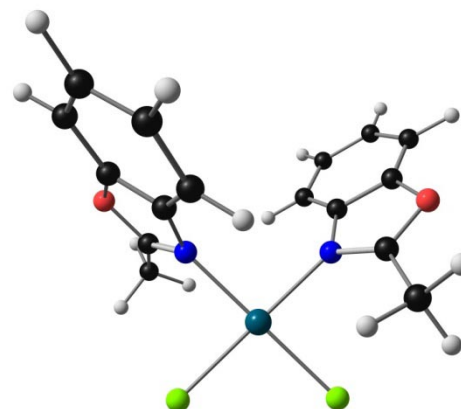


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C	3.507100000	-2.938427000	1.740407000
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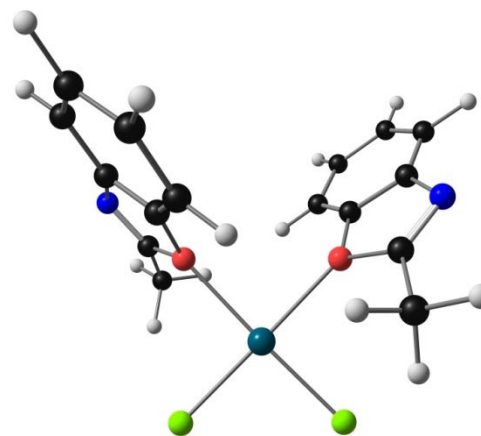


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H	1.021208000	0.981221000	-2.892101000
H	2.707340000	1.452138000	-2.751464000
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H	-3.905634000	-3.784211000	-2.314342000
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Cl	-1.605609000	3.126819000	0.286616000
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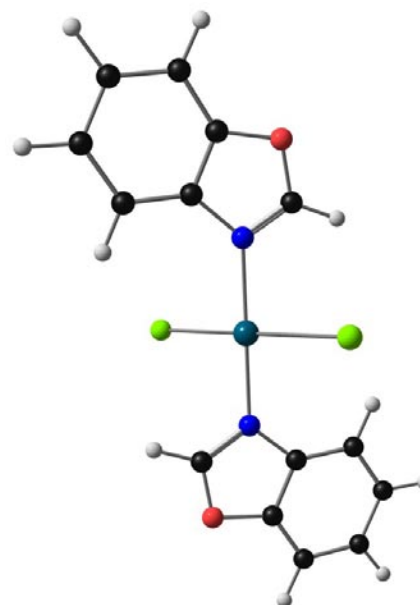


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H	-2.132771000	1.600918000	2.536276000
H	-2.592047000	0.249670000	3.618206000
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C	4.193356000	-0.855747000	0.230437000
C	3.472890000	1.352510000	-0.460709000

H	1.618649000	-2.631394000	0.804599000
C	5.543396000	-0.569578000	0.094733000
C	4.823676000	1.661689000	-0.607023000
H	2.688407000	2.076199000	-0.642222000
C	5.839134000	0.724215000	-0.335170000
H	6.310487000	-1.305885000	0.306566000
H	5.102912000	2.657951000	-0.936274000
H	6.877694000	1.014258000	-0.462816000
O	3.611400000	-2.046737000	0.621168000
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C	-2.288925000	1.819339000	-0.572474000
C	-4.193421000	0.855823000	-0.230184000
C	-3.472991000	-1.352820000	0.459757000
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C	-4.823785000	-1.662078000	0.605824000
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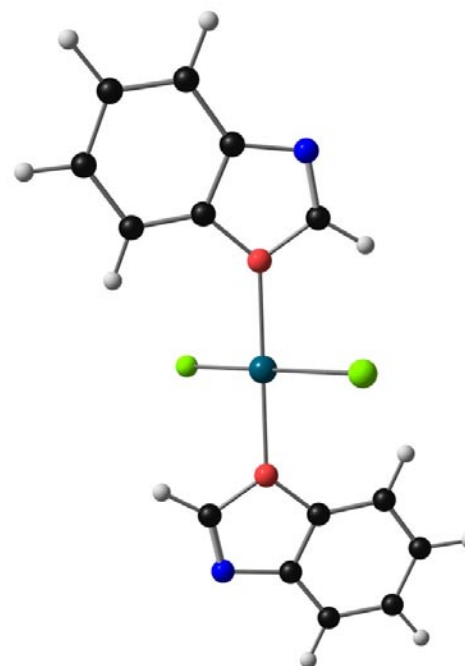


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N	-1.959032000	0.613595000	-0.207001000
Cl	0.469232000	2.081993000	1.041595000
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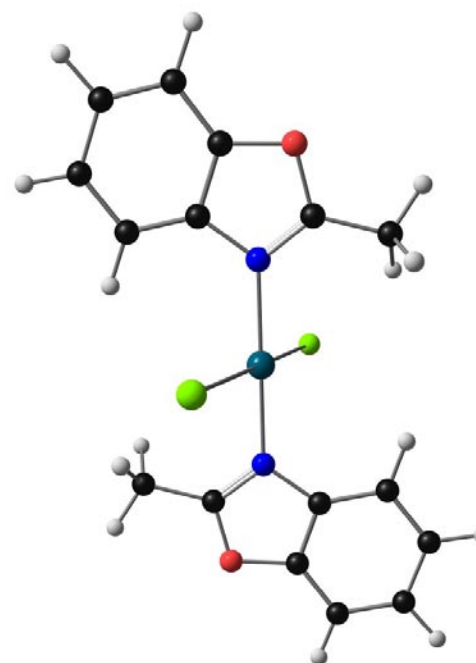
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C	-5.568844000	0.523440000	-0.031997000
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O	2.023858000	-0.594656000	0.333788000
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H	1.606758000	-2.561169000	0.949554000



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C	-3.262719000	1.543705000	0.340875000
C	-5.516249000	-0.218623000	0.044086000
C	-4.573548000	1.998593000	0.476015000
H	-2.409419000	2.205735000	0.426126000
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H	-6.355862000	-0.894569000	-0.073427000
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O	-3.741176000	-1.915466000	-0.368296000
N	-1.960187000	-0.609129000	-0.134079000
C	3.095443000	-0.187911000	-0.058896000
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C	4.204178000	0.647061000	0.084636000

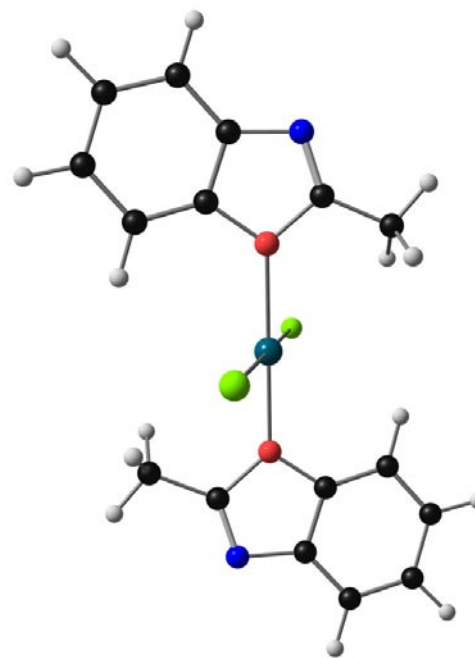


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C	5.516232000	0.218464000	-0.044265000
C	4.573381000	-1.998737000	-0.475931000
H	2.409247000	-2.205765000	-0.425850000
C	5.678168000	-1.137884000	-0.332912000
H	6.355888000	0.894377000	0.073129000
H	4.748910000	-3.048210000	-0.692284000
H	6.681233000	-1.537950000	-0.446120000
O	3.741283000	1.915440000	0.368090000
N	1.960201000	0.609187000	0.134133000
Cl	-0.319913000	1.406484000	-1.886427000
Cl	0.319898000	-1.406423000	1.886512000
C	-1.602998000	-3.042867000	-0.670195000
H	-1.077046000	-2.936036000	-1.625754000
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H	-2.267506000	-3.907602000	-0.721390000
C	1.603194000	3.042988000	0.670068000
H	0.856514000	3.184980000	-0.117356000
H	1.077419000	2.936319000	1.625744000
H	2.267735000	3.907713000	0.721013000



Trans-PdCl<sub>2</sub>(Mebox)<sub>2</sub>-O-bound

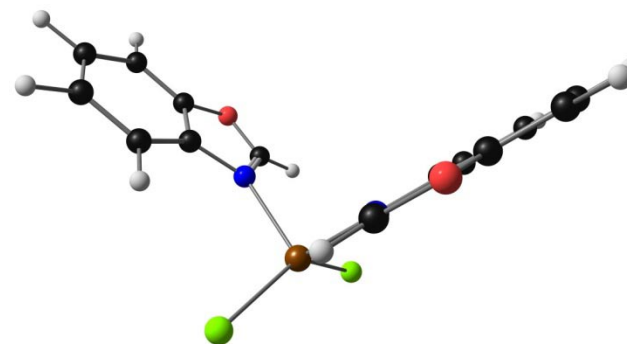
Pd	0.000111000	0.000082000	0.001276000
C	-3.133753000	0.178627000	-0.047961000
C	-2.525856000	-1.935443000	-0.416304000
C	-4.233614000	-0.679753000	-0.067989000
C	-3.208652000	1.545747000	0.144761000
C	-5.516022000	-0.165004000	0.125696000
C	-4.499470000	2.048342000	0.339803000
H	-2.332440000	2.183245000	0.126255000
C	-5.628194000	1.210404000	0.332529000
H	-6.382582000	-0.817508000	0.112015000
H	-4.629337000	3.114968000	0.495784000
H	-6.610038000	1.647456000	0.487940000
C	3.133574000	-0.178792000	0.049015000
C	2.526333000	1.936046000	0.414179000
C	4.233304000	0.679852000	0.063755000
C	3.208196000	-1.546381000	-0.140496000
C	5.515247000	0.164901000	-0.132432000



C	4.498548000	-2.049178000	-0.338121000
H	2.332170000	-2.183993000	-0.117678000
C	5.627102000	-1.210986000	-0.336260000
H	6.381709000	0.817607000	-0.122831000
H	4.628190000	-3.116162000	-0.491824000
H	6.608579000	-1.648209000	-0.493499000
Cl	-0.093025000	1.164871000	-2.037141000
Cl	0.093268000	-1.165232000	2.039387000
C	-1.539628000	-3.009451000	-0.680310000
H	-0.936359000	-2.772533000	-1.564466000
H	-0.867106000	-3.127788000	0.176374000
H	-2.082436000	-3.940591000	-0.851755000
C	1.540762000	3.010516000	0.678777000
H	0.866623000	3.127934000	-0.176761000
H	0.939189000	2.774780000	1.564394000
H	2.084059000	3.941784000	0.847968000
N	-3.800729000	-1.990253000	-0.307917000
N	3.800870000	1.990807000	0.302024000
O	2.014593000	0.619063000	0.276585000
O	-2.014310000	-0.618962000	-0.274008000

ZnCl<sub>2</sub>(box)<sub>2</sub>-N-bound

Zn	0.000000000	1.500395000	0.000005000
C	-2.585796000	-0.546664000	0.020411000
C	-1.772635000	-0.085283000	1.955410000
C	-3.332670000	-1.225994000	0.986633000
C	-2.913136000	-0.649271000	-1.333697000
H	-1.202210000	0.312380000	2.783344000
C	-4.413372000	-2.044252000	0.693615000
C	-3.996246000	-1.467110000	-1.651605000
H	-2.361590000	-0.092653000	-2.084024000
C	-4.728352000	-2.152684000	-0.662156000
H	-4.974470000	-2.558097000	1.466013000
H	-4.290986000	-1.573651000	-2.691179000
H	-5.565667000	-2.776507000	-0.960179000
C	2.585795000	-0.546666000	-0.020414000
C	1.772635000	-0.085271000	-1.955410000
C	3.332671000	-1.225985000	-0.986641000

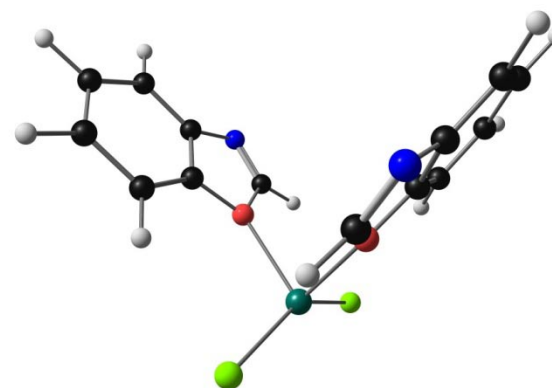


C	2.913133000	-0.649285000	1.333693000
H	1.202210000	0.312398000	-2.783342000
C	4.413374000	-2.044245000	-0.693629000
C	3.996244000	-1.467125000	1.651595000
H	2.361585000	-0.092674000	2.084025000
C	4.728352000	-2.152689000	0.662141000
H	4.974474000	-2.558080000	-1.466031000
H	4.290981000	-1.573675000	2.691169000
H	5.565668000	-2.776513000	0.960161000
N	-1.583539000	0.169399000	0.693965000
N	1.583538000	0.169402000	-0.693964000
O	2.797637000	-0.916824000	-2.223187000
O	-2.797633000	-0.916845000	2.223181000
Cl	0.694665000	2.315233000	2.014311000
Cl	-0.694664000	2.315245000	-2.014296000

ZnCl<sub>2</sub>(box)<sub>2</sub>-O-bound

Zn	-0.000043000	1.874676000	0.000131000
C	-2.274059000	-0.591444000	0.212592000

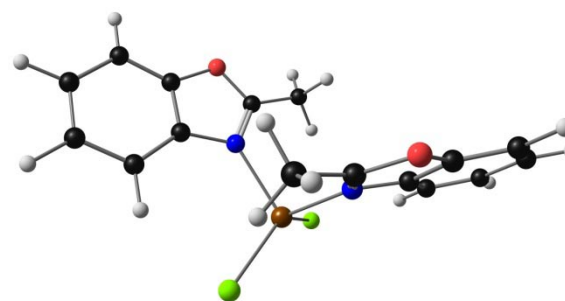
C	-1.282294000	-0.200714000	2.138019000
C	-2.645872000	-1.527682000	1.181632000
C	-2.752846000	-0.577096000	-1.087437000
H	-0.625559000	0.367042000	2.781823000
C	-3.549009000	-2.541954000	0.857327000
C	-3.655283000	-1.599524000	-1.396711000
H	-2.460978000	0.181774000	-1.804769000
C	-4.043205000	-2.561766000	-0.446604000
H	-3.847812000	-3.275855000	1.598167000
H	-4.070348000	-1.645366000	-2.398986000
H	-4.748466000	-3.334534000	-0.737373000
C	2.274048000	-0.591360000	-0.212635000
C	1.282667000	-0.200035000	-2.138140000
C	2.646086000	-1.527273000	-1.181904000
C	2.752572000	-0.577421000	1.087496000
H	0.626073000	0.367930000	-2.781902000
C	3.549195000	-2.541618000	-0.857750000
C	3.654984000	-1.599917000	1.396615000
H	2.460520000	0.181194000	1.805023000
C	4.043131000	-2.561837000	0.446274000



H	3.848166000	-3.275273000	-1.598766000
H	4.069845000	-1.646076000	2.398961000
H	4.748356000	-3.334679000	0.736933000
Cl	0.906527000	2.563881000	1.913526000
Cl	-0.906700000	2.564015000	-1.913172000
O	-1.375154000	0.280722000	0.825528000
O	1.375249000	0.280984000	-0.825477000
N	1.991166000	-1.235083000	-2.387134000
N	-1.990743000	-1.235840000	2.386833000

#### ZnCl<sub>2</sub>(Mebox)<sub>2</sub>-N-bound

Zn	0.000955000	1.341950000	-0.010983000
C	2.798593000	-0.341423000	-0.124183000
C	1.419313000	-0.911724000	-1.691262000
C	3.410030000	-1.321441000	-0.909176000
C	3.477729000	0.217979000	0.961535000
C	4.688733000	-1.808414000	-0.687193000
C	4.766133000	-0.258255000	1.205333000
H	3.016999000	0.988180000	1.571034000



C	5.360625000	-1.249423000	0.402045000
H	5.133369000	-2.568590000	-1.319784000
H	5.329456000	0.151784000	2.038192000
H	6.367418000	-1.585960000	0.630749000
C	-2.801897000	-0.331370000	0.123515000
C	-1.423142000	-0.887824000	1.696014000
C	-3.415888000	-1.300039000	0.920513000
C	-3.480096000	0.217454000	-0.968153000
C	-4.696413000	-1.785296000	0.705382000
C	-4.770318000	-0.257262000	-1.205197000
H	-3.017252000	0.978832000	-1.587061000
C	-5.367412000	-1.236901000	-0.389776000
H	-5.143034000	-2.536470000	1.347259000
H	-5.333011000	0.144848000	-2.042339000
H	-6.375538000	-1.572706000	-0.613631000
N	1.517995000	-0.111730000	-0.660677000
N	-1.520086000	-0.099648000	0.656207000
O	-2.526737000	-1.645250000	1.916774000
O	2.520596000	-1.675354000	-1.902115000
Cl	-0.742308000	2.338716000	-1.926532000

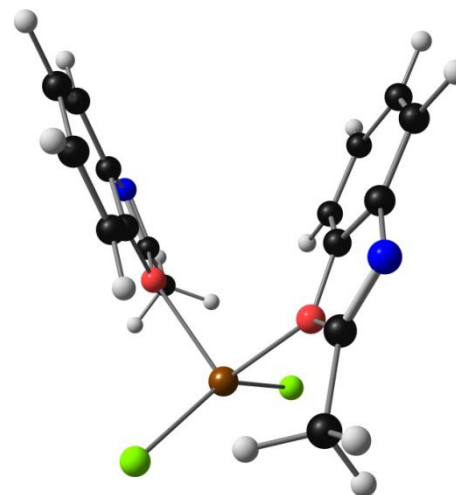
Cl	0.746613000	2.359811000	1.892455000
C	-0.278121000	-1.064433000	2.626350000
H	-0.639288000	-1.421586000	3.593657000
H	0.428598000	-1.803900000	2.229414000
H	0.246934000	-0.113226000	2.752517000
C	0.274602000	-1.095653000	-2.620571000
H	0.635788000	-1.463844000	-3.583731000
H	-0.433966000	-1.829443000	-2.216432000
H	-0.248363000	-0.144769000	-2.757304000

ZnCl<sub>2</sub>(Mebox)<sub>2</sub>-O-bound

Zn	1.924143000	-0.000877000	-0.000001000
C	-0.766966000	1.698987000	-0.732912000
C	0.076586000	2.653744000	1.081265000
C	-1.664487000	2.607993000	-0.168019000
C	-1.012168000	0.988316000	-1.896690000
C	-2.906632000	2.825222000	-0.765757000
C	-2.260983000	1.214546000	-2.485296000
H	-0.277024000	0.330327000	-2.344701000



C	-3.190552000	2.109873000	-1.929315000
H	-3.611576000	3.529479000	-0.336770000
H	-2.510179000	0.688851000	-3.402037000
H	-4.146331000	2.253575000	-2.424362000
C	-0.768464000	-1.698359000	0.732948000
C	0.074013000	-2.653647000	-1.081446000
C	-1.666903000	-2.606423000	0.168001000
C	-1.012871000	-0.987649000	1.896866000
C	-2.909201000	-2.822556000	0.765822000
C	-2.261841000	-1.212783000	2.485564000
H	-0.277055000	-0.330438000	2.344912000
C	-3.192326000	-2.107119000	1.929521000
H	-3.614857000	-3.526072000	0.336793000
H	-2.510445000	-0.686997000	3.402414000
H	-4.148195000	-2.249982000	2.424635000
Cl	2.684225000	-0.307453000	2.069855000
Cl	2.684619000	0.305010000	-2.069821000
O	0.366472000	1.693009000	0.080443000
O	0.364893000	-1.693316000	-0.080524000
N	-1.088904000	-3.184639000	-0.966793000

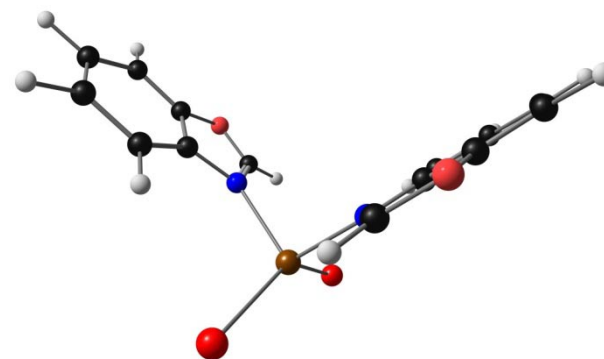


N	-1.085838000	3.185820000	0.966644000
C	1.143325000	-2.957764000	-2.064891000
H	2.022227000	-3.376031000	-1.559251000
H	0.756677000	-3.694768000	-2.770667000
H	1.472724000	-2.063025000	-2.601806000
C	1.146280000	2.956993000	2.064566000
H	2.025495000	3.374444000	1.558797000
H	0.760362000	3.694392000	2.770331000
H	1.474957000	2.062006000	2.601511000

ZnBr2(box)2-N-bound

Zn	0.000000000	-1.169702000	0.000004000
C	-2.515161000	0.971134000	-0.234247000
C	-1.545067000	0.497842000	-2.091776000
C	-3.140149000	1.692745000	-1.254926000
C	-2.961758000	1.073629000	1.085316000
H	-0.914433000	0.086559000	-2.867948000
C	-4.208141000	2.553505000	-1.050486000

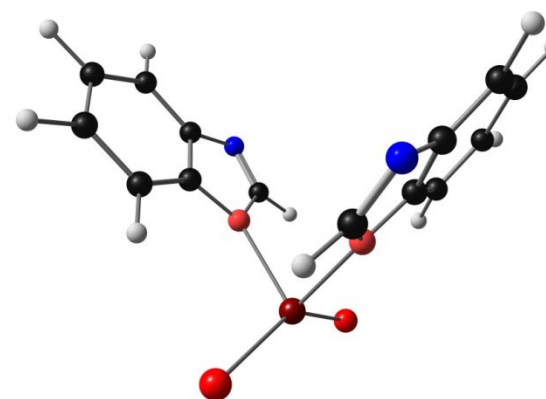
C	-4.034474000	1.933791000	1.314354000
H	-2.505372000	0.484359000	1.873787000
C	-4.642692000	2.660721000	0.271961000
H	-4.673008000	3.099690000	-1.863560000
H	-4.419184000	2.041915000	2.323955000
H	-5.477093000	3.316849000	0.500759000
C	2.515161000	0.971136000	0.234241000
C	1.545060000	0.497865000	2.091772000
C	3.140144000	1.692760000	1.254914000
C	2.961764000	1.073615000	-1.085321000
H	0.914422000	0.086591000	2.867945000
C	4.208136000	2.553517000	1.050469000
C	4.034480000	1.933775000	-1.314365000
H	2.505383000	0.484335000	-1.873787000
C	4.642693000	2.660718000	-0.271978000
H	4.673000000	3.099712000	1.863538000
H	4.419195000	2.041887000	-2.323966000
H	5.477095000	3.316844000	-0.500780000
N	-1.485292000	0.220073000	-0.822734000
N	1.485290000	0.220082000	0.822732000



O	2.505571000	1.375467000	2.441092000
O	-2.505580000	1.375440000	-2.441103000
Br	0.916370000	-2.066527000	-2.042926000
Br	-0.916367000	-2.066517000	2.042940000

ZnBr<sub>2</sub>(box)<sub>2</sub>-O-bound

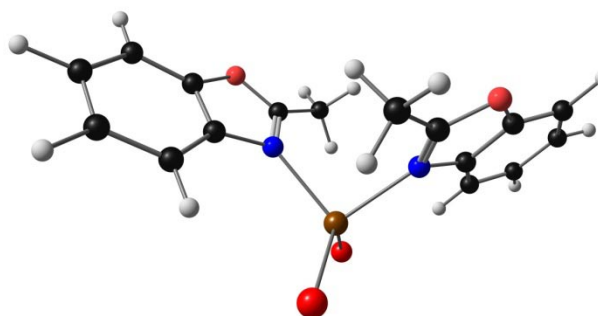
Zn	-0.000016000	-1.480559000	-0.000004000
C	2.182784000	1.049240000	0.582049000
C	0.872230000	0.669695000	2.306002000
C	2.362784000	2.007119000	1.584353000
C	2.885858000	1.024844000	-0.611752000
H	0.121333000	0.099811000	2.834678000
C	3.293870000	3.032410000	1.407076000
C	3.813422000	2.058387000	-0.774682000
H	2.737442000	0.249208000	-1.354683000
C	4.011429000	3.041925000	0.211400000
H	3.445264000	3.782563000	2.175932000
H	4.399294000	2.096392000	-1.688084000
H	4.745126000	3.823150000	0.036544000



C	-2.182774000	1.049281000	-0.582049000
C	-0.872203000	0.669738000	-2.305992000
C	-2.362714000	2.007202000	-1.584324000
C	-2.885883000	1.024863000	0.611730000
H	-0.121315000	0.099844000	-2.834671000
C	-3.293771000	3.032517000	-1.407035000
C	-3.813418000	2.058430000	0.774673000
H	-2.737507000	0.249200000	1.354641000
C	-4.011366000	3.042010000	-0.211380000
H	-3.445121000	3.782702000	-2.175868000
H	-4.399312000	2.096423000	1.688061000
H	-4.745043000	3.823251000	-0.036516000
O	1.202796000	0.170416000	1.040543000
O	-1.202785000	0.170457000	-1.040538000
N	-1.508768000	1.721548000	-2.659220000
N	1.508850000	1.721462000	2.659258000
Br	-1.280121000	-2.244561000	1.823661000
Br	1.280069000	-2.244576000	-1.823679000

ZnBr<sub>2</sub>(Mebox)<sub>2</sub>-N-bound

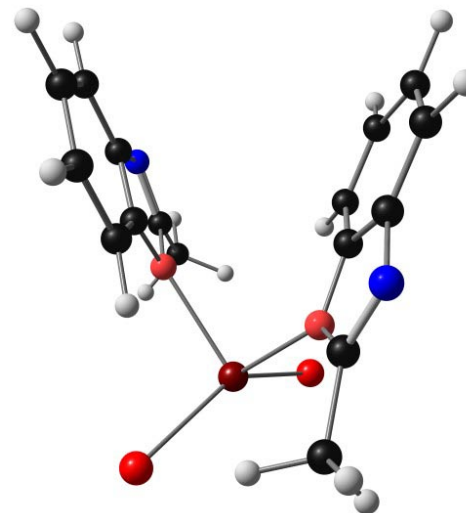
Zn	0.000007000	0.973665000	-0.000082000
C	-2.808794000	-0.707006000	0.240512000
C	-1.336792000	-1.319879000	1.702865000
C	-3.383980000	-1.683969000	1.056239000
C	-3.548775000	-0.126355000	-0.792844000
C	-4.683858000	-2.145159000	0.917366000
C	-4.859567000	-0.576002000	-0.952699000
H	-3.113287000	0.637898000	-1.427999000
C	-5.417455000	-1.563044000	-0.118627000
H	-5.098874000	-2.903560000	1.571854000
H	-5.469567000	-0.148413000	-1.742768000
H	-6.443704000	-1.878627000	-0.281164000
C	2.808783000	-0.707080000	-0.240437000
C	1.336717000	-1.320283000	-1.702590000
C	3.383938000	-1.684223000	-1.055968000
C	3.548797000	-0.126200000	0.792765000
C	4.683821000	-2.145382000	-0.917037000
C	4.859598000	-0.575806000	0.952671000



H	3.113331000	0.638198000	1.427761000
C	5.417456000	-1.563034000	0.118799000
H	5.098813000	-2.903931000	-1.571370000
H	5.469625000	-0.148039000	1.742622000
H	6.443711000	-1.878580000	0.281370000
N	-1.490433000	-0.506056000	0.689784000
N	1.490412000	-0.506216000	-0.689712000
O	2.435270000	-2.066190000	-1.981132000
O	-2.435353000	-2.065724000	1.981533000
C	0.136103000	-1.531747000	-2.552341000
H	0.427764000	-1.999514000	-3.495172000
H	-0.583302000	-2.187253000	-2.046642000
H	-0.352197000	-0.571118000	-2.745492000
C	-0.136219000	-1.531117000	2.552728000
H	-0.427903000	-1.998759000	3.495613000
H	0.583275000	-2.186637000	2.047174000
H	0.351993000	-0.570417000	2.745752000
Br	0.797598000	2.069659000	2.000647000
Br	-0.797533000	2.069419000	-2.000967000

ZnBr<sub>2</sub>(Mebox)<sub>2</sub>-O-bound

Zn	-1.553795000	-0.000065000	0.000020000
C	1.212246000	-1.795199000	-0.220170000
C	0.392201000	-2.191890000	1.798017000
C	2.138924000	-2.459487000	0.587050000
C	1.437726000	-1.463525000	-1.546578000
C	3.390881000	-2.803119000	0.075383000
C	2.696446000	-1.813168000	-2.047110000
H	0.679880000	-1.002089000	-2.168666000
C	3.655134000	-2.463745000	-1.251731000
H	4.118041000	-3.319888000	0.692799000
H	2.930685000	-1.581793000	-3.081766000
H	4.617943000	-2.716534000	-1.685740000
C	1.212105000	1.795289000	0.220091000
C	0.391979000	2.192009000	-1.798058000
C	2.138754000	2.459549000	-0.587179000
C	1.437667000	1.463569000	1.546477000
C	3.390753000	2.803144000	-0.075591000
C	2.696428000	1.813171000	2.046923000





H	0.679849000	1.002121000	2.168586000
C	3.655085000	2.463741000	1.251500000
H	4.117887000	3.319889000	-0.693058000
H	2.930737000	1.581747000	3.081553000
H	4.617926000	2.716496000	1.685456000
O	0.074985000	-1.585735000	0.559252000
O	0.074823000	1.585817000	-0.559318000
N	1.573902000	2.691711000	-1.845227000
N	1.574099000	-2.691682000	1.845101000
C	-0.675191000	2.231088000	-2.829003000
H	-1.529140000	2.820592000	-2.473236000
H	-0.267751000	2.702219000	-3.724988000
H	-1.048936000	1.230868000	-3.069274000
C	-0.674962000	-2.231092000	2.828965000
H	-1.528757000	-2.820830000	2.473215000
H	-0.267442000	-2.702079000	3.724992000
H	-1.048910000	-1.230938000	3.069164000
Br	-2.380199000	-0.986590000	-1.971581000
Br	-2.379792000	0.986570000	1.971806000

<b>ZnCl<sub>2</sub> energy calculations</b>	single point energy (a.u.)	single point energy ( kJ/mol)	difference in energy ( <i>N</i> -minus <i>O</i> -bound) in kJ/mol	
Complexes containing H-substituted benzoxazoles				
N-bound ligand	-3499.793613100	-9188708.131194050		
O-bound ligand	-3499.753674200	-9188603.271612100	-104.859581949	N-binding favoured
Complexes containing Me-substituted benzoxazoles				
N-bound ligand	-3578.467126700	-9395265.441150850		
O-bound ligand	-3578.422476900	-9395148.213100950	-117.228049899	N-binding favoured

**ZnBr<sub>2</sub> energy calculations**

	single point energy (a.u.)	single point energy ( kJ/mol)	difference in energy (N- minus O-bound) in kJ/mol	
Complexes containing H-substituted benzoxazoles				
N-bound ligand	-7727.628977100	-20288889.879376100		
O-bound ligand	-7727.588667500	-20288784.046521300	-105.832854800	N-binding favoured
Complexes containing Me-substituted benzoxazoles				
N-bound ligand	-7806.301483000	-20495444.543616500		
O-bound ligand	-7806.257328100	-20495328.614926600	-115.928689949	N-binding favoured

<b>Pd trans energy calculations</b>	single point energy (a.u.)	single point energy ( kJ/mol)	difference in energy ( <i>N</i> - minus <i>O</i> -bound) in kJ/mol	
Complexes containing H-substituted benzoxazoles				
N-bound ligand	-1847.014300400	-4849336.045700200		
O-bound ligand	-1846.936916800	-4849132.875058400	-203.170641799	N-binding favoured
Complexes containing Me-substituted benzoxazoles				
N-bound ligand	-1925.690555000	-5055900.552152500		
O-bound ligand	-1925.613915100	-5055699.334095050	-201.218057450	N-binding favoured

<b>Pd cis energy calculations</b>	single point energy (a.u.)	single point energy ( kJ/mol)	difference in energy ( <i>N</i> -minus <i>O</i> -bound) in kJ/mol	
Complexes containing H-substituted benzoxazoles				
N-bound ligand	-1846.999764500	-4849297.881694750		
O-bound ligand	-1846.939918800	-4849140.756809400	-157.124885350	N-binding favoured
Complexes containing Me-substituted benzoxazoles				
N-bound ligand	-1925.676529600	-5055863.728464800		
O-bound ligand	-1925.614694400	-5055701.380147200	-162.348317600	N-binding favoured

<b>Pd trans energy calculations</b>	energy in kJ/mol Trans	energy in kJ/mol Cis	difference in energy in kJ/mol	
Complexes containing H-substituted benzoxazoles				
N-bound ligand	-4849336.045700200	4849297.881694750	-38.164005450	Trans-binding favoured
O-bound ligand	-4849132.875058400	4849140.756809400	7.881751000	Cis-binding favoured
Complexes containing Me-substituted benzoxazoles				
N-bound ligand	-5055900.552152500	5055863.728464800	-36.823687700	Trans-binding favoured
O-bound ligand	-5055699.334095050	5055701.380147200	2.046052150	Cis-binding favoured

## Calculated Selected Bond Lengths and Angles

# Selected Bond Lengths and Angles

## PdCl<sub>2</sub>box-N-cis

Pd-N(1)	2.11901
Pd-N(2)	2.11892
Pd-Cl(1)	2.32922
Pd-Cl(2)	2.32924
N(1)-Pd-N(2)	93.832
Cl(1)-Pd-Cl(2)	91.454
N(1)-Pd-Cl(1)	87.413
N(2)-Pd-Cl(2)	87.405

## PdCl<sub>2</sub>box-O-cis

Pd-O(1)	2.25763
Pd-O(2)	2.25918
Pd-Cl(1)	2.28039
Pd-Cl(2)	2.28035
O(1)-Pd-O(2)	91.117
Cl(1)-Pd-Cl(2)	91.482
O(1)-Pd-Cl(1)	88.627
O(2)-Pd-Cl(2)	88.781

## PdCl<sub>2</sub>Mebox-N-cis

Pd-N(1)	2.11531
Pd-N(2)	2.11540
Pd-Cl(1)	2.33082
Pd-Cl(2)	2.33072
N(1)-Pd-N(2)	92.145
Cl(1)-Pd-Cl(2)	91.837
N(1)-Pd-Cl(1)	88.027
N(2)-Pd-Cl(2)	88.010

## PdClMe<sub>2</sub>box-O-cis

Pd-O(1)	2.26467
Pd-O(2)	2.26505
Pd-Cl(1)	2.28310
Pd-Cl(2)	2.28312
O(1)-Pd-O(2)	87.918
Cl(1)-Pd-Cl(2)	90.844
O(1)-Pd-Cl(1)	90.773
O(2)-Pd-Cl(2)	90.787



### **PdCl<sub>2</sub>box-N-trans**

Pd-N(1)	2.06329
Pd-N(2)	2.06323
Pd-Cl(1)	2.37477
Pd-Cl(2)	2.37478
N(1)-Pd-N(2)	179.996
Cl(1)-Pd-Cl(2)	179.994
N(1)-Pd-Cl(1)	91.673
N(2)-Pd-Cl(2)	91.665

### **PdCl<sub>2</sub>box-O-trans**

Pd-O(1)	2.13562
Pd-O(2)	2.13562
Pd-Cl(1)	2.34905
Pd-Cl(2)	2.34905
O(1)-Pd-O(2)	179.999
Cl(1)-Pd-Cl(2)	179.994
O(1)-Pd-Cl(1)	91.488
O(2)-Pd-Cl(2)	91.489

### **PdCl<sub>2</sub>Mebox-N-trans**

Pd-N(1)	2.05704
Pd-N(2)	2.05704
Pd-Cl(1)	2.37470
Pd-Cl(2)	2.37470
N(1)-Pd-N(2)	179.999
Cl(1)-Pd-Cl(2)	179.999
N(1)-Pd-Cl(1)	89.726
N(2)-Pd-Cl(2)	89.727

### **PdCl<sub>2</sub>Mebox-O-trans**

Pd-O(1)	2.12530
Pd-O(2)	2.12534
Pd-Cl(1)	2.34959
Pd-Cl(2)	2.34958
O(1)-Pd-O(2)	179.998
Cl(1)-Pd-Cl(2)	179.985
O(1)-Pd-Cl(1)	89.682
O(2)-Pd-Cl(2)	89.685

# Selected Bond Lengths and Angles

## ZnCl<sub>2</sub>box-N

Zn-N(1)	2.18191
Zn-N(2)	2.18191
Zn-Cl(1)	2.28122
Zn-Cl(2)	2.28122
N(1)-Zn-N(2)	104.819
Cl(1)-Zn-Cl(2)	138.144
N(1)-Zn-Cl(1)	106.125
N(2)-Zn-Cl(2)	106.125
N(1)-Zn-Cl(2)	99.094
N(2)-Zn-Cl(1)	99.094

## ZnCl<sub>2</sub>box-O

Zn-O(1)	2.26177
Zn-O(2)	2.26177
Zn-Cl(1)	2.22665
Zn-Cl(2)	2.22664
O(1)-Zn-O(2)	90.363
Cl(1)-Zn-Cl(2)	143.935
O(1)-Zn-Cl(1)	106.516
O(2)-Zn-Cl(2)	106.515
O(1)-Zn-Cl(2)	98.750
O(2)-Zn-Cl(1)	98.750

## ZnCl<sub>2</sub>Mebox-N

Zn-N(1)	2.19925
Zn-N(2)	2.19930
Zn-Cl(1)	2.28366
Zn-Cl(2)	2.28371
N(1)-Zn-N(2)	97.667
Cl(1)-Zn-Cl(2)	127.652
N(1)-Zn-Cl(1)	108.398
N(2)-Zn-Cl(2)	108.389
N(1)-Zn-Cl(2)	105.380
N(2)-Zn-Cl(1)	105.374

## ZnCl<sub>2</sub>Mebox-O

Zn-O(1)	2.30263
Zn-O(2)	2.30262
Zn-Cl(1)	2.22621
Zn-Cl(2)	2.22622
O(1)-Zn-O(2)	94.809
Cl(1)-Zn-Cl(2)	140.062
O(1)-Zn-Cl(1)	99.352
O(2)-Zn-Cl(2)	99.351
O(1)-Zn-Cl(2)	107.445
O(2)-Zn-Cl(1)	107.445

# Selected Bond Lengths and Angles

## ZnBr<sub>2</sub>box-N

Zn-N(1)	2.19419
Zn-N(2)	2.19419
Zn-Br(1)	2.41197
Zn-Br(2)	2.41197
N(1)-Zn-N(2)	101.399
Br(1)-Zn-Br(2)	136.344
N(1)-Zn-Br(1)	107.213
N(2)-Zn-Br(2)	107.213
N(1)-Zn-Br(2)	100.084
N(2)-Zn-Br(1)	100.084

## ZnBr<sub>2</sub>box-O

Zn-O(1)	2.29243
Zn-O(2)	2.29243
Zn-Br(1)	2.35545
Zn-Br(2)	2.35545
O(1)-Zn-O(2)	87.859
Br(1)-Zn-Br(2)	142.147
O(1)-Zn-Br(1)	107.451
O(2)-Zn-Br(2)	107.451
O(1)-Zn-Br(2)	99.632
O(2)-Zn-Br(1)	99.632

## ZnBr<sub>2</sub>Mebox-N

Zn-N(1)	2.21063
Zn-N(2)	2.21064
Zn-Br(1)	2.41667
Zn-Br(2)	2.41667
N(1)-Zn-N(2)	95.958
Br(1)-Zn-Br(2)	126.068
N(1)-Zn-Br(1)	109.839
N(2)-Zn-Br(2)	109.839
N(1)-Zn-Br(2)	105.529
N(2)-Zn-Br(1)	105.530

## ZnBr<sub>2</sub>Mebox-O

Zn-O(1)	2.34094
Zn-O(2)	2.34100
Zn-Br(1)	2.35444
Zn-Br(2)	2.35450
O(1)-Zn-O(2)	91.828
Br(1)-Zn-Br(2)	138.914
O(1)-Zn-Br(1)	99.233
O(2)-Zn-Br(2)	99.233
O(1)-Zn-Br(2)	109.140
O(2)-Zn-Br(1)	109.145

**Comparison of the derived R values for the crystallographic datasets of complexes 1, 2 and 6 upon 'swapping' of the N-atom for the O-atom of the benzoxazole ligands.**

Comparison of R values for correct refinement and refinement with O and N swapped.

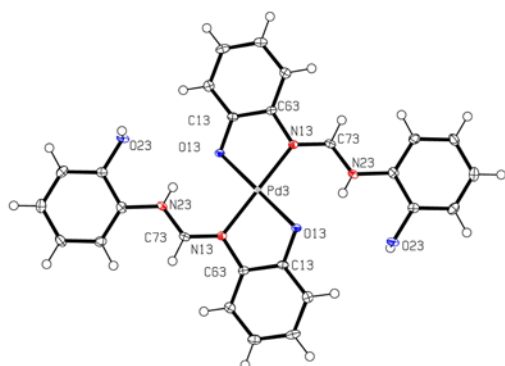
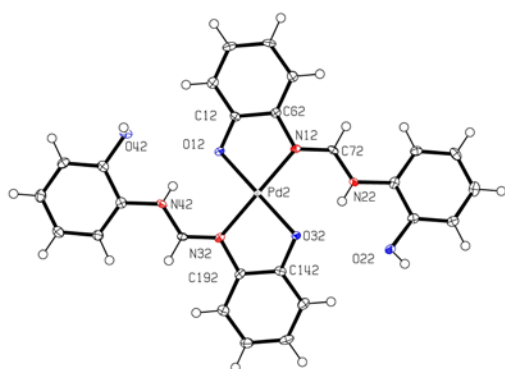
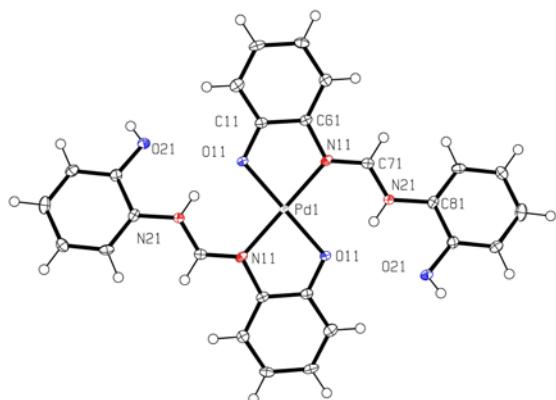
	R1 ( $I > 2\sigma(I)$ )	R1 (all)
Complex <b>6</b>	0.0317	0.0448
Complex <b>6</b> swap	0.0391	0.0523
Complex <b>1</b>	0.0422	0.0569
Complex <b>1</b> swap	0.0519	0.0665
Complex <b>2</b>	0.0322	0.0482
Complex <b>2</b> swap	0.0390	0.0551

**Comparison of the derived R values for the crystallographic datasets of complex 4 upon 'swapping' of the N-atom for the O-atom of the benzoxazole ligands**

<u>Switch</u>	<u>wR2</u>	<u>R1</u>
no switch (both N-bound)	8.09	3.14
switch positions 1 $\leftrightarrow$ 3	9.29	3.46
switch positions 11 $\leftrightarrow$ 13	9.37	3.48
switch both positions	10.47	3.77



Alternative pictorial (ORTEP) presentations of the Pd units found in the solid-state for complex **7**.



## Syntheses

### Synthesis of $\text{ZnCl}_2(\text{box})_2$ (1)<sup>1</sup>

A 1.0 g sample of  $\text{ZnCl}_2$  (7.3 mmol) was dissolved in ~80 mL of  $\text{Et}_2\text{O}$  and stirred at RT for about 10 min. The mixture was then filtered into a round bottomed flask equipped with a stir bar. To the clear solution was added, dropwise with stirring, a 50 mL solution ( $\text{Et}_2\text{O}$ ) of 1.90 g of box (16 mmol). A colourless precipitate began to form in about 15 s. Stirring was continued for 12 h and then the off-white solid was removed by filtration, and then washed with  $\text{Et}_2\text{O}$  (30 mL  $\times$  2) and petroleum ether (20 mL) and then dried in a dessicator. Yield: 2.35 g (86%).

### Synthesis of $\text{ZnBr}_2(\text{box})_2$ (2)<sup>1</sup>

A 0.89 g sample of  $\text{ZnBr}_2$  (4.0 mmol) was dissolved in ~70 mL of  $\text{Et}_2\text{O}$  and stirred at RT for about 10 min. The mixture was filtered into a round bottomed flask equipped with a stir bar. To the clear solution was added, dropwise with stirring, a 40 mL solution ( $\text{Et}_2\text{O}$ ) of 0.99 g of box (8.3 mmol). A colourless precipitate began to form in about 30 s. Stirring was continued for 14 h and then the colourless solids were removed by filtration and then washed with  $\text{Et}_2\text{O}$  (25 mL  $\times$  2) and petroleum ether (20 mL) and then dried in a dessicator. Yield: 1.34 g (72%).

### Synthesis of $\text{ZnCl}_2(\text{Mebox})_2$ (3)<sup>2</sup>

A 0.049 g sample of  $\text{ZnCl}_2$  (0.36 mmol) was dissolved in ~80 mL of  $\text{Et}_2\text{O}$  and stirred at RT for about 10 min. The mixture was filtered into a round bottomed flask equipped with a stir bar. To the clear solution was added, dropwise with stirring, a 50 mL solution ( $\text{Et}_2\text{O}$ ) of 0.24g of Mebox (1.8 mmol). A colourless precipitate began to form in about 15 s. Stirring was continued for 12 h and then the colourless solids were removed by filtration, washed with  $\text{Et}_2\text{O}$  (30 mL  $\times$  2) and petroleum ether (20 mL) and then dried in a dessicator. Yield: 0.144 g (99%).

#### **Synthesis of $\text{ZnBr}_2(\text{Mebox})_2$ (4)<sup>2, 3</sup>**

A 2.79 g sample of  $\text{ZnBr}_2$  (12.4 mmol) was dissolved in ~125 mL of  $\text{Et}_2\text{O}$  and stirred at RT for about 20 min. The mixture was filtered into a beaker containing a stirring bar. To the clear solution was added, dropwise with stirring, a 6.0 mL portion of Mebox (51 mmol). A colourless precipitate began to form in about 30 s. Stirring was continued for 3 h and then the colourless solids were removed by filtration, washed with  $\text{Et}_2\text{O}$  (60 mL  $\times$  2) and pentane (50 mL) and then dried in a dessicator. Yield: 4.98 g (82%).

#### **Synthesis of $\text{PdCl}_2(\text{box})_2$ (5)<sup>4</sup>**

A 1.8 mL portion of a 0.2 M methanolic solution of  $\text{Li}_2\text{PdCl}_4$  (0.36 mmol) was added to a stirring MeOH (20 mL) solution of box (0.85 g: 7.1 mmol). A light yellow precipitate formed in about 5 s. Stirring was continued for 1.5 h and then the solids were removed by filtration,

washed with MeOH (20 mL × 2) and *t*-BuOMe (20 mL × 2) and then dried overnight in a dessicator. Yield: 0.15 g (>99%).

### Synthesis of *trans*-PdCl<sub>2</sub>(Mebox)<sub>2</sub> (**6**)<sup>4, 5</sup>

A 6.8 mL quantity of 0.2 M methanolic solution of Li<sub>2</sub>PdCl<sub>4</sub> (1.4 mmol) was added to a stirring MeOH (15 mL) solution of Mebox (0.90 g: 6.7 mmol). A light orange precipitate formed in about 5 seconds. Stirring was continued for a further 1.5 h and then the solids were removed by filtration, washed with MeOH (20 mL × 2), *t*-BuOMe (20 mL × 2) and then dried overnight in a dessicator. Yield: 0.57 g (92%).

### References:

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4. A. I. P. Sinha and S. P. Tewari, *Current Sci.*, 1987, **56**, 257.
5. M. Massacesi, R. Pinna, M. Biddau, G. Ponticelli and I. A. Zakharova, *Inorg. Chim. Acta*, 1983, **80**, 151.