# Supplementary Information

# Sulfur containing platium(II) complexes with *N*-heterocyclic carbene ligands obtained by reactions of a hydrosulfido complex

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**Table S1** Optimised atomic coordinates of $C_{3h}$-isomer of $[\mathbf{5}]^{2+}$ obtained from DFT calculations

| Number | Atom | Coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | Pt | 0.060737 | 1.894589 | -0.004828 |
| 2 | C | 0.259037 | 3.294587 | 1.428528 |
| 3 | C | 0.082007 | 3.381159 | -1.399033 |
| 4 | S | -0.007502 | -0.015188 | -1.546782 |
| 5 | S | -0.001498 | -0.012186 | 1.520980 |
| 6 | Pt | -1.692643 | -0.903434 | 0.000254 |
| 7 | Pt | 1.623282 | -1.012281 | -0.003899 |
| 8 | N | 1.335373 | 4.126651 | 1.480201 |
| 9 | N | -0.516531 | 3.663022 | 2.478188 |
| 10 | N | -0.834960 | 3.560813 | -2.392494 |
| 11 | N | 0.932257 | 4.448409 | -1.530895 |
| 12 | C | -3.011176 | -1.426001 | 1.432008 |
| 13 | C | -2.995138 | -1.623721 | -1.391538 |
| 14 | C | 2.909965 | -1.760791 | -1.397153 |
| 15 | C | 2.758915 | -1.856044 | 1.430131 |
| 16 | C | 2.420487 | 4.042055 | 0.510381 |
| 17 | C | 1.234445 | 5.009105 | 2.549225 |
| 18 | C | -2.035600 | 2.754071 | -2.607371 |
| 19 | C | -0.566066 | 4.705187 | -3.126735 |
| 20 | C | 2.150451 | 4.803745 | -0.783458 |
| 21 | C | 0.542265 | 5.262798 | -2.590846 |
| 22 | C | -1.801763 | 3.065431 | 2.832285 |
| 23 | C | 0.068770 | 4.714533 | 3.176331 |
| 24 | N | -4.262737 | -0.892024 | 1.481385 |
| 25 | N | -2.958001 | -2.286623 | 2.477743 |
| 26 | N | -4.342776 | -1.411035 | -1.523175 |
| 27 | N | -2.699681 | -2.516970 | -2.378986 |
| 28 | N | 3.517901 | -1.046066 | -2.387339 |
| 29 | C | 3.385332 | 0.393283 | -2.609740 |
| 30 | N | 3.432266 | -3.021540 | -1.525193 |
| 31 | N | 3.464225 | -1.353225 | 2.472845 |
| 32 | N | 2.967210 | -3.200640 | 1.483161 |
| 33 | C | 3.568714 | 0.061910 | 2.819458 |
| 34 | C | -4.714837 | 0.096566 | 0.509694 |
| 35 | C | -5.244608 | -0.509168 | -0.787010 |
| 36 | C | 4.389795 | -1.837582 | -3.118133 |
| 37 | C | -4.987870 | -1.415948 | 2.544994 |
| 38 | C | 4.109541 | -2.372088 | 3.166720 |
| 39 | C | -4.860264 | -2.159867 | -2.576797 |
| 40 | C | -1.402058 | -3.155078 | -2.596991 |
| 41 | C | -3.829046 | -2.852522 | -3.109203 |
| 42 | C | -1.814944 | -3.127771 | 2.823277 |
| 43 | C | -4.164512 | -2.293122 | 3.170924 |
| 44 | C | 2.356785 | -4.110598 | 0.521175 |
| 45 | C | 3.799091 | -3.536448 | 2.544417 |
| 46 | C | 3.146825 | -4.256470 | -0.775624 |
| 47 | C | 4.337316 | -3.076934 | -2.581718 |
| 48 | H | 2.601931 | 2.984536 | 0.309888 |
| 49 | H | -1.825136 | 1.718146 | -2.352429 |
| 50 | H | -1.908947 | 2.132836 | 2.280839 |
| 51 | H | 2.353333 | 0.693024 | -2.442297 |
| 52 | H | -2.857528 | 3.129853 | -1.990710 |
| 53 | H | 2.782221 | 0.601876 | 2.294776 |

| | | | | |
|---|---|---|---|---|
| 54 | H | -3.877682 | 0.768346 | 0.312299 |
| 55 | H | -2.617727 | 3.747974 | 2.578478 |
| 56 | H | 4.045874 | 0.942026 | -1.932364 |
| 57 | H | 3.015722 | 4.661868 | -1.441360 |
| 58 | H | 3.321955 | 4.468138 | 0.959443 |
| 59 | H | 2.078726 | 5.873717 | -0.564110 |
| 60 | H | -2.315247 | 2.821859 | -3.660197 |
| 61 | H | -1.823472 | 2.857124 | 3.904104 |
| 62 | H | -0.608881 | -2.446756 | -2.369459 |
| 63 | H | 4.549080 | 0.450833 | 2.529884 |
| 64 | H | -0.952325 | -2.782221 | 2.255996 |
| 65 | H | 3.667597 | 0.610051 | -3.641274 |
| 66 | H | 1.992431 | 5.742510 | 2.775565 |
| 67 | H | -1.183773 | 5.017840 | -3.953623 |
| 68 | H | 1.091634 | 6.148902 | -2.867306 |
| 69 | H | -0.388226 | 5.147560 | 4.052140 |
| 70 | H | 1.347799 | -3.745906 | 0.321552 |
| 71 | H | -5.526941 | 0.676629 | 0.956721 |
| 72 | H | 3.435601 | 0.182592 | 3.896569 |
| 73 | H | -5.527785 | 0.317220 | -1.449370 |
| 74 | H | -1.304821 | -4.039354 | -1.960391 |
| 75 | H | -2.028716 | -4.172439 | 2.580492 |
| 76 | H | -1.335538 | -3.455982 | -3.643929 |
| 77 | H | -6.152056 | -1.083070 | -0.574558 |
| 78 | H | -1.606372 | -3.039765 | 3.891698 |
| 79 | H | 4.966150 | -1.449876 | -3.943041 |
| 80 | H | 2.593766 | -4.941820 | -1.428441 |
| 81 | H | -5.998775 | -1.113388 | 2.769062 |
| 82 | H | 2.283445 | -5.102305 | 0.976068 |
| 83 | H | 4.718836 | -2.178931 | 4.035519 |
| 84 | H | -5.902191 | -2.120153 | -2.852834 |
| 85 | H | -4.322781 | -2.907946 | 4.042883 |
| 86 | H | -3.797449 | -3.549592 | -3.931477 |
| 87 | H | 4.115038 | -4.719552 | -0.560945 |
| 88 | H | 4.845774 | -3.987858 | -2.855660 |
| 89 | H | 4.079193 | -4.553828 | 2.768255 |

**Table S2** Orbital energies and kinetic energies (alpha) for $C_{3h}$ isomer of $[\mathbf{5}]^{2+}$obtained from DFT calculations

| | | orbital energies | kinetic energies |
|---|---|---|---|
| 191 | (A)--O | -0.38122 | 1.98704 |
| 192 | (A)--O | -0.37073 | 1.95085 |
| 193 | (A)--O | -0.36580 | 1.97617 |
| 194 | (A)--O | -0.36022 | 2.09940 |
| 195 | (A)--O | -0.35991 | 2.09898 |
| 196 | (A)--V | -0.17363 | 2.12901 |
| 197 | (A)--V | -0.17070 | 1.30744 |
| 198 | (A)--V | -0.17016 | 1.31593 |
| 199 | (A)--V | -0.16071 | 2.48837 |
| 200 | (A)--V | -0.16018 | 2.50050 |

**Table S3** Optimised atomic coordinates of $C_s$ isomer of $[\mathbf{5}]^{2+}$ obtained from DFT calculations

| Number | Atom | Coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | Pt | -1.828516 | -0.823424 | 0.024011 |
| 2 | C | -3.229887 | -1.132836 | 1.444907 |
| 3 | C | -3.259291 | -1.230520 | -1.370453 |
| 4 | S | -0.039694 | -0.201134 | -1.532907 |
| 5 | S | -0.008132 | -0.206885 | 1.528983 |
| 6 | Pt | 1.608885 | -1.187446 | -0.027860 |
| 7 | Pt | 0.166421 | 1.711030 | 0.009491 |
| 8 | N | -4.340455 | -0.348448 | 1.533586 |
| 9 | N | -3.373610 | -2.046626 | 2.436128 |
| 10 | N | -3.155715 | -2.131514 | -2.386580 |
| 11 | N | -4.517079 | -0.705092 | -1.514540 |
| 12 | C | 2.922450 | -1.878220 | 1.371480 |
| 13 | C | 2.915001 | -1.781234 | -1.447235 |
| 14 | C | 0.270516 | 3.173449 | -1.408082 |
| 15 | C | 0.442233 | 3.087967 | 1.452612 |
| 16 | C | -4.593286 | 0.742344 | 0.600072 |
| 17 | C | -5.168229 | -0.766276 | 2.569413 |
| 18 | C | -2.003250 | -2.989777 | -2.646866 |
| 19 | C | -4.306278 | -2.159358 | -3.158896 |
| 20 | C | -5.240194 | 0.293359 | -0.707770 |
| 21 | C | -5.163078 | -1.267435 | -2.613331 |
| 22 | C | -2.437560 | -3.126807 | 2.728804 |
| 23 | C | -4.555778 | -1.833603 | 3.138356 |
| 24 | N | 2.631547 | -2.726954 | 2.395776 |
| 25 | C | 1.321362 | -3.310318 | 2.668485 |
| 26 | N | 4.261214 | -1.624493 | 1.515504 |
| 27 | N | 2.871632 | -2.705332 | -2.437925 |
| 28 | N | 4.161890 | -1.241007 | -1.531309 |
| 29 | C | 1.735504 | -3.570100 | -2.735006 |
| 30 | N | -0.603760 | 3.341379 | -2.441853 |
| 31 | C | -1.774549 | 2.515190 | -2.727823 |
| 32 | N | 1.169687 | 4.196708 | -1.563683 |
| 33 | N | -0.295845 | 3.466383 | 2.526406 |
| 34 | N | 1.550480 | 3.877422 | 1.498691 |
| 35 | C | 3.749439 | -2.984473 | 3.173533 |
| 36 | C | -1.597682 | 2.920448 | 2.899594 |
| 37 | C | -0.253875 | 4.425819 | -3.230239 |
| 38 | C | 4.074587 | -2.737555 | -3.136650 |
| 39 | C | 0.343477 | 4.481009 | 3.231309 |
| 40 | C | 4.622784 | -0.223843 | -0.595310 |
| 41 | C | 4.890050 | -1.817587 | -2.565123 |
| 42 | C | 5.171860 | -0.793855 | 0.709321 |
| 43 | C | 4.774068 | -2.296380 | 2.622389 |
| 44 | C | 2.613704 | 3.782209 | 0.507066 |
| 45 | C | 1.506624 | 4.741922 | 2.586059 |
| 46 | C | 2.342661 | 4.581599 | -0.761335 |
| 47 | C | 0.856135 | 4.965901 | -2.681122 |
| 48 | H | -3.645083 | 1.251034 | 0.418253 |
| 49 | H | 0.762615 | -3.359933 | 1.735418 |
| 50 | H | -1.422523 | -3.072011 | -1.730119 |
| 51 | H | -1.642961 | -3.091388 | 1.985939 |
| 52 | H | -2.037477 | 1.956444 | -1.832599 |
| 53 | H | 0.951418 | -3.351190 | -2.012835 |

| | | | | |
|---|---|---|---|---|
| 54 | H | -2.358154 | -3.976563 | -2.952088 |
| 55 | H | -1.738197 | 1.975264 | 2.378552 |
| 56 | H | -2.952302 | -4.089368 | 2.673790 |
| 57 | H | 0.772366 | -2.694905 | 3.384667 |
| 58 | H | -2.600672 | 3.167156 | -3.021773 |
| 59 | H | -5.399131 | 1.185279 | -1.324721 |
| 60 | H | -5.279107 | 1.450743 | 1.073294 |
| 61 | H | -6.224906 | -0.133258 | -0.491273 |
| 62 | H | -1.377729 | -2.560423 | -3.432786 |
| 63 | H | -2.014867 | -2.997722 | 3.728451 |
| 64 | H | 1.370960 | -3.375837 | -3.746905 |
| 65 | H | -2.392804 | 3.622134 | 2.631083 |
| 66 | H | 1.460284 | -4.315921 | 3.070734 |
| 67 | H | -1.555338 | 1.809942 | -3.532549 |
| 68 | H | -6.095999 | -0.272294 | 2.812223 |
| 69 | H | -4.414524 | -2.811763 | -4.010944 |
| 70 | H | 2.032882 | -4.618565 | -2.651227 |
| 71 | H | -6.165930 | -0.987981 | -2.895753 |
| 72 | H | -4.848543 | -2.451547 | 3.972593 |
| 73 | H | 3.783566 | 0.447549 | -0.405264 |
| 74 | H | 2.761410 | 2.725234 | 0.279490 |
| 75 | H | -1.620251 | 2.744848 | 3.977154 |
| 76 | H | 3.717041 | -3.634526 | 4.033492 |
| 77 | H | -0.824392 | 4.715839 | -4.098372 |
| 78 | H | 5.505914 | 0.047223 | 1.327828 |
| 79 | H | 5.427347 | 0.345038 | -1.069663 |
| 80 | H | 4.236593 | -3.400236 | -3.972122 |
| 81 | H | 3.228539 | 4.503387 | -1.401845 |
| 82 | H | 3.532730 | 4.174921 | 0.950815 |
| 83 | H | -0.078677 | 4.914230 | 4.124303 |
| 84 | H | 6.050744 | -1.409349 | 0.491349 |
| 85 | H | 2.219790 | 5.637955 | -0.499884 |
| 86 | H | 5.812181 | -2.226821 | 2.906747 |
| 87 | H | 5.898694 | -1.520893 | -2.806457 |
| 88 | H | 1.445699 | 5.820213 | -2.974484 |
| 89 | H | 2.297341 | 5.440679 | 2.809794 |

**Table S4** Orbital energies and kinetic energies (alpha) for $C_s$ isomer of $[\mathbf{5}]^{2+}$obtained from DFT calculations

| | | orbital energies | kinetic energies |
|---|---|---|---|
| 191 | (A)--O | -0.37862 | 1.94337 |
| 192 | (A)--O | -0.37070 | 1.99316 |
| 193 | (A)--O | -0.36591 | 1.96156 |
| 194 | (A)--O | -0.36122 | 2.08077 |
| 195 | (A)--O | -0.35737 | 2.07792 |
| 196 | (A)--V | -0.17388 | 1.26215 |
| 197 | (A)--V | -0.17270 | 2.11448 |
| 198 | (A)--V | -0.16766 | 1.38777 |
| 199 | (A)--V | -0.16277 | 2.49602 |
| 200 | (A)--V | -0.15355 | 2.57674 |

**Table S5** Dipole moment (field-independent basis, Debye) of $[\mathbf{5}]^{2+}$ obtained from DFT calculations

| | x | y | z | total |
|---|---|---|---|---|
| $C_{3h}$-isomer | 0.0447 | 0.1071 | 0.5376 | 0.5500 |
| $C_s$-isomer | 0.3469 | 1.6257 | 0.1006 | 1.6654 |

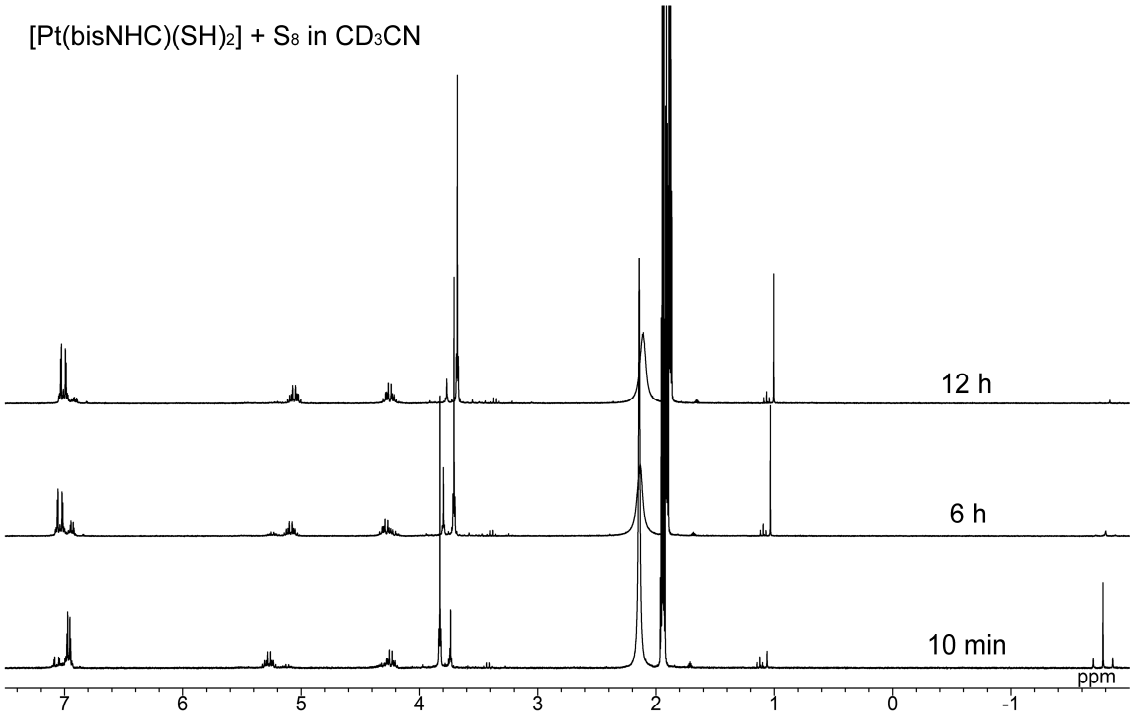


**Fig. S1** $^{1}$H NMR spectra of the reaction mixture of **2** and elemental sulfur.