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Experimental and Theoretical Insights into trans influence of organo-sulfur and -selenium ligands in 5,6-Membered Palladium(II) Cationic Pincer Complexes Based on Iminophosphoranes

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Spectroscopy data for compound 3a



Figure S1. Mass Spectrum (FAB+) for compound 3a.



Figure S2. Infrared spectrum for compound **3a**.



Figure S3. ^{31}P NMR spectrum for compound 3a in CDCl3 (202 MHz).



Figure S4. ¹H NMR spectrum for compound **3a** in CDCl₃ (500 MHz).



Figure S5. ¹³C NMR spectrum for compound **3a** in CDCl₃ (125 MHz).



Figure S6. COSY NMR spectrum for compound **3a** in CDCl_{3.}



Figure S7. HSQC NMR spectrum for compound 3a in CDCl_{3.}



Figure S8. HMBC NMR spectrum for compound 3a in CDCI₃.



Spectroscopy data for compound 3b

Figure S9. Mass Spectrum (FAB+) for compound 3b.



Figure S10. Infrared spectrum for compound 3b.



Figure S11. ³¹P NMR spectrum for compound **3b** in CDCl₃ (202 MHz).



Figure S12. ¹H NMR spectrum for compound **3b** in CDCl₃ (500 MHz).



Figure S13. ¹³C NMR spectrum for compound **3b** in CDCl₃ (125 MHz).

Spectroscopy data for compound 3c



Figure S14. Mass Spectrum (FAB+) for compound 3c.



Figure S15. Infrared spectrum for compound 3c.



Figure S16. ³¹P NMR spectrum for compound **3b** in CDCI₃ (202 MHz).



Figure S17. ¹H NMR spectrum for compound 3c in CDCl₃ (500 MHz).



Figure S18. ¹³C NMR (DEPTQ) spectrum for compound **3c** in CDCl₃ (125 MHz).



Figure S19. ⁷⁷Se NMR spectrum for compound 3c in CDCl₃ (95 MHz).

Spectroscopy data for compound 3d



Figure S20. Mass Spectrum (FAB+) for compound **3d**.



Figure S21. Infrared spectrum for compound 3d.



Figure S22. ¹H NMR spectrum for compound **3d** in CDCl₃ (500 MHz).



Figure S23. ^{13}C NMR spectrum for compound 3d in CDCl3 (125 MHz).





Figure S25. ⁷⁷Se NMR spectrum for compound **3d** in CDCl₃ (95 MHz).

Spectroscopy data for compound 4a



Figure 26. Mass Spectrum (FAB+) for compound 4a.



Figure 27. Infrared spectrum for compound 4a.



Figure 28. ¹H NMR spectrum for compound 4**a** in CDCl₃ (500 MHz).



Figure 29. ¹³C NMR (DEPTQ) spectrum for compound 4**a** in CDCl₃ (126 MHz).



Figure 30. ³¹P NMR spectrum for compound 4**a** in CDCl₃ (202 MHz).



Figure 31. COSY NMR spectrum for compound 4a in CDCl_{3.}



Figure 32. HMBC NMR spectrum for compound 4a in CDCl_{3.}



Figure 33. HSQC NMR spectrum for compound 4a in CDCl_{3.}

Spectroscopy data for compound 4b



Figure 34. Mass Spectrum (FAB+) for compound 4b.



Figure 35. Infrared spectrum for compound 4b.



Figure S36. ¹H NMR spectrum for compound 4**b** in CDCl₃ (500 MHz).



Figure S37. ¹³C NMR (DEPTQ) spectrum for compound 4**b** in CDCl₃ (126 MHz).



Figure S38. ³¹P NMR spectrum for compound **4b** in CDCl₃ (202 MHz).

Spectroscopy data for compound 4c



Figure S39. Mass Spectrum (FAB+) for compound 4c.



Figure S40. Infrared spectrum for compound 4c.



Figure S41. ¹H NMR spectrum for compound **4c** in CDCl₃ (500 MHz).



Figure S42. ¹³C NMR (DEPTQ) spectrum for compound 4**c** in CDCl₃ (126 MHz).



Figure S43. ³¹P NMR spectrum for compound **4c** in CDCl₃ (202 MHz).



Figure S44. ^{77}Se NMR spectrum for compound 4c in CDCl₃ (95 MHz).

Spectroscopy data for compound 4d



Figure S45. Mass Spectrum (FAB+) for compound 4d.



Figure S46. Infrared spectrum for compound 4d.



Figure S47. ¹H NMR spectrum for compound 4**c** in CDCI₃ (500MHz).



Figure S50. ⁷⁷Se NMR spectrum for compound **4c** in CDCl₃ (95 MHz).

Crystallography data for 3d, 4a, 4b, 4c and 4b

Table S1. Crystal data and structure refinement for 3d.

Identification code	2132462
Empirical formula	C ₃₁ H ₂₆ NPSSe
Formula weight	554.52
Temperature/K	101(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.3859(4)
b/Å	12.4127(5)
c/Å	12.8167(6)
α/°	62.093(5)
β/°	74.683(4)
$\gamma^{\prime \circ}$	87.704(4)
Volume/Å ³	1266.55(11)
Z	2
Q _{calc} g/cm ³	1.454
μ/mm ⁻¹	3.526
F(000)	568.0
Crystal size/mm ³	$0.1 \times 0.07 \times 0.05$
Radiation	$CuK\alpha \ (\lambda = 1.54184)$
2Θ range for data collection/°	8.1 to 146.056
Index ranges	$-11 \le h \le 11, -15 \le k \le 15, -15 \le l \le 15$
Reflections collected	18864
Independent reflections	$4957 \ [R_{int} = 0.0524, R_{sigma} = 0.0383]$
Data/restraints/parameters	4957/0/317
Goodness-of-fit on F ²	1.065
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0537, wR_2 = 0.1412$
Final R indexes [all data]	$R_1 = 0.0560, wR_2 = 0.1446$
Largest diff. peak/hole / e Å-3	1.57/-1.00

Table S2. Crystal data and structure refinement for 4a

Identification code	2132186
Empirical formula	$C_{27}H_{26}BCl_3F_4NPPdS_2$
Formula weight	759.14
Temperature/K	100.0(4)
Crystal system	triclinic
Space group	P-1
a/Å	10.3604(4)
b/Å	12.8764(5)
c/Å	12.9364(7)
α/°	65.103(5)
β/°	73.145(4)
γ/°	74.459(4)
Volume/Å ³	1476.84(13)
Z	2
Q _{calc} g/cm ³	1.707
μ/mm ⁻¹	1.141
F(000)	760.0
Crystal size/mm ³	$0.18 \times 0.14 \times 0.11$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/°	5.868 to 58.468
Index ranges	$-13 \le h \le 8, -17 \le k \le 16, -17 \le l \le 17$
Reflections collected	12349
Independent reflections	$6823 [R_{int} = 0.0434, R_{sigma} = 0.0791]$
Data/restraints/parameters	6823/98/437
Goodness-of-fit on F ²	0.999
Final R indexes [I>= 2σ (I)]	R1 = 0.0389, wR2 = 0.0687
Final R indexes [all data]	R1 = 0.0521, $wR2 = 0.0748$
Largest diff. peak/hole / e Å-3	0.68/-0.85

Table S3. Crystal data and structure refinement for 4b

Identification code	2132185
Empirical formula	$C_{32}H_{30}BCl_3F_4NOPPdS_2$
Formula weight	839.22
Temperature/K	100.0(4)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.5136(7)
b/Å	15.1765(5)
c/Å	19.8095(6)
α/°	90
β/°	92.705(3)
γ/°	90
Volume/Å ³	6760.9(3)
Z	8
Q _{calc} g/cm ³	1.649
µ/mm⁻¹	1.008
F(000)	3376.0
Crystal size/mm ³	$0.34 \times 0.25 \times 0.15$
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.17 to 58.314
Index ranges	$-29 \le h \le 30, -20 \le k \le 19, -26 \le l \le 16$
Reflections collected	29675
Independent reflections	$8127 [R_{int} = 0.0460, R_{sigma} = 0.0456]$
Data/restraints/parameters	8127/0/407
Goodness-of-fit on F ²	1.044
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0377, wR_2 = 0.0837$
Final R indexes [all data]	$R_1 = 0.0468, wR_2 = 0.0894$
Largest diff. peak/hole / e Å-3	1.88/-0.99

Table S4. Crystal data and structure refinement for 4c

Identification code	2132447
Empirical formula	$C_{27}H_{26}BCl_3F_4NPPdSSe$
Formula weight	805.03
Temperature/K	99.9(4)
Crystal system	triclinic
Space group	P-1
a/Å	10.3865(5)
b/Å	12.8750(7)
c/Å	12.9927(7)
α/°	65.113(5)
β/°	72.940(4)
γ/°	74.721(5)
Volume/Å ³	1486.99(15)
Z	2
Q _{calc} g/cm ³	1.798
μ/mm ⁻¹	2.287
F(000)	794.0
Crystal size/mm ³	$0.3 \times 0.2 \times 0.2$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/°	5.856 to 58.426
Index ranges	$-14 \le h \le 14, -17 \le k \le 16, -17 \le l \le 12$
Reflections collected	12602
Independent reflections	$6826 [R_{int} = 0.0524, R_{sigma} = 0.0800]$
Data/restraints/parameters	6826/98/437
Goodness-of-fit on F ²	1.033
Final R indexes [I>= 2σ (I)]	R1 = 0.0425, wR2 = 0.0844
Final R indexes [all data]	R1 = 0.0589, wR2 = 0.0940
Largest diff. peak/hole / e Å-3	0.91/-0.95

Table S5. Crystal data and structure refinement for 4d

Identification code	2132458
Empirical formula	C ₃₂ H ₂₇ Cl ₇ NPPd ₂ SSe
Formula weight	1028.48
Temperature/K	99.9(3)
Crystal system	trigonal
Space group	P3221
a/Å	15.9613(6)
b/Å	15.9613(6)
c/Å	25.1755(10)
a/°	90
β/°	90
γ/°	120
Volume/Å3	5554.5(5)
Z	6
Q _{calc} g/cm ³	1.845
μ/mm-1	2.584
F(000)	3012.0
Crystal size/mm3	$0.25 \times 0.2 \times 0.15$
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.354 to 58.208
Index ranges	$-16 \le h \le 20, -21 \le k \le 18, -33 \le l \le 25$
Reflections collected	28648
Independent reflections	8831 [Rint = 0.0431, Rsigma = 0.0537]
Data/restraints/parameters	8831/48/444
Goodness-of-fit on F2	1.032
Final R indexes [I>= 2σ (I)]	R1 = 0.0380, wR2 = 0.0692
Final R indexes [all data]	R1 = 0.0512, $wR2 = 0.0743$
Largest diff. peak/hole / e Å-3	0.78/-0.67
Flack parameter	0.000(6)

Table S6. Cartesian	coordinates for optimized g	geometry 4a (PBE0/SDD/6-31+G(d)).	

Pd	-1.5049270000	0.2551210000	-0.9942370000
Cl	-3.3543620000	-0.0857390000	-2.3219150000
S	-1.2486900000	-1.9706530000	-0.3647480000
S	-1.7639640000	2.5181840000	-1.2186060000
Р	1.4870640000	-0.3968800000	0.0677080000
F	-2.1643390000	0.7941660000	1.7861060000
F	-4.2918890000	0.4559350000	2.6089220000
F	-3.1826390000	-1.2536800000	1.5330640000
F	-2.4818160000	-0.5568210000	3.6129730000
N	0.3119630000	0.7283210000	-0.1082370000
C	3.2974040000	1.2075950000	-1.2671260000
С	4.5261400000	1.8207240000	-1.4859330000
С	5.5848020000	1.5965920000	-0.6047690000
С	5.4112480000	0.7626340000	0.4974930000
С	4.1819130000	0.1450240000	0.7217730000
С	3.1227600000	0.3605680000	-0.1642570000
С	2.2878780000	-2.3755730000	1.8746780000
C	2.2127960000	-3.0525680000	3.0857680000
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С	0.4300120000	-1.5812860000	3.8093290000
С	0.5061150000	-0.8848600000	2.6030580000
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С	1.3206410000	-1.6656970000	-1.2350930000
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С	2.3668670000	-2.9984250000	-2.9759490000
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C	-0.3911250000	4.3427830000	0.3057110000
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C	1.3132140000	2.4354600000	1.3957580000
С	0.4085310000	2.0314290000	0.4009860000
В	-3.0583010000	-0.1324140000	2.4029040000

Н	-0.1075620000	2.5557570000	-2.9980860000
Н	-1.7993460000	2.5394940000	-3.5844390000
Н	-1.0929160000	4.0561800000	-2.9452740000
Н	2.4680120000	1.3906590000	-1.9462320000
Н	4.6559590000	2.4796580000	-2.3401330000
Н	6.5434800000	2.0795720000	-0.7748550000
Н	6.2310890000	0.5954460000	1.1908610000
Н	4.0465530000	-0.4888630000	1.5935300000
Н	2.9831780000	-2.7138770000	1.1084630000
Н	2.8623330000	-3.9045520000	3.2696660000
Н	1.2201100000	-3.1937420000	4.9924420000
Н	-0.3351650000	-1.2957780000	4.5241540000
Н	-0.2033710000	-0.0846440000	2.4013140000
Н	3.3666740000	-1.4528060000	-1.8756240000
Н	3.2422530000	-3.2323430000	-3.5748300000
Н	1.1102550000	-4.4757040000	-3.9114180000
Н	-0.8671140000	-3.9328860000	-2.5491220000
Н	-2.3856090000	-4.0377170000	-0.7404030000
Н	-2.8445110000	-2.7929040000	-1.9875430000
Н	-3.4510790000	-2.6626390000	-0.3135620000
Н	-1.1049370000	5.0624790000	-0.0882220000
Н	0.5957180000	5.7621630000	1.5908810000
Н	2.0973210000	4.0355310000	2.5801440000
Н	1.9492360000	1.7019660000	1.8817750000

Pd0.2801970000-1.56624900000.3961270000CI0.7528240000-3.55052300001.4629280000S-1.6781770000-1.1398100001.57255000S2.0257390000-1.8573210000.2514780000P-0.59991700001.5615620000.2514780000F-1.5736780000-1.995990000-2.326271000F-2.661721000-3.8892670000-2.32671000F-2.9163250000-2.8827540000-0.268750000F-3.850553000-1.9233480000-0.268750000C1.7309090003.01719700000.066873000C1.913940005.314723000-0.630166000C0.5347500005.370845000-0.179658000C0.5347500005.3708450000-0.9811000C0.34139600003.075969000-0.090811000C-3.0985540002.082730000-0.4749360000C-4.448520002.9322040000.167617000C-4.448520002.932204000-0.1505150000C-5.0456570002.058162000-0.1650150000C-2.9403750000.9202530002.05293000C-0.6536650001.2991030002.872422000C-0.6670600002.2010780004.840866000C-0.6546940001.0329200004.840866000C-0.16570100001.0329200004.840866000C-0.657600002.2101780004.840866000C-0.6576900001.179830002.655772000C <th></th> <th></th> <th></th> <th></th>				
Cl0.7528240000-3.55052300001.462928000S-1.6781770000-1.1398100001.572955000P-0.59991700001.5615620000.2514780000F-1.5736780000-1.9095990000-1.861586000F-2.6617210000-3.8892670000-2.3262710000F-2.9163250000-2.827540000-0.2687500000F-3.850553000-1.9233480000-2.141308000N0.1090720000.23898000-0.50744000C1.7309900003.0171970000.086873000C1.9139400005.314723000-0.6301660000C1.9139400005.3147230000-0.6301660000C0.5347500005.3708450000-0.519200000C0.3413960003.0759690000.0908110000C-3.0985400002.8027300000.1676170000C-3.0985400002.05816200000.1676170000C-4.485220002.058162000-0.745906000C-4.489320001.050183000-1.350059000C-2.9403750001.2991030002.05523000C-0.5396550001.2991030002.872422000C-0.6694700002.2010780004.468740000C-0.1026701000-0.042310004.643574000C-1.026701000-1.4527100001.393221000C5.189960000-1.4527100001.393221000C5.2837970000.411728000-0.131309000C5.2837970000.411728000-0.3139000C <td>Pd</td> <td>0.2801970000</td> <td>-1.5662490000</td> <td>0.3961270000</td>	Pd	0.2801970000	-1.5662490000	0.3961270000
S-1.6781770000-1.13981000001.5729550000S2.0257390000-1.8573210000-1.0863610000F-0.59991700001.5615620000.2514780000F-1.5736780000-1.9095990000-1.861586000F-2.6617210000-3.882670000-2.326271000F-2.9163250000-2.88275400000.02687500000F-3.8505530000-1.9233480000-2.1413080000C1.7309900003.01719700000.0868730000C1.9139400005.314723000-0.630166000C0.5347500005.370845000-0.51920000C0.3413960003.0759690000.098811000C0.3413960002.8027300000.167617000C-3.9855400002.8027300000.167617000C-3.9855400002.8027300000.167617000C-3.9855400002.05816200000.167617000C-3.9855400002.05816200000.167617000C-3.9855400001.806050000-0.165315000C-4.4983200001.806050000-0.16571000C-2.94037500001.2991300002.055293000C-2.94037500001.03222000004.840866000C-2.14152600002.2017800002.655772000C-1.03257500000.11798300002.655772000C-1.0325750000-1.4527100003.93221000C-1.045750000-1.4527100000.131309000C-2.84181000-0.293860000.293463000 <tr< td=""><td>Cl</td><td>0.7528240000</td><td>-3.5505230000</td><td>1.4629280000</td></tr<>	Cl	0.7528240000	-3.5505230000	1.4629280000
S2.0257390000-1.8573210000-1.0863610000P-0.59991700001.5615620000.2514780000F-1.5736780000-1.9095990000-1.861586000F-2.6617210000-2.8827540000-0.268750000F-3.8505530000-1.923480000-2.141308000N0.10907200000.2938980000-0.5007440000C1.7309900003.01719700000.0868730000C1.7309900003.01719700000.0868730000C1.9139400005.314723000-0.630166000C0.5347500005.370845000-0.818936000C0.3413960002.8027300000.074590000C0.3413960002.8027300000.167617000C-3.985540002.8027300000.167617000C-5.0456570002.05816200000.167617000C-5.9456570002.0581620000-1.05315000C-2.9403750001.806050000-0.165071000C-2.94337500001.2991030002.65273000C-0.06694700002.210780004.84086000C-1.025750000-1.0329700002.655772000C-1.0325750000-1.4527100002.655772000C-1.0325750000-1.4527100002.6549390000C-1.0325750000-1.4527100002.654939000C-1.0325750000-1.4527100002.654939000C-1.0325750000-1.4527100002.654939000C-1.0325750000-1.4527100002.654939000 <tr< td=""><td>S</td><td>-1.6781770000</td><td>-1.1398100000</td><td>1.5729550000</td></tr<>	S	-1.6781770000	-1.1398100000	1.5729550000
P.0.5999170001.5615620000.251478000F.1.573678000.1.99599000.1.861586000F.2.661721000.3.889267000.2.326271000F.2.916325000.2.882754000.0.268750000F.3.850553000.1.923348000.2.141308000N0.1090720000.293898000.0.500744000C1.739990003.0171970000.086873000C1.9139440005.314723000.0.630166000C.0.5347500005.370845000.0.818936000C0.5347500005.370845000.0.90811000C0.3413960003.075969000.0.90811000C.0.3413960002.8027300000.167617000C.3.985540002.8027300000.167617000C.4.485220002.9322040000.167617000C.4.48520002.058162000.1.35059000C.4.298390001.050183000.1.35059000C.4.298390001.050183000.2.523300C.2.398530001.291030002.872422000C.0.65396650001.299130002.857242000C.0.6545690001.329200004.4666000C.1.174330002.655772000C.1.302575000.1.4527100003.93221000C.1.302575000.1.452710000.3.93221000C.1.302575000.1.452710000.3.93221000C.1.31097000.4.29836000.1.333221000C.1.31309000.1.452710000.3.9322	S	2.0257390000	-1.8573210000	-1.0863610000
F.1.573678000.1.909599000.1.861586000F.2.661721000.3.889267000.2.326271000F.2.916325000.2.882754000.0.268750000F.3.850553000.1.9233480000.2.141308000N0.1090720000.293898000.0.500744000C1.7309900003.0171970000.086873000C1.7309900003.0171970000.086873000C1.9139440005.314723000.0.630166000C0.5347500005.370845000.0.51920000C0.3413960003.075969000.0.90811000C0.3413960002.8027300000.470346000C0.3413960002.0581620000.167617000C-2.9403750000.920253000.1.065315000C-4.448520002.329440002.055293000C-4.298390001.806050002.055293000C-2.398530001.2991030002.85242000C-0.659650001.2991030002.85242000C-0.669470002.3296430002.85742000C-0.67060002.210780004.46577000C-0.67060002.3296430000.75545000C-1.026701000-0.042310004.36374000C-1.026701000-1.4527100003.93221000C5.824181000-1.4527100003.93221000C5.824181000-1.4527100003.93221000C5.824181000-0.293680000.75545000C5.180960000-1.452710000<	Р	-0.5999170000	1.5615620000	0.2514780000
F-2.661721000-3.8892670000-2.326271000F-2.9163250000-2.8827540000-0.268750000F-3.8505530000-1.9233480000-2.141308000N0.1090720000.293898000-0.500744000C1.7309900003.0171970000.086873000C2.5115490004.136839000-0.630166000C1.9139440005.314723000-0.631189000C0.5347500005.370845000-0.618936000C0.5347500002.8027300000.470346000C0.3413960002.9322040000.167617000C-3.0985540002.0581620000.167617000C-3.0985540002.058162000-1.350059000C-3.0985540002.0523000-1.65315000C-3.0985540002.0523000-1.65315000C-2.9403750000.920253000-1.65315000C-0.0669470002.201780002.05293000C-0.0669470002.201780004.260177000C-0.0570600001.0329200004.840866000C-1.025750000.1179830002.65577200C-1.025750000.1179830002.655772000C5.84181000-2.998840000.975545000C5.824181000-0.293680000.942569000C5.839770000.411728000-0.313309000C5.84181000-0.293680000.275755000C5.839770000.411728000-0.29363000C5.839770000.41172800	F	-1.5736780000	-1.9095990000	-1.8615860000
F2.9163250002.882754000-0.268750000F3.850553000-1.923480000-2.141308000N0.10907200000.2938980000-0.5007440000C1.7309090003.0171970000.086873000C2.5115490004.136839000-0.179658000C1.9139440005.314723000-0.630166000C0.5347500005.3708450000-0.818936000C0.5347500005.3708450000-0.6511920000C0.3413960003.0759690000.470346000C-3.985540002.8027300000.167617000C-3.0985540002.0581620000.167617000C-4.4485220002.058162000-1.350059000C-5.0456570000.920253000-1.065315000C-2.398530001.806050000-0.165071000C-0.05396650001.2991030002.85242000C-0.669470002.201780004.840866000C-0.10267010000.042310004.840866000C-0.1026701000-0.042310004.66177000C-1.025750000.1179830002.655772000C-1.0325750000.1179830000.75545000C5.84181000-1.8995340000.9425699000C5.824181000-0.293680000.942569000C5.824181000-0.293680000.4231309000C5.8397700000.1174335000-0.29363000C5.834770000-1.817435000-0.29363000C5.834777000 </td <td>F</td> <td>-2.6617210000</td> <td>-3.8892670000</td> <td>-2.3262710000</td>	F	-2.6617210000	-3.8892670000	-2.3262710000
F-3.8505530000-1.9233480000-2.141308000N0.1090720000.02938980000.0500744000C1.7309090003.0171970000.086873000C2.5115490004.136839000-0.179658000C1.9139440005.3147230000.0630166000C0.5347500005.3708450000.0818936000C0.02542860004.253155000-0.090811000C0.3413960003.0759690000.0470346000C0.3413960002.8027300000.167617000C-3.0985540002.9322400000.167617000C-4.4485220002.9322400000.167617000C-5.0456570002.0581620000-0.745906000C-5.4398530001.806050000-1.055192000C-2.9403750000.9202530001.065917000C-0.669470002.201780002.055293000C-0.669470002.210780004.260177000C-0.0669470002.201780004.403574000C-1.026701000-0.0042310004.643574000C-1.032575000-1.4895340002.655972000C5.180960000-1.4527100001.393221000C5.180960000-1.4527100000.913309000C5.2937970000.4117280000.131309000C5.2937970000.4117335000-0.298163000C3.4927570000.589150000-0.2344950000C3.4927570000.589150000-2.234495000C3.492757000 <td>F</td> <td>-2.9163250000</td> <td>-2.8827540000</td> <td>-0.2687500000</td>	F	-2.9163250000	-2.8827540000	-0.2687500000
N0.10907200000.2938980000-0.500744000C1.7309090003.01719700000.086873000C2.51154900004.1368390000-0.179658000C1.9139440005.3147230000-0.630166000C0.5347500005.3708450000-0.818936000C0.5347500004.2531550000-0.0551920000C0.3413960003.075969000-0.090811000C0.3413960002.8027300000.470346000C-3.0985540002.8027300000.167617000C-4.4485220002.93220400000.167617000C-5.0456570002.058162000-1.350059000C-4.298390001.050183000-1.655315000C-2.9403750000.920253000-1.065315000C-2.9403750001.2991030002.055293000C-0.5396650001.2991030002.872422000C-0.669470002.2010780004.480866000C-0.669470002.2010780004.480866000C-1.026701000-0.042310004.643574000C-1.026701000-2.4980720002.654939000C-1.032575000-1.4527100001.393221000C5.80960000-1.4527100001.393221000C5.824181000-0.293680000.942569000C5.2937970000.4117280000.757543000C5.293797000-1.174335000-2.234495000C3.492757000-1.174335000-2.234495000	F	-3.8505530000	-1.9233480000	-2.1413080000
C1.7309090003.01719700000.086873000C2.51154900004.1368390000-0.179658000C1.91394400005.3147230000-0.630166000C0.5347500005.3708450000-0.818936000C0.025428600004.2531550000-0.551920000C0.34139600003.07596900000.470346000C-3.09855400002.8027300000.470346000C-3.09855400002.93220400000.167617000C-4.44852200002.0581620000-0.745906000C-5.04565700002.0581620000-1.350059000C-2.94037500000.9202530000-1.065315000C-2.94037500001.2991030002.055293000C-0.06694700002.32964300002.055293000C-0.06694700002.32964300004.260177000C-0.0570600001.0329200004.840866000C-0.06701600002.2010780004.840866000C-1.02670100001.0329200004.840866000C-1.02670100001.0329200004.654939000C-1.0267010000-2.4980720002.655493000C-1.015560000-1.4527100001.33221000C5.824181000-0.293680000.942569000C5.824181000-0.293680000.942569000C5.82937970000.411728000-0.757953000C3.492757000-1.174335000-2.234495000C1.531107000-0.588150000-3.529735000 <td>Ν</td> <td>0.1090720000</td> <td>0.2938980000</td> <td>-0.5007440000</td>	Ν	0.1090720000	0.2938980000	-0.5007440000
C2.5115490004.136839000-0.179658000C1.9139440005.314723000-0.630166000C0.5347500005.370845000-0.818936000C-0.2542860004.253155000-0.551920000C0.3413960003.0759690000.4090811000C-3.0985540002.8027300000.470346000C-3.0985540002.9322040000.167617000C-4.485220002.058162000-0.745906000C-5.0456570002.058162000-0.745906000C-2.9403750000.920253000-1.065315000C-2.3398530001.8060500002.055293000C-0.0669470002.3296430002.872422000C-0.0669470002.2010780004.260177000C-0.057060001.0329200004.840866000C-0.05456940001.0329200004.84086000C-1.0267010000.1179830002.655772000C-1.0267010000.1179830002.655772000C-2.141526000-2.4980720002.654939000C5.180960000-1.4527100001.393221000C5.180960000-1.4527100000.131309000C5.2937970000.411728000-0.131309000C5.2937970000.411728000-0.298163000C3.492757000-1.174335000-2.234495000C3.492757000-1.17435000-3.52935000C2.040165000-0.66413000-3.52935000	С	1.7309090000	3.0171970000	0.0868730000
C1.91394400005.3147230000-0.6301660000C0.53475000005.3708450000-0.8189360000C-0.25428600004.2531550000-0.090811000C0.34139600003.0759690000-0.090811000C-3.09855400002.80273000000.470346000C-3.09855400002.93220400000.167617000C-4.44852200002.0581620000-0.745906000C-5.04565700002.0581620000-0.165071000C-4.2983900001.0501830000-1.350059000C-2.94037500000.9202530000-1.0653150000C-2.3985300001.80605500002.0552930000C-0.0694700002.3296430002.872422000C-0.06700600002.20107800004.840866000C-0.0670100000.10329200004.840866000C-1.02670100001.0329200004.643574000C-1.02670100000.1179830002.655772000C-2.1415260000-2.49807200002.654939000C-1.0325750000.1179830000.75545000C5.1809600000-1.4527100001.393221000C5.1809600000.411728000-0.131309000C5.2937970000.411728000-0.131309000C3.4927570000.1174335000-0.2934495000C3.492757000-1.174335000-2.234495000C1.531107000-0.589150000-3.529735000	С	2.5115490000	4.1368390000	-0.1796580000
C0.0.5347500005.370845000-0.818936000C-0.2542860004.253155000-0.090811000C0.3413960003.0759690000.470346000C-3.0985540002.8027300000.470346000C-3.0985540002.09322040000.167617000C-4.4485220002.0581620000.167617000C-5.0456570002.058162000-0.745906000C-4.298390001.050183000-1.050315000C-2.9403750000.920253000-1.065315000C-2.398530001.806050002.055293000C-0.5396650001.2991030002.055293000C-0.0669470002.2010780004.260177000C-0.0670060002.2010780004.840866000C-0.05456940001.0329200004.043574000C-1.026701000-0.0042310004.043574000C-1.026701000-2.4980720002.654939000C-2.141526000-2.4980720002.654939000C5.180960000-1.4527100001.333221000C5.180960000-0.293680000.0131309000C5.2937970000.411728000-0.131309000C3.492757000-1.174335000-2.234495000C1.531107000-0.606413000-2.234495000	С	1.9139440000	5.3147230000	-0.6301660000
C-0.25428600004.2531550000-0.551920000C0.34139600003.07596900000.470346000C-3.09855400002.80273000000.470346000C-4.44852200002.93220400000.167617000C-5.04565700002.0581620000-0.745906000C-4.2983390001.0501330000-1.350059000C-2.94037500000.9202530000-1.065315000C-2.3385300001.8060500002.055293000C-2.33965500001.29910300002.055293000C-0.6694700002.32964300002.872422000C-0.06700600002.20107800004.840866000C-0.06700600002.20107800004.840866000C-0.167010000-0.00423100004.840866000C-1.0267010000-0.0423100004.655772000C-1.0267010000-1.179830002.655792000C-1.0325750000-1.4527100001.393221000C5.1809600000-1.4527100001.393221000C5.824181000-0.29388000-0.75753000C5.824181000-0.20187000-0.75753000C3.492757000-1.174335000-0.298163000C1.531107000-0.589150000-2.234495000C2.0401650000-0.666413000-3.529735000	С	0.5347500000	5.3708450000	-0.8189360000
C0.34139600003.0759690000-0.0908110000C-3.09855400002.80273000000.4703460000C-4.44852200002.93220400000.1676170000C-5.04565700002.0581620000-0.7459060000C-4.29983900001.0501830000-1.3500590000C-2.94037500000.9202530000-1.0653150000C-2.33985300001.8060550000-0.1650710000C-0.53966500001.29910300002.055293000C-0.06694700002.20107800004.260177000C-0.06700600002.20107800004.840866000C-0.06700600002.20107800004.840866000C-0.1657500000.11798300002.655772000C-1.0257500000.11798300002.655772000C-1.0325750000-1.4527100001.3332210000C5.824181000-0.2936800000.942569000C5.824181000-0.293680000-0.757953000C3.4927570000.4117280000-0.757953000C3.492757000-0.11743350000-0.298163000C3.4927570000-1.1743350000-2.2344950000C1.5311070000-0.5891500000-3.5297350000	С	-0.2542860000	4.2531550000	-0.5519200000
C-3.09855400002.8027300000.470346000C-4.44852200002.05216200000.167617000C-5.04565700002.0581620000-0.745906000C-4.2998390001.0501830000-1.350059000C-2.3403750000.920253000-1.065315000C-2.33985300001.806050000-0.165071000C-0.53966500001.29910300002.055293000C-0.06694700002.32964300002.872422000C-0.06700600002.20107800004.8606000C-0.06700600002.20107800004.840866000C-0.067010000-0.00423100004.043574000C-1.0267010000-0.11798300002.655772000C-1.03257500000.11798300002.655439000C-1.0325750000-1.4527100001.393221000C5.180960000-1.4527100000.942569000C5.2937970000.011728000-0.75753000C5.2937970000.011728000-0.75753000C3.492757000-1.174335000-0.298163000C3.492757000-1.174335000-0.298163000C1.5311070000-0.589150000-3.529735000C2.0401650000-0.666413000-3.529735000	С	0.3413960000	3.0759690000	-0.0908110000
C-4.44852200002.93220400000.1676170000C-5.04565700002.058162000-0.745906000C-4.29983900001.0501830000-1.350059000C-2.94037500000.9202530000-1.065315000C-2.33985300001.8060050000-0.165071000C-0.53966500001.29910300002.055293000C-0.06694700002.20107800002.872422000C-0.06700600002.20107800004.260177000C-0.06700600002.20107800004.840866000C-0.054569400001.0329200004.840866000C-1.0257010000-0.00423100004.043574000C-1.0257500000.11798300002.655772000C-2.1415260000-1.89953400000.775545000C5.1809600000-1.45271000001.393221000C5.8241810000-0.2936800000.942569000C5.29379700000.4117280000-0.131309000C3.4927570000-1.1743350000-0.298163000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-3.0985540000	2.8027300000	0.4703460000
C5.04565700002.05816200000.745906000C4.2998390001.05018300001.350059000C2.94037500000.92025300001.065315000C2.33985300001.80600500002.0552930000C0.53966500001.29910300002.055293000C0.6694700002.32964300002.872422000C0.0670060002.20107800004.2601770000C0.0670060002.20107800004.8408660000C0.54569400001.03292000004.8408660000C1.0267010000.0.00423100002.6557720000C1.03257500000.11798300002.654939000C2.14152600002.49807200000.775545000C.5.8241810001.89953400000.775545000C.5.824181000.0.2993680000.942569000C.5.2937970000.411728000.0.757953000C.5.293797000.1.174335000.0.298163000C.5.31107000.0.5891500002.234495000C.2.040165000.0.606413000.3.529735000	С	-4.4485220000	2.9322040000	0.1676170000
C-4.29933900001.0501830000-1.3500590000C-2.34037500000.9202530000-1.0653150000C-2.33985300001.80600500002.0552930000C-0.53966500002.29107300002.8724220000C-0.06694700002.32964300002.8724220000C-0.06700600002.20107800004.2601770000C-0.06700600001.03292000004.8408660000C-0.54569400001.03292000004.8408660000C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C5.1809600000-1.45271000001.3932210000C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-5.0456570000	2.0581620000	-0.7459060000
C2.94037500000.92025300001.0653150000C2.33985300001.8060050000-0.1650710000C-0.53966500001.29910300002.0552930000C-0.06694700002.32964300002.8724220000C-0.06700600002.20107800004.2601770000C-0.06700600001.03292000004.8408660000C-0.54569400001.0329200004.8408660000C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C4.0167560000-1.89953400000.7755450000C5.1809600000-1.4527100001.3932210000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-4.2998390000	1.0501830000	-1.3500590000
C-2.33985300001.8060050000-0.1650710000C-0.53966500001.29910300002.0552930000C-0.06694700002.32964300002.8724220000C-0.06700600002.20107800004.2601770000C-0.54569400001.03292000004.8408660000C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C-2.1415260000-1.45271000000.7755450000C5.1809600000-1.45271000000.9425690000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-2.9403750000	0.9202530000	-1.0653150000
C-0.53966500001.29910300002.0552930000C-0.06694700002.32964300002.872422000C-0.06700600002.20107800004.2601770000C-0.54569400001.03292000004.8408660000C-0.5456940000-0.00423100004.0435740000C-1.0267010000-0.00423100002.6557720000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C-2.1415260000-1.89953400000.7755450000C5.1809600000-1.45271000001.3932210000C5.29379700000.4117280000-0.1313090000C5.2937970000-0.201870000-0.7579530000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-2.3398530000	1.8060050000	-0.1650710000
C-0.06694700002.32964300002.8724220000C-0.06700600002.20107800004.2601770000C-0.54569400001.03292000004.8408660000C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C4.0167560000-1.89953400000.7755450000C5.1809600000-1.45271000001.3932210000C5.82418100000.029936800000.9425690000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-0.5396650000	1.2991030000	2.0552930000
C-0.06700600002.20107800004.2601770000C-0.54569400001.03292000004.8408660000C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.65549390000C-2.1415260000-1.89953400000.7755450000C5.1809600000-1.45271000001.3932210000C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-0.0669470000	2.3296430000	2.8724220000
C-0.54569400001.03292000004.8408660000C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C4.0167560000-1.89953400000.7755450000C5.1809600000-1.45271000001.3932210000C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-0.0670060000	2.2010780000	4.2601770000
C-1.0267010000-0.00423100004.0435740000C-1.03257500000.11798300002.6557720000C-2.1415260000-2.49807200002.6549390000C4.0167560000-1.89953400000.7755450000C5.1809600000-1.45271000001.3932210000C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-0.5456940000	1.0329200000	4.8408660000
C -1.0325750000 0.1179830000 2.6557720000 C -2.1415260000 -2.4980720000 2.6549390000 C 4.0167560000 -1.8995340000 0.7755450000 C 5.1809600000 -1.4527100000 1.3932210000 C 5.8241810000 -0.2993680000 0.9425690000 C 5.2937970000 0.4117280000 -0.1313090000 C 4.1244970000 -0.0201870000 -0.7579530000 C 3.4927570000 -1.1743350000 -0.2981630000 C 1.5311070000 -0.5891500000 -2.2344950000 C 2.0401650000 -0.6064130000 -3.5297350000	С	-1.0267010000	-0.0042310000	4.0435740000
C-2.1415260000-2.49807200002.6549390000C4.0167560000-1.89953400000.7755450000C5.1809600000-1.45271000001.3932210000C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C4.1244970000-0.0201870000-0.7579530000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	-1.0325750000	0.1179830000	2.6557720000
C 4.0167560000 -1.8995340000 0.7755450000 C 5.1809600000 -1.4527100000 1.3932210000 C 5.8241810000 -0.2993680000 0.9425690000 C 5.2937970000 0.4117280000 -0.1313090000 C 4.1244970000 -0.0201870000 -0.7579530000 C 3.4927570000 -1.1743350000 -0.2981630000 C 1.5311070000 -0.5891500000 -2.2344950000 C 2.0401650000 -0.6064130000 -3.5297350000	С	-2.1415260000	-2.4980720000	2.6549390000
C5.1809600000-1.45271000001.3932210000C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C4.1244970000-0.0201870000-0.7579530000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	4.0167560000	-1.8995340000	0.7755450000
C5.8241810000-0.29936800000.9425690000C5.29379700000.4117280000-0.1313090000C4.1244970000-0.0201870000-0.7579530000C3.4927570000-1.1743350000-0.2981630000C1.5311070000-0.5891500000-2.2344950000C2.0401650000-0.6064130000-3.5297350000	С	5.1809600000	-1.4527100000	1.3932210000
C 5.2937970000 0.4117280000 -0.1313090000 C 4.1244970000 -0.0201870000 -0.7579530000 C 3.4927570000 -1.1743350000 -0.2981630000 C 1.5311070000 -0.5891500000 -2.2344950000 C 2.0401650000 -0.6064130000 -3.5297350000	С	5.8241810000	-0.2993680000	0.9425690000
C 4.1244970000 -0.0201870000 -0.7579530000 C 3.4927570000 -1.1743350000 -0.2981630000 C 1.5311070000 -0.5891500000 -2.2344950000 C 2.0401650000 -0.6064130000 -3.5297350000	С	5.2937970000	0.4117280000	-0.1313090000
C 3.4927570000 -1.1743350000 -0.2981630000 C 1.5311070000 -0.5891500000 -2.2344950000 C 2.0401650000 -0.6064130000 -3.5297350000	С	4.1244970000	-0.0201870000	-0.7579530000
C 1.5311070000 -0.5891500000 -2.2344950000 C 2.0401650000 -0.6064130000 -3.5297350000	С	3.4927570000	-1.1743350000	-0.2981630000
C 2.0401650000 -0.6064130000 -3.5297350000	С	1.5311070000	-0.5891500000	-2.2344950000
	С	2.0401650000	-0.6064130000	-3.5297350000

Table S7. Cartesian coordinates for optimized geometry **4b** (PBE0/SDD/6-31+G(d)).

с	1.6161730000	0.3426880000	-4.4550760000
с	0.6596410000	1.2790150000	-4.0683100000
С	0.1348400000	1.2812330000	-2.7801320000
С	0.5672410000	0.3510960000	-1.8222840000
В	-2.7611530000	-2.6777170000	-1.6688850000
н	2.1989880000	2.0943340000	0.4230370000
н	3.5882310000	4.0876610000	-0.0404260000
н	2.5264280000	6.1873980000	-0.8415980000
н	0.0693820000	6.2834430000	-1.1815150000
н	-1.3270330000	4.2963800000	-0.7179620000
н	-2.6451370000	3.4599500000	1.2101220000
н	-5.0400100000	3.7028140000	0.6553830000
н	-6.1058580000	2.1533230000	-0.9669690000
н	-4.7578640000	0.3280890000	-2.0188610000
н	-2.3764570000	0.1012280000	-1.5082230000
н	0.3123910000	3.2427110000	2.4236030000
н	0.3104220000	3.0110810000	4.8774610000
н	-0.5454970000	0.9176160000	5.9214680000
н	-1.3905990000	-0.9129810000	4.5108190000
н	-2.9729740000	-2.1776140000	3.2884820000
Н	-1.2877210000	-2.8632700000	3.2276010000
Н	-2.4788210000	-3.2709060000	1.9598060000
Н	3.5029810000	-2.7885170000	1.1343610000
н	5.5863510000	-2.0126770000	2.2318360000
Н	6.7368470000	0.0403600000	1.4250050000
н	5.7934670000	1.3067990000	-0.4943790000
Н	3.7154070000	0.5335110000	-1.5983550000
Н	2.7555730000	-1.3751670000	-3.8110660000
н	2.0004450000	0.3275070000	-5.4704030000
н	0.2891400000	2.0046900000	-4.7878190000
Н	-0.6494110000	1.9907700000	-2.5333100000
-			

Pd	2.305240	-0.957124	-0.128313
Se	3.738414	0.784042	-0.923434
Cl	3.977922	-2.496300	-0.525665
S	0.819861	-2.542265	0.749877
Р	-0.697458	0.273697	0.210234
Ν	0.938193	0.557900	0.202944
С	-2.858449	3.661745	-1.987192
С	-1.555109	1.635642	-0.601286
С	2.730919	2.173574	-0.078074
С	-2.617772	-0.483937	2.086663
С	-1.318265	0.003033	1.886985
С	-2.547825	-2.306453	-2.335029
С	-0.455269	-2.472820	-0.495842
С	0.754079	2.878358	1.069895
С	-0.989826	2.150706	-1.778634
С	5.213977	0.657370	0.354748
С	3.262869	3.455890	0.022891
С	1.290882	4.154873	1.187875
С	1.488841	-4.208593	0.609073
С	-0.860854	-3.603674	-1.194072
С	-3.422770	3.140501	-0.828071
С	-3.075665	-0.680082	3.387718
С	-2.132614	-1.166420	-1.648114
С	2.544087	4.461231	0.660623
С	-0.946854	0.053073	4.271915
С	-0.478677	0.261109	2.978259
С	-2.770429	2.129773	-0.124666
С	-1.078463	-1.229634	-0.734021
С	-1.907652	-3.515478	-2.114917
С	1.449836	1.849430	0.406338
С	-1.641408	3.167204	-2.463577
С	-2.246802	-0.411252	4.475746
В	-5.474728	-0.221943	-0.529119
н	-3.375299	4.444275	-2.536585
н	-3.281534	-0.717797	1.253871
н	-3.392778	-2.231514	-3.011846
н	-0.221185	2.682433	1.504197

Table S8. Cartesian coordinates for optimized geometry **4c** (PBE0/SDD/6-31+G(d)).

н	-0.047074	1.758153	-2.152154
Н	4.812654	0.664634	1.368130
Н	5.886570	1.501655	0.190846
н	5.716700	-0.288841	0.146166
н	4.245249	3.667481	-0.393056
н	0.716000	4.918545	1.705011
н	1.829213	-4.419270	-0.405809
н	0.731739	-4.919695	0.949350
н	2.351031	-4.236683	1.278232
н	-0.382086	-4.561964	-1.026987
н	-4.390577	3.484074	-0.476755
н	-4.087932	-1.044351	3.538428
Н	-2.681233	-0.243764	-1.806731
Н	2.958313	5.460797	0.750893
Н	-0.296128	0.250863	5.119725
Н	0.538407	0.607689	2.814494
Н	-3.246514	1.713718	0.756653
Н	-2.225525	-4.410844	-2.642156
Н	-1.205991	3.568705	-3.374727
н	-2.611959	-0.569302	5.487499
F	-5.434523	0.787987	0.459227
F	-4.858836	0.264514	-1.708795
F	-6.775458	-0.619761	-0.783338
F	-4.702984	-1.324677	-0.058117

Pd	0.3511060000	-1.4271590000	0.5441280000
Se	2.2485270000	-1.6123450000	-0.9006840000
CI	1.0690740000	-3.2393950000	1.7740490000
S	-1.7051750000	-1.2064330000	1.6349420000
Р	-0.9384020000	1.5211480000	0.1791590000
F	-1.1889910000	-2.2037470000	-1.8007990000
F	-2.0229920000	-4.3242700000	-2.1535280000
F	-2.4894520000	-3.2092640000	-0.1911640000
F	-3.4338670000	-2.5013990000	-2.1673940000
N	-0.0291880000	0.3358400000	-0.4901130000
С	1.1537030000	3.2972220000	-0.0501910000
C	1.7607580000	4.5089600000	-0.3622160000
C	0.9974100000	5.5662570000	-0.8587630000
C	-0 3740550000	5.4096140000	-1 0480740000
C	-0.9895810000	4 1985340000	-0 7363160000
C	-0.2280020000	3 1419390000	-0.2296920000
C	-3 6094390000	2 3552490000	0.2859830000
C	-4.9533220000	2.3552450000	-0.0537930000
C	-4.3333220000	1 2650210000	-0.9449590000
C	-3.3702330000	0.2687820000	-0.9449530000
C	-3 1080720000	0.4686730000	-1 1669270000
C	-2 6826670000	1.4707830000	-0.2890250000
C	-2.0820070000	1.4707830000	1 9975110000
C	-0.8990290000	2 5020680000	2 761 2250000
C	-0.5780410000	2.5020680000	4 1538070000
C	-0.0038750000	2.4343530000	4.1538970000
C	-0.9612250000	0.1406640000	4.7932320000
C	-1.2901080000	0.1406640000	4.0496550000
C	-1.2657310000	0.1810630000	2.6573100000
C	-2.0094790000	-2.5581330000	2.7794560000
C	4.0527430000	-0.9771650000	1.2186140000
C	5.0658520000	-0.2700610000	1.8614850000
C	5.6146680000	0.8697780000	1.2734700000
C	5.1447860000	1.3050590000	0.0358510000
C	4.1294600000	0.6065270000	-0.6184480000
C	3.5891560000	-0.5285960000	-0.0191550000
С	1.5575640000	-0.3673130000	-2.1758890000
C	2.0941610000	-0.3345850000	-3.4584200000

Table S9. Cartesian coordinates for optimized geometry **4d** (PBE0/SDD/6-31+G(d)).

С	1.5517080000	0.5154720000	-4.4184550000
С	0.4517080000	1.2973230000	-4.0752050000
С	-0.0971020000	1.2448410000	-2.7980100000
С	0.4508160000	0.4181120000	-1.8041450000
В	-2.2896990000	-3.0879840000	-1.5956550000
Н	1.7519970000	2.4680610000	0.3216250000
Н	2.8322990000	4.6250100000	-0.2231350000
Н	1.4747100000	6.5109530000	-1.1060270000
Н	-0.9678970000	6.2278770000	-1.4464410000
Н	-2.0557910000	4.0750300000	-0.9043900000
Н	-3.2891420000	3.1032110000	1.0090120000
Н	-5.6741740000	2.9387620000	0.3882820000
Н	-6.4309130000	1.1809150000	-1.1950540000
Н	-4.7774380000	-0.4401690000	-2.1412940000
Н	-2.4094220000	-0.2644650000	-1.5648000000
Н	-0.2971550000	3.4270210000	2.2669780000
Н	-0.3465880000	3.3381340000	4.7295270000
Н	-0.9817550000	1.2214560000	5.8786000000
Н	-1.5573820000	-0.7771890000	4.5623080000
Н	-2.8961660000	-2.3287670000	3.3765370000
Н	-1.1301840000	-2.7691130000	3.3902320000
Н	-2.2117230000	-3.4060780000	2.1201430000
Н	3.6115310000	-1.8565860000	1.6829870000
Н	5.4251000000	-0.6138180000	2.8280290000
Н	6.4086530000	1.4147260000	1.7774200000
Н	5.5728300000	2.1886470000	-0.4318520000
Н	3.7647720000	0.9464270000	-1.5840950000
Н	2.9252080000	-0.9891460000	-3.7096130000
Н	1.9597940000	0.5391230000	-5.4243430000
Н	-0.0113110000	1.9401470000	-4.8194870000
Н	-0.9879230000	1.8293220000	-2.5878640000



Figure S51:The average percent errors between calculated and experimental bond angles of 4b.

Table S10. bond distances (Å) of PBE0/SDD/6-31+G(d) optimized geometries (E= S(2), Se).

comp.	Pd–S(1)	Pd–S(2)/Se	Pd–N	Pd–Cl
4a	2.3272	2.2889	2.0761	2.302
4b	2.3242	2.3086	2.0722	2.3019
4c	2.3431	2.3912	2.0673	2.3076
4d	2.3381	2.3921	2.0791	2.3049

Table S11. Bond angles (degree) of PBE0/SDD/6-31+G(d) optimized geometries (E= S(2), Se).

comp.	S(1)-Pd-E	S(1)–Pd–N	E-Pd-N	CI–Pd–N	CI-Pd-S(1)	CI–Pd–E
4a	169.93	90.36	85.15	169.42	95.9	89.94
4b	170.19	89.13	84.13	172.46	95.54	91.93
4c	175.7	90.95	85.18	174.71	94.18	89.65
4d	170.64	89.49	84.85	171.56	95.69	90.82

Table S12. Experimental bond angles for 4a-d (X-ray) (E= S(2), Se).

comp.	S(1)-Pd-E	S(1)–Pd–N	E-Pd-N	CI–Pd–N	Cl-Pd-S(1)	CI–Pd–E
4a	175.04	93.64	85.21	173.46	92.9	88.28
4b	171.35	87.92	84.06	176.23	95.44	92.68
4c	176.2	93.79	85.84	172.72	93.49	86.92
4d	172.71	87.46	85.40	174.79	96.43	90.79

comp.	S(1)-Pd-E	S(1)-Pd-N	E-Pd-N	Cl–Pd–N	Cl-Pd-S(1)	CI-Pd-E	T.% Error
4a	2.9193	3.5028	0.0704	2.3291	3.2293	1.8804	2.3219
4b	0.6770	1.3763	0.0833	2.1392	0.1048	0.8092	0.8650
4c	0.2894	3.0074	0.7573	1.1522	0.7165	3.1408	1.5106
4d	1.1985	2.3211	0.6440	1.8479	0.7674	0.0330	1.1353

Table S13. % error on bond angles calculated (PBE0/SDD/6-31+G(d)) (E= S(2), Se).

Table S14. Experimental and calculated bond lengths and the percent error.

comp.	bonds	exp (Å)	calc. (Å)	% error
4a	Pd–Cl	2.2814	2.30203	0.90427
	Pd-S (1)	2.3323	2.32723	0.21738
	Pd–S(2)	2.2728	2.28886	0.70662
	Pd–N	2.059	2.07605	0.82807
4b	Pd–Cl	2.2919	2.3019	0.43632
	Pd-S (1)	2.2989	2.3242	1.10053
	Pd–S(2)	2.3040	2.3086	0.19965
	Pd–N	2.042	2.0722	1.47894
4c	Pd–Cl	2.2828	2.3076	1.08639
	Pd-S (1)	2.3440	2.3431	0.03712
	Pd–Se	2.3673	2.3912	1.00959
	Pd–N	2.064	2.0673	0.16134
4d	Pd–Cl	2.2938	2.3049	0.48391
	Pd-S (1)	2.3183	2.3381	0.85407
	Pd–Se	2.3921	2.3880	0.17140
	Pd–N	2.034	2.0761	2.06981

comp.	E–BCP	S(1)-BCP	N–BCP	CI–BCP
4a	1.18342	1.20906	1.01341	1.18985
4b	1.19459	1.20463	1.01265	1.1912
4c	1.125502	1.21706	1.00885	1.19561
4d	1.125562	1.2137	1.01573	1.19263

Table S15. Distance (Å) from L to the bond critical points in Pd–L bonds (E= S(2), Se).

Table S16. Distance (A) from Pd to the bond critical points (PBE0/SDD/6-31+G(d)) (E=	S(2), Se	e).
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comp.	Pd–E	Pd-S(1)	Pd–N	Pd–Cl
4a	1.10561	1.11827	1.06294	1.11204
4b	1.11418	1.11933	1.05957	1.11152
4c	1.13601	1.12576	1.05848	1.11218
4d	1.13715	1.12434	1.06331	1.1121

Table S17. Topologica	al values of the electror	n density in the bond	critical point (a.u.)	(PBE0/SDD/
6-31+G(d)).				

comp	bond	ρ(r)	∇2ρ(r)	G (r)	V (r)	H(r)	V(r) /G(r)	ε	H/rho
4a	Pd-S(1)	0.08752	0.22389	0.07987	-0.10377	-0.02390	1.29923	0.09774	-0.27308
	Pd–Cl	0.08661	0.23637	0.08039	-0.10169	-0.02130	1.26493	0.07566	-0.24592
	Pd–S(2)	0.09651	0.22681	0.08596	-0.11523	-0.02926	1.34041	0.05773	-0.30323
	Pd-N	0.09562	0.40853	0.12027	-0.13841	-0.01814	1.15082	0.06185	-0.18970
4b	Pd-S(1)	0.08832	0.22084	0.07962	-0.10402	-0.02441	1.30656	0.08657	-0.27634
	Pd–Cl	0.08656	0.23703	0.08055	-0.10185	-0.02130	1.26439	0.07908	-0.24605
	Pd-S(2)	0.09201	0.22008	0.08168	-0.10834	-0.02666	1.32640	0.06546	-0.28975
	Pd-N	0.09640	0.41110	0.12135	-0.13993	-0.01858	1.15310	0.06565	-0.19273
4c	Pd-S(1)	0.08556	0.21445	0.07654	-0.09946	-0.02293	1.29954	0.08273	-0.26795
	Pd–Cl	0.08535	0.23772	0.08012	-0.10080	-0.02069	1.25819	0.06587	-0.24237
	Pd–Se	0.09045	0.16013	0.07006	-0.10009	-0.03003	1.42861	0.02503	-0.33199
	Pd-N	0.09859	0.40538	0.12120	-0.14106	-0.01986	1.16383	0.05202	-0.20139
4d	Pd-S(1)	0.08571	0.21949	0.07778	-0.10069	-0.02291	1.29453	0.09615	-0.26726
	Pd–Cl	0.08593	0.23643	0.08007	-0.10103	-0.02096	1.26182	0.07452	-0.24395
	Pd–Se	0.08926	0.16528	0.07051	-0.09971	-0.02920	1.41405	0.04629	-0.32710
	Pd-N	0.09477	0.40543	0.11899	-0.13662	-0.01763	-1.14818	0.06761	-0.18605

AIM charge	4a	4b	4c	4d
Pd	0.549	0.570	0.476	0.541
CI	-0.530	-0.534	-0.547	-0.538
S	0.245	0.223	0.127	0.221
E	0.209	0.205	0.428	0.505
N	-1.562	-1.618	-1.591	-1.616
Р	2.782	2.955	2.934	2.946

Table S18. Atomic Charge (QTAIM) (PBE0/SDD/6-31+G(d)) (E= S(2), Se).



Figure S52. Relevant NBOs of complex 4b.



Figure S53. Relevant NBOs of complex 4c.



Figure S54. Relevant NBOs of complex 4d.