Electronic supplementary materials *Mendeleev Commun*., 2015, **25**, 196−198

Unexpected N,N'-coordination of tris(2-pyridyl)phosphine chalcogenides to $PdCl_2$

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General remarks

Tris(2-pyridyl)phosphine oxide, sulfide and selenide were synthesized by treatment of tris(2-pyridyl)phosphine with H_2O_2 (H_2O/acetone), powdered sulfur and selenium, respectively.[1] The initial tris(2-pyridyl)phosphine was prepared directly from 2-bromopyridine and red phosphorus according to the published method.[2,3] $PdCl_2$ was used as purchased, while Li_2PdCl_4 was prepared by reaction of $PdCl_2$ with LiCl in water. ^1H (400.13 MHz) and ^{31}P NMR (161.98 MHz) spectra were recorded on a Bruker DPX-400 spectrometer at ambient temperature and referenced to internal HDMS (^1H) and external 85% H_3PO_4 (^{31}P) standards. UV-Vis spectra were measured on a Lambda 35 spectrophotometer. FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer. The microanalyses were performed on a Flash EA 1112 analyzer.

Computation details

The DFT calculations were performed using the Gaussian 09 pakage.[4] Geometry optimization and subsequent vibrational analysis were carried out at the B3LYP level[5] with SDD[6] basis set and pseudopotential on Pd and Se, and 6-311+G(d,p) on all other atoms.

References

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Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian Inc., Wallingford CT, 2009.

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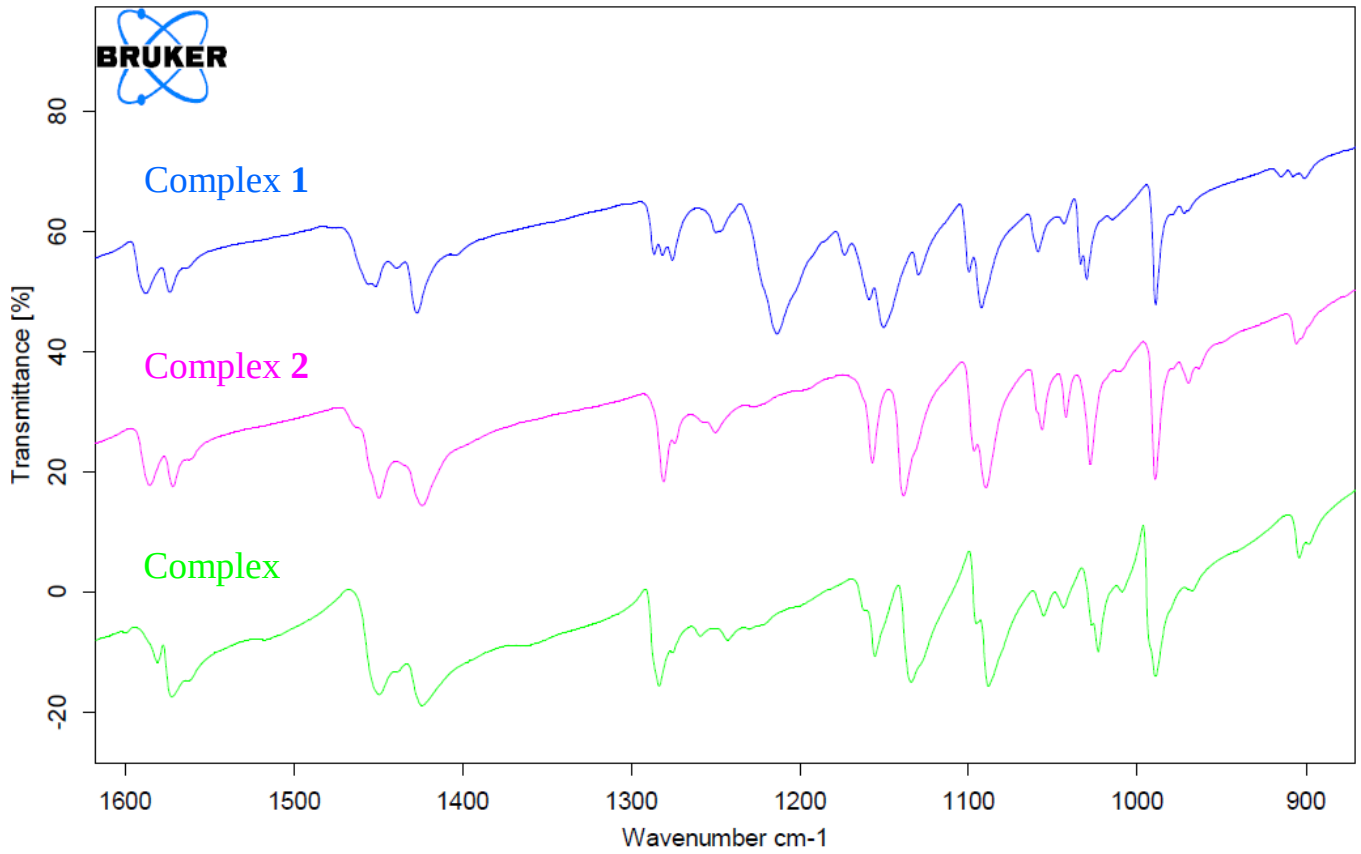
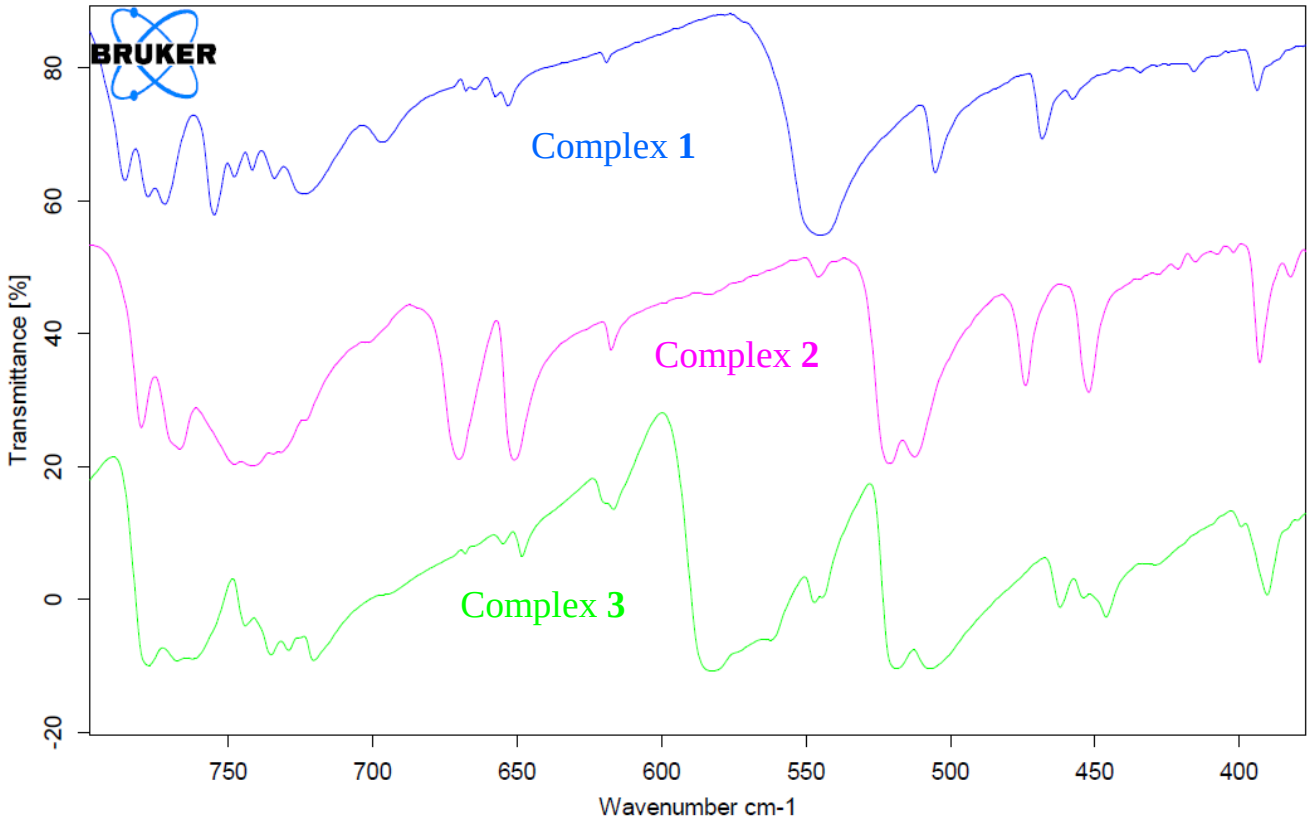
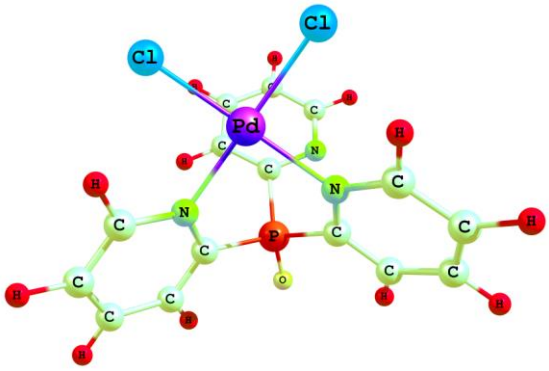
Figure S1. Copies of FT-IR spectra of complexes 1-3 (selected ranges)




BRUKER
Complex 1
Complex 2
Complex 3
Transmittance [%]
80
60
40
20
0
-20
750
700
650
600
550
500
450
400
Wavenumber cm-1

Structural data for possible isomers of complexes 1-3 from DFT calculations

Structure of [Pd(*N*,*N*′-Py_3P=O)Cl_2]



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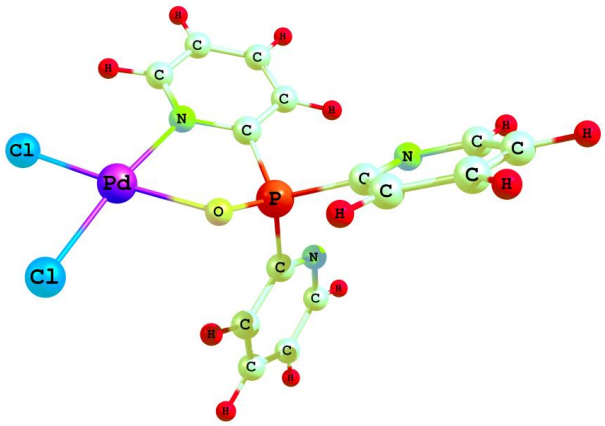
17	-1.665945000	-2.682732000	-0.777990000
17	1.529288000	-2.332765000	-1.610967000
15	0.094632000	1.591977000	1.220443000
7	-1.754430000	0.394496000	-0.458989000
7	1.137557000	0.725485000	-1.187144000
7	1.884074000	-0.101046000	2.194181000
6	1.944004000	0.810430000	-2.258466000
1	1.882509000	-0.006234000	-2.963950000
6	2.825119000	1.872006000	-2.432378000
1	3.454182000	1.897101000	-3.313162000
6	2.884694000	2.872457000	-1.469555000
1	3.567459000	3.707071000	-1.578410000
6	2.053617000	2.781193000	-0.356343000
1	2.053714000	3.522627000	0.432829000
6	1.198318000	1.690743000	-0.250694000
6	-2.962614000	0.262080000	-1.031873000
1	-3.064663000	-0.547887000	-1.740434000
6	-4.025182000	1.098935000	-0.707303000
1	-4.979187000	0.955912000	-1.198810000
6	-3.841130000	2.095354000	0.243909000
1	-4.654174000	2.757747000	0.517405000
6	-2.590009000	2.228728000	0.841303000
1	-2.376656000	2.987445000	1.584114000
6	-1.572314000	1.358084000	0.464544000
6	0.558895000	0.033338000	2.067009000
6	2.335505000	-1.172098000	2.846285000
1	3.413915000	-1.266005000	2.925988000
6	1.492882000	-2.139647000	3.395201000
1	1.912417000	-2.999836000	3.902526000
6	0.118165000	-1.983443000	3.263100000
1	-0.565993000	-2.722708000	3.662096000
6	-0.368392000	-0.869045000	2.584993000
1	-1.431992000	-0.728525000	2.440619000
8	0.136578000	2.839789000	2.045996000

Zero-point correction = 0.247126 (Hartree/Particle)
Thermal correction to Energy = 0.268450
Thermal correction to Enthalpy = 0.269394
Thermal correction to Gibbs Free Energy = 0.195031
Sum of electronic and zero-point Energies = -2208.142159
Sum of electronic and thermal Energies = -2208.120835
Sum of electronic and thermal Enthalpies = -2208.119891
Sum of electronic and thermal Free Energies = -2208.194254

Structure of [Pd(*N*,*O*-$Py_3P{=}O)Cl_2$]



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7	-1.036736000	-1.450205000	0.646781000
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1	2.745189000	2.203637000	3.661135000
6	1.522883000	3.608082000	2.561027000
1	1.682440000	4.421421000	3.258789000
6	0.720777000	3.772556000	1.437102000
1	0.232085000	4.718667000	1.235854000
6	0.543686000	2.693858000	0.571894000
1	-0.085501000	2.759509000	-0.308186000
6	1.190876000	1.501473000	0.896146000
6	4.685658000	-1.264418000	-0.648341000
1	5.419586000	-1.689564000	0.029321000
6	4.986894000	-1.079455000	-1.998406000
1	5.962514000	-1.356877000	-2.379009000
6	4.013826000	-0.542934000	-2.834705000
1	4.209746000	-0.393638000	-3.890179000
6	2.775452000	-0.203650000	-2.293923000
1	1.974251000	0.206113000	-2.896683000
6	2.585292000	-0.418034000	-0.928201000
6	0.302428000	-1.317404000	0.805649000
6	-1.669818000	-2.419937000	1.321974000
1	-2.741352000	-2.468064000	1.169699000
6	-0.990537000	-3.285444000	2.175304000
1	-1.545284000	-4.055158000	2.697171000
6	0.380430000	-3.141159000	2.346147000
1	0.928406000	-3.798136000	3.011400000
6	1.044949000	-2.132689000	1.649271000
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46	-2.022337000	-0.037636000	-0.618754000
17	-2.860246000	1.639046000	-1.939958000
17	-4.110017000	-0.569392000	0.186342000
8	-0.024887000	0.349192000	-1.326242000

Zero-point correction = 0.246157 (Hartree/Particle)
Thermal correction to Energy = 0.267866
Thermal correction to Enthalpy = 0.268810
Thermal correction to Gibbs Free Energy = 0.191421
Sum of electronic and zero-point Energies = -2208.124303
Sum of electronic and thermal Energies = -2208.102595
Sum of electronic and thermal Enthalpies = -2208.101650
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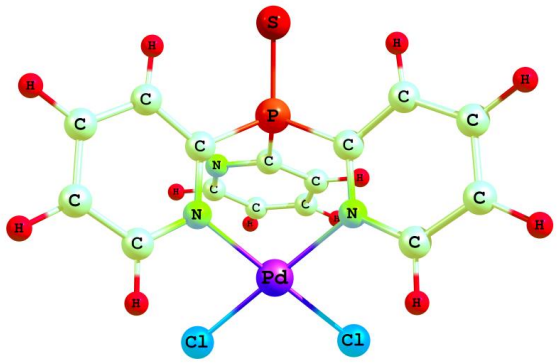
Structure of [Pd(*N*,*N*′-Py_3P=S)Cl_2]



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1	-1.197196000	-1.946469000	-2.718201000
6	0.737318000	-2.906728000	-2.889755000
1	0.433170000	-3.554486000	-3.702109000
6	2.018441000	-2.961400000	-2.356165000
1	2.751566000	-3.660276000	-2.741668000
6	2.346426000	-2.105111000	-1.308941000
1	3.325853000	-2.107817000	-0.847792000
6	1.380895000	-1.226907000	-0.833691000
6	-0.251696000	2.905316000	-1.202497000
1	-1.264546000	2.976957000	-1.572940000
6	0.630315000	3.978563000	-1.252796000
1	0.306652000	4.908797000	-1.702198000
6	1.903307000	3.833882000	-0.716312000
1	2.610063000	4.655314000	-0.733220000
6	2.259629000	2.611371000	-0.153012000
1	3.238265000	2.437674000	0.276444000
6	1.329626000	1.577508000	-0.144672000
6	0.574432000	-0.482344000	1.869208000
6	-0.408396000	-2.200441000	3.002423000
1	-0.535967000	-3.273116000	3.106416000
6	-1.084845000	-1.315522000	3.841933000
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6	-0.894800000	0.050644000	3.666943000
1	-1.414858000	0.768029000	4.290355000
6	-0.041181000	0.487140000	2.658135000
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16	3.689142000	-0.150866000	1.109999000

Zero-point correction = 0.245066 (Hartree/Particle)
Thermal correction to Energy = 0.266838
Thermal correction to Enthalpy = 0.267782
Thermal correction to Gibbs Free Energy = 0.192494
Sum of electronic and zero-point Energies = -2531.111268
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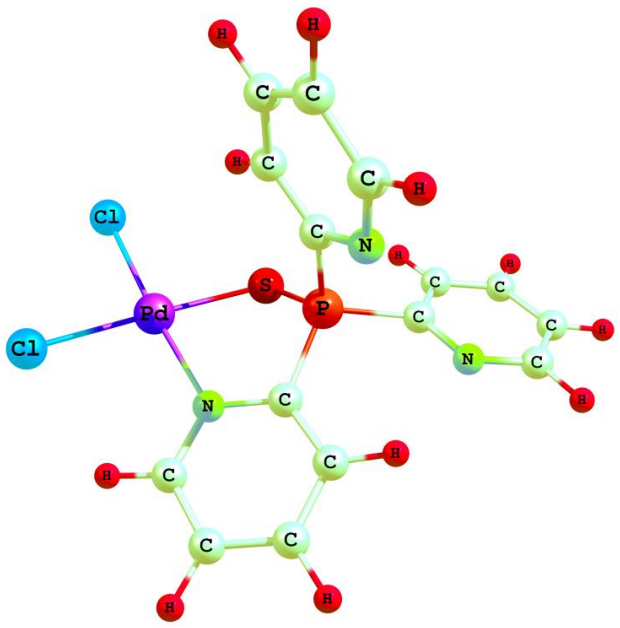
Structure of [Pd(*N*,*S*-Py_3P=S)Cl_2]



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1	-2.270138000	-1.565455000	4.028419000
6	-0.907854000	-3.006936000	3.164373000
1	-0.917118000	-3.661171000	4.027870000
6	-0.141815000	-3.306847000	2.043310000
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6	-0.951275000	-1.291703000	1.071980000
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1	-6.532398000	0.383036000	-1.559439000
6	-4.649389000	-0.481584000	-2.174485000
1	-5.050331000	-0.998906000	-3.038314000
6	-3.293877000	-0.571886000	-1.870403000
1	-2.617090000	-1.148207000	-2.488509000
6	-2.828296000	0.111496000	-0.745236000
6	-0.390325000	1.521157000	0.408873000
6	1.555093000	2.748449000	0.691286000
1	2.628913000	2.776693000	0.559620000
6	0.849987000	3.774952000	1.313730000
1	1.384760000	4.654374000	1.649819000
6	-0.518349000	3.642088000	1.501807000
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6	-1.155602000	2.487846000	1.047166000
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46	2.042959000	0.032981000	-0.626598000
17	3.095270000	-1.824526000	-1.509526000
17	3.959496000	0.615832000	0.574487000
16	0.078347000	-0.513185000	-1.903877000

Zero-point correction = 0.243974 (Hartree/Particle)
Thermal correction to Energy = 0.266253
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Thermal correction to Gibbs Free Energy = 0.188657
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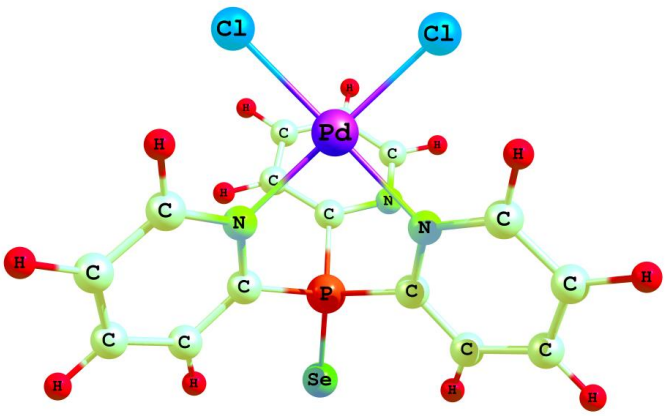
Sum of electronic and thermal Energies = -2531.077971
Sum of electronic and thermal Enthalpies = -2531.077027
Sum of electronic and thermal Free Energies = -2531.155568

Structure of [Pd(*N*,*N*′-Py_3P=Se)Cl_2]



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17	-3.194920000	-1.614815000	-0.167205000
15	1.573830000	-0.025302000	0.207056000
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7	-0.353376000	-1.188894000	-1.386358000
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6	0.013239000	-2.934332000	-2.979465000
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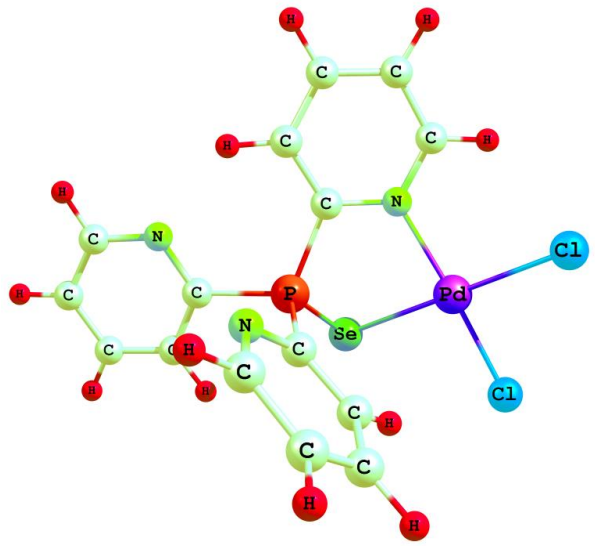
6	1.849485000	-2.072999000	-1.707110000
1	2.893135000	-2.049995000	-1.419739000
6	0.959262000	-1.207846000	-1.084789000
6	-0.811917000	2.882979000	-1.223248000
1	-1.874616000	2.925344000	-1.415721000
6	0.020697000	3.975760000	-1.434898000
1	-0.398491000	4.891304000	-1.832542000
6	1.369249000	3.869067000	-1.120437000
1	2.041836000	4.706405000	-1.265331000
6	1.847479000	2.664462000	-0.611243000
1	2.888449000	2.523110000	-0.348159000
6	0.959992000	1.609011000	-0.434352000
6	0.577326000	-0.431220000	1.702431000
6	-0.234215000	-2.142702000	2.971462000
1	-0.363235000	-3.213942000	3.086770000
6	-0.743383000	-1.254771000	3.918741000
1	-1.281259000	-1.629786000	4.780710000
6	-0.555370000	0.109498000	3.725984000
1	-0.947351000	0.829494000	4.434291000
6	0.126660000	0.541337000	2.592617000
1	0.275000000	1.596164000	2.399705000
34	3.704157000	-0.063001000	0.494820000

Zero-point correction = 0.244171 (Hartree/Particle)
Thermal correction to Energy = 0.266368
Thermal correction to Enthalpy = 0.267312
Thermal correction to Gibbs Free Energy = 0.190194
Sum of electronic and zero-point Energies = -2142.243177
Sum of electronic and thermal Energies = -2142.220980
Sum of electronic and thermal Enthalpies = -2142.220036
Sum of electronic and thermal Free Energies = -2142.297153

Structure of [Pd(*N*,*Se*-Py_3P=Se)Cl_2]



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7	0.859030000	1.613309000	0.596817000
6	-1.439561000	-2.327196000	3.026754000
1	-2.037434000	-2.226682000	3.927246000
6	-0.571645000	-3.407549000	2.860238000
1	-0.485057000	-4.157388000	3.637372000
6	0.177447000	-3.492319000	1.692201000
1	0.871070000	-4.309292000	1.532843000
6	0.038688000	-2.497507000	0.724807000
1	0.620951000	-2.511914000	-0.188261000
6	-0.854654000	-1.464046000	0.994992000
6	-4.589338000	1.508831000	-1.116271000
1	-4.885564000	2.513227000	-1.402362000
6	-5.516759000	0.467219000	-1.100610000
1	-6.547231000	0.651486000	-1.379075000
6	-5.087257000	-0.800994000	-0.724150000
1	-5.778363000	-1.635456000	-0.698658000
6	-3.751125000	-0.985309000	-0.378674000
1	-3.382037000	-1.955746000	-0.074517000
6	-2.905017000	0.123004000	-0.432993000
6	-0.472448000	1.428565000	0.735284000
6	1.426963000	2.668955000	1.199941000
1	2.499168000	2.752482000	1.082971000
6	0.686509000	3.573195000	1.955327000
1	1.189792000	4.414746000	2.414240000
6	-0.677940000	3.371292000	2.112126000
1	-1.276659000	4.053518000	2.704148000
6	-1.271634000	2.273909000	1.492148000
1	-2.330673000	2.083194000	1.584513000
46	2.030403000	0.197491000	-0.477598000
17	3.189830000	-1.452168000	-1.607307000
17	3.853495000	0.585788000	0.942370000
34	0.054908000	-0.208465000	-2.031093000

Zero-point correction = 0.243121 (Hartree/Particle)
Thermal correction to Energy = 0.265860
Thermal correction to Enthalpy = 0.266804
Thermal correction to Gibbs Free Energy = 0.187124
Sum of electronic and zero-point Energies = -2142.233434
Sum of electronic and thermal Energies = -2142.210695
Sum of electronic and thermal Enthalpies = -2142.209750
Sum of electronic and thermal Free Energies = -2142.289431