

## Supplementary Material to:

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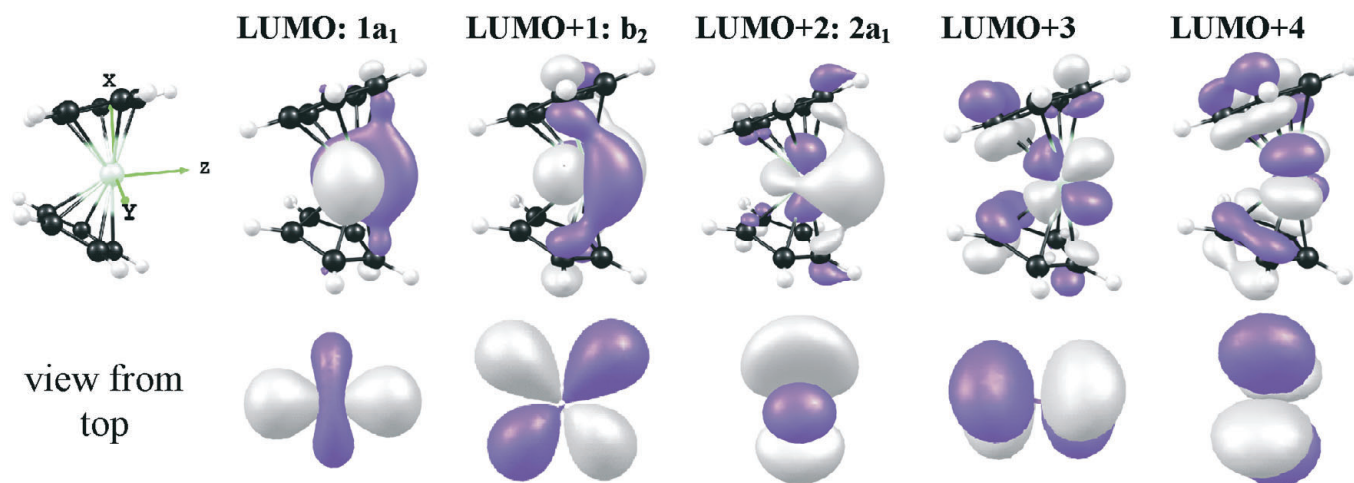


Fig. S1 The frontier MOs of  $[\text{Cp}_2\text{Ti}^{\text{IV}}]^{2+}$ . Colour code for atoms: Ti (lime green), C (black) and H (white).

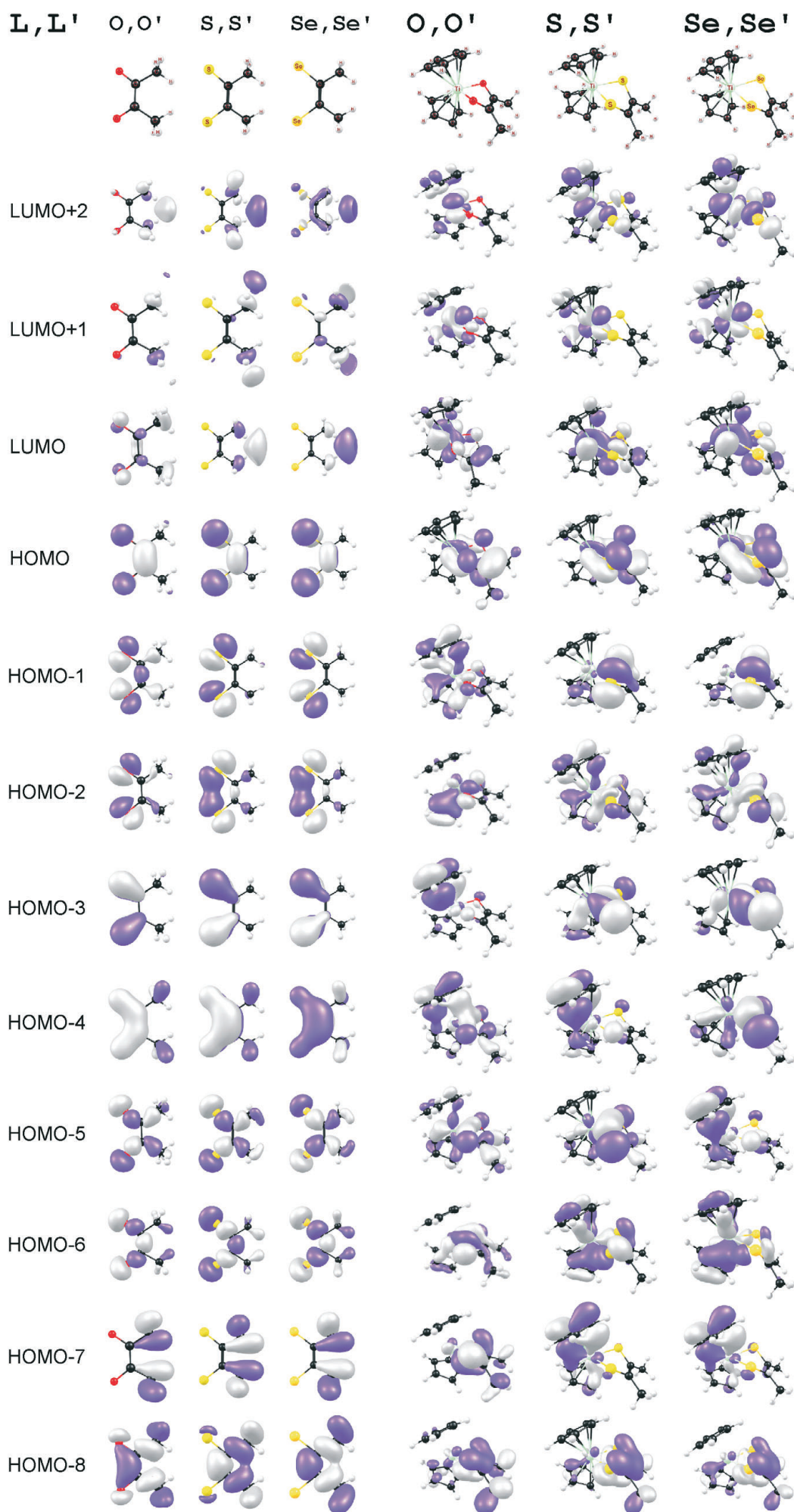


Fig. S2 The frontier MOs of simplified  $[Cp_2Ti^{IV}(L,L'-BID)]$  models,  $L,L'-BID$  = dioxolene, dithiolene or diselenolene. Colour code for atoms: Ti (lime green), C (black), H (white), S (green-yellow), Se (bright yellow) and O (red). A  $C_s$  symmetry constraint was imposed.

**Optimized Cartesian coordinates/Å**

All compounds were optimized with Gaussian/PW91/6-311G(d,p).

1  $\text{Cp}_2\text{Ti}(\eta^2\text{-OC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{O})$  complex 1

Ti	-0.000626000	-0.473026000	0.000000000
O	-0.741253000	0.799931000	1.286331000
O	-0.741253000	0.799931000	-1.286331000
C	-0.580075000	1.999171000	0.694059000
C	-0.580075000	1.999171000	-0.694059000
C	2.112621000	-0.744718000	-1.151447000
H	2.110844000	-1.075524000	-2.186170000
C	2.117500000	0.605825000	-0.704946000
H	2.079103000	1.483280000	-1.342743000
C	2.117500000	0.605825000	0.704946000
H	2.079103000	1.483280000	1.342743000
C	2.112621000	-0.744718000	1.151447000
H	2.110844000	-1.075524000	2.186170000
C	2.150126000	-1.577135000	0.000000000
H	2.187567000	-2.661525000	0.000000000
C	-1.585096000	-1.853386000	-1.149295000
H	-1.810087000	-1.590117000	-2.178178000
C	-0.546772000	-2.712980000	-0.711717000
H	0.135519000	-3.263619000	-1.352596000
C	-0.546772000	-2.712980000	0.711717000
H	0.135519000	-3.263619000	1.352596000
C	-1.585096000	-1.853386000	1.149295000
H	-1.810087000	-1.590117000	2.178178000
C	-2.226589000	-1.319902000	0.000000000
H	-3.018448000	-0.579043000	0.000000000
C	-0.495118000	3.184792000	-1.604820000
H	-1.321106000	3.146895000	-2.331725000
H	-0.545501000	4.137160000	-1.063569000
H	0.440776000	3.173275000	-2.187841000
C	-0.495118000	3.184792000	1.604820000
H	-0.545501000	4.137160000	1.063569000
H	-1.321106000	3.146895000	2.331725000
H	0.440776000	3.173275000	2.187841000

2  $\text{Cp}_2\text{Ti}^{\text{IV}}(\text{O},\text{O}'\text{-BID})$  complex:  $\text{Cp}_2\text{Ti}^{\text{IV}}(\eta^2\text{-OC}(\text{Ph})=\text{C}(\text{Ph})\text{O})$ 

Ti	-0.554125000	3.452367000	2.963736000
O	0.438262000	4.146894000	4.513461000
O	0.478435000	4.841844000	2.057139000
C	1.671146000	4.877002000	2.687044000
C	2.835352000	5.218573000	1.853002000
C	1.622403000	4.584446000	4.062182000
C	2.662044000	4.796401000	5.085207000
C	2.660688000	3.977461000	6.232808000
C	2.640146000	6.010509000	0.701533000
C	1.309042000	1.886461000	2.700469000
C	3.599655000	5.847933000	5.014907000
C	3.589372000	4.176507000	7.255289000
C	4.128148000	4.713230000	2.104423000
C	5.191160000	5.021978000	1.255784000
C	-2.218537000	4.672147000	4.229558000
C	4.524741000	6.043951000	6.038957000
C	0.354248000	1.301927000	3.580808000
C	-2.900744000	3.232690000	2.573167000
C	3.706877000	6.320570000	-0.141330000
C	0.705622000	2.032435000	1.425554000
C	-0.829194000	1.064546000	2.840136000
C	-0.617248000	1.531585000	1.508188000
C	-2.475222000	4.440882000	1.958392000
C	4.530189000	5.206339000	7.161350000
C	-2.065911000	5.332641000	2.987544000
C	-2.718909000	3.367375000	3.978151000
C	4.989094000	5.831517000	0.132244000
H	1.911423000	3.189791000	6.309462000
H	1.635438000	6.372215000	0.484100000
H	2.320179000	2.177858000	2.961991000

H	3.587715000	6.523214000	4.160028000
H	3.576317000	3.526674000	8.131675000
H	4.297858000	4.071305000	2.968758000
H	6.182178000	4.617118000	1.466164000
H	-1.915620000	5.063134000	5.195096000
H	5.237382000	6.867057000	5.968937000
H	0.511255000	1.068994000	4.629752000
H	-3.293967000	2.360733000	2.061176000
H	3.536981000	6.944360000	-1.020329000
H	1.164657000	2.484626000	0.551859000
H	-1.741126000	0.615542000	3.222471000
H	-1.338670000	1.500680000	0.696478000
H	-2.454093000	4.646537000	0.891751000
H	5.254632000	5.364760000	7.961141000
H	-1.631221000	6.315088000	2.840417000
H	-2.932428000	2.610614000	4.727984000
H	5.821927000	6.068891000	-0.530783000

3 Cp<sub>2</sub>Ti(η<sup>2</sup>-SC(CH<sub>3</sub>)=C(CH<sub>3</sub>)S) complex 2

Ti	0.037273000	-0.741144000	0.000000000
S	-0.814025000	0.863632000	1.587956000
S	-0.814025000	0.863632000	-1.587956000
C	-0.349489000	2.307547000	0.691053000
C	-0.349489000	2.307547000	-0.691053000
C	2.121148000	-1.067829000	-1.150410000
H	2.111118000	-1.398503000	-2.185004000
C	2.133801000	0.284771000	-0.704985000
H	2.125426000	1.159977000	-1.344502000
C	2.133801000	0.284771000	0.704985000
H	2.125426000	1.159977000	1.344502000
C	2.121148000	-1.067829000	1.150410000
H	2.111118000	-1.398503000	2.185004000
C	2.154467000	-1.898907000	0.000000000
H	2.175682000	-2.984184000	0.000000000
C	-1.596625000	-2.051226000	-1.150493000
H	-1.849867000	-1.822723000	-2.181785000
C	-0.570872000	-2.926724000	-0.711435000
H	0.096300000	-3.494216000	-1.353056000
C	-0.570872000	-2.926724000	0.711435000
H	0.096300000	-3.494216000	1.353056000
C	-1.596625000	-2.051226000	1.150493000
H	-1.849867000	-1.822723000	2.181785000
C	-2.233302000	-1.510268000	0.000000000
H	-3.035714000	-0.781033000	0.000000000
C	-0.037839000	3.515770000	-1.537398000
H	-0.705869000	3.545781000	-2.409838000
H	-0.145524000	4.459221000	-0.986911000
H	0.992646000	3.474997000	-1.927525000
C	-0.037839000	3.515770000	1.537398000
H	-0.145524000	4.459221000	0.986911000
H	-0.705869000	3.545781000	2.409838000
H	0.992646000	3.474997000	1.927525000

4 Cp<sub>2</sub>Ti<sup>IV</sup>(S,S'-BID) complex: Cp<sub>2</sub>Ti<sup>IV</sup>(1,2-benzene-dithionato)

C	1.666361000	2.759608000	-0.277016000
C	3.293669000	-1.410800000	-0.543622000
C	2.227895000	-0.588210000	-0.095339000
C	5.523153000	2.065624000	-2.050889000
C	5.180414000	1.437456000	-3.277552000
C	5.347384000	0.037307000	-3.115984000
C	5.801133000	-0.200339000	-1.789066000
C	5.901344000	1.051306000	-1.127883000
C	0.782300000	3.186780000	0.734945000
C	-0.504880000	3.613232000	0.424340000
C	-0.942901000	3.613736000	-0.910576000
C	-0.092573000	3.185335000	-1.924984000
C	1.219739000	2.756636000	-1.636243000
C	1.405879000	-0.289791000	-1.207086000
C	1.954907000	-0.934650000	-2.352721000
C	3.106194000	-1.644519000	-1.939762000
S	2.320214000	2.292170000	-2.937072000

S	3.333437000	2.323845000	0.109713000
Ti	3.599602000	0.683447000	-1.644967000
H	-0.429189000	3.174523000	-2.962117000
H	-1.951806000	3.948122000	-1.155448000
H	-1.172661000	3.945210000	1.220140000
H	1.128101000	3.179600000	1.769128000
H	0.518825000	0.333152000	-1.191823000
H	2.081384000	-0.233563000	0.919066000
H	1.554233000	-0.887167000	-3.360413000
H	3.741200000	-2.256354000	-2.573043000
H	4.088201000	-1.818373000	0.074439000
H	6.032498000	-1.168903000	-1.357899000
H	6.205840000	1.211547000	-0.097344000
H	5.171045000	-0.714287000	-3.879430000
H	4.844064000	1.945710000	-4.176103000
H	5.465531000	3.128486000	-1.845134000

5 Cp<sub>2</sub>Ti<sup>IV</sup>(S,S'-BID) complex: Cp<sub>2</sub>Ti<sup>IV</sup>(ethylene-1,2-dithiolato)

C	2.660535000	3.531938000	-0.890948000
C	1.720821000	-0.157142000	2.809770000
C	3.034530000	0.200084000	3.220731000
C	3.082141000	1.612305000	3.353848000
C	1.804835000	2.130123000	3.012055000
C	0.964223000	1.035131000	2.665825000
C	3.977478000	3.471991000	-0.517804000
C	4.243014000	-0.299517000	-0.197706000
C	3.524032000	0.456180000	-1.167714000
C	2.159971000	0.080576000	-1.101079000
C	2.025363000	-0.903691000	-0.089934000
C	3.321682000	-1.150747000	0.456200000
H	2.373166000	4.076341000	-1.794018000
H	1.359153000	-1.165537000	2.639003000
H	3.856025000	-0.483652000	3.414009000
H	3.941630000	2.200896000	3.658269000
H	1.529823000	3.178559000	2.995746000
H	-0.073117000	1.104668000	2.349940000
H	4.737628000	3.968851000	-1.126899000
H	5.309121000	-0.237526000	-0.005234000
H	3.944493000	1.201075000	-1.832208000
H	1.355487000	0.482444000	-1.707242000
H	1.102720000	-1.399433000	0.196737000
S	1.375220000	2.872205000	0.083075000
S	4.515307000	2.723833000	0.961249000
Ti	2.707261000	1.083699000	1.042538000
H	3.557467000	-1.865470000	1.238893000

6 Cp<sub>2</sub>Ti<sup>IV</sup>(S,S'-BID) complex: Cp<sub>2</sub>Ti<sup>IV</sup>(1,3-dithiole-2-thione-4,5-dithiolato)

Ti	10.227679000	9.846347000	6.520282000
S	8.397369000	9.697498000	4.904430000
S	11.210158000	8.015890000	5.214993000
S	7.031931000	6.995680000	4.545575000
S	9.537780000	5.500922000	4.805155000
S	6.985788000	3.994319000	4.224697000
C	8.477801000	7.963983000	4.846195000
C	9.668499000	7.254181000	4.970168000
C	7.796458000	5.401586000	4.502059000
C	8.449524000	9.031716000	7.960403000
C	9.026266000	10.187438000	8.550972000
C	10.370230000	9.869819000	8.903186000
C	10.635190000	8.542993000	8.483595000
C	9.437473000	8.022354000	7.913296000
C	10.250586000	12.058581000	5.630336000
C	11.094622000	11.272676000	4.795998000
C	12.197295000	10.831071000	5.575445000
C	12.036375000	11.340076000	6.889764000
C	10.835611000	12.104728000	6.921771000
H	7.431107000	8.945211000	7.596701000
H	8.520217000	11.131760000	8.729793000
H	11.070283000	10.534049000	9.399975000
H	11.571904000	8.005676000	8.595350000
H	9.305825000	7.019703000	7.522600000

H	9.324658000	12.539421000	5.326476000
H	10.913361000	11.026699000	3.755425000
H	13.016835000	10.212621000	5.221093000
H	12.721887000	11.185077000	7.717136000
H	10.438287000	12.633924000	7.782129000
7	Cp <sub>2</sub> Ti <sup>IV</sup> (S,S'-BID) complex: Cp <sub>2</sub> Ti <sup>IV</sup> (5,6-dihydro-1,4-dithiine-2,3-dithiolato)		
Ti	4.658798000	7.324612000	7.510050000
S	2.617551000	7.349364000	6.176592000
S	5.582962000	8.451392000	5.567632000
S	5.734185000	7.087043000	3.001484000
S	2.449961000	6.090306000	3.511355000
C	3.434196000	6.999537000	4.676620000
C	4.729983000	7.433556000	4.426569000
C	4.610405000	6.305965000	1.760283000
C	3.155326000	6.704465000	1.933788000
C	4.962817000	5.308760000	8.735158000
C	4.277364000	4.946451000	7.550929000
C	5.149291000	5.185165000	6.452212000
C	6.370537000	5.703477000	6.957907000
C	6.258081000	5.786447000	8.367325000
C	3.598942000	8.092853000	9.490267000
C	3.299198000	9.062897000	8.496672000
C	4.516476000	9.670633000	8.091700000
C	5.574307000	9.077538000	8.835176000
C	5.003030000	8.118331000	9.713423000
H	4.720448000	5.216261000	1.814032000
H	4.994817000	6.653036000	0.789224000
H	3.022520000	7.793325000	1.889956000
H	2.537818000	6.242910000	1.150152000
H	4.571077000	5.236203000	9.745482000
H	3.269149000	4.550401000	7.488653000
H	4.923496000	4.996012000	5.409418000
H	7.235003000	5.988275000	6.367535000
H	7.030318000	6.133601000	9.047464000
H	2.878186000	7.461152000	10.001765000
H	2.314255000	9.305674000	8.111882000
H	4.615930000	10.443700000	7.337947000
H	6.628656000	9.327590000	8.754213000
H	5.543136000	7.514681000	10.434596000
8	Cp <sub>2</sub> Ti(η <sup>2</sup> -SeC(CH <sub>3</sub> )=C(CH <sub>3</sub> )Se) complex 3		
Ti	0.165859000	-0.977115000	0.000000000
Se	-0.652695000	0.758030000	1.674191000
Se	-0.652695000	0.758030000	-1.674191000
C	-0.025935000	2.277217000	0.686122000
C	-0.025935000	2.277217000	-0.686122000
C	2.232132000	-1.387293000	-1.150230000
H	2.209136000	-1.717925000	-2.184584000
C	2.291493000	-0.035056000	-0.705443000
H	2.315802000	0.839261000	-1.345262000
C	2.291493000	-0.035056000	0.705443000
H	2.315802000	0.839261000	1.345262000
C	2.232132000	-1.387293000	1.150230000
H	2.209136000	-1.717925000	2.184584000
C	2.236236000	-2.218772000	0.000000000
H	2.217536000	-3.304255000	0.000000000
C	-1.530543000	-2.210503000	-1.150734000
H	-1.783568000	-1.982103000	-2.182230000
C	-0.539478000	-3.125818000	-0.711669000
H	0.102213000	-3.721630000	-1.353374000
C	-0.539478000	-3.125818000	0.711669000
H	0.102213000	-3.721630000	1.353374000
C	-1.530543000	-2.210503000	1.150734000
H	-1.783568000	-1.982103000	2.182230000
C	-2.146167000	-1.645508000	0.000000000
H	-2.920987000	-0.886679000	0.000000000
C	0.390946000	3.450043000	-1.537789000
H	-0.277159000	3.549976000	-2.405155000
H	0.380496000	4.399504000	-0.985735000
H	1.408989000	3.310690000	-1.937079000



C	0.390946000	3.450043000	1.537789000
H	0.380496000	4.399504000	0.985735000
H	-0.277159000	3.549976000	2.405155000
H	1.408989000	3.310690000	1.937079000

9 Cp<sub>2</sub>Ti<sup>IV</sup>(Se,Se'-BID) complex: Cp<sub>2</sub>Ti<sup>IV</sup>(1,2-benzene-diselenato)

Ti	0.694089000	10.156462000	14.509038000
Se	0.315115000	8.282767000	12.778293000
Se	-0.422154000	8.515940000	16.076160000
C	0.721950000	6.897505000	14.002724000
C	0.445993000	6.976490000	15.350031000
C	1.330453000	5.683147000	13.357719000
C	3.319480000	4.443814000	13.112011000
H	4.379857000	4.575361000	13.346624000
H	3.162847000	4.363223000	12.028799000
H	2.920666000	3.548190000	13.605852000
C	0.695629000	5.795953000	16.217058000
C	0.694337000	4.956362000	18.418901000
H	0.519007000	5.348774000	19.424836000
H	1.709744000	4.548180000	18.330027000
H	-0.027141000	4.164520000	18.178077000
C	2.468024000	10.995997000	15.844971000
H	2.245205000	11.665061000	16.671190000
C	2.577909000	9.580174000	15.921693000
H	2.432426000	8.978850000	16.812618000
C	2.885226000	9.092465000	14.631276000
H	3.027477000	8.051591000	14.359888000
C	2.980319000	10.206829000	13.746338000
H	3.199713000	10.156165000	12.684176000
C	2.754390000	11.381015000	14.501754000
H	2.776552000	12.398126000	14.122208000
C	-1.077439000	11.559190000	15.300000000
H	-1.387058000	11.532465000	16.341186000
C	-0.069264000	12.389992000	14.746608000
H	0.527055000	13.114418000	15.291963000
C	0.022428000	12.107164000	13.355562000
H	0.696179000	12.579259000	12.646828000
C	-0.941557000	11.110692000	13.046879000
H	-1.147602000	10.696030000	12.064597000
C	-1.624038000	10.773337000	14.247258000
H	-2.409288000	10.031557000	14.342134000
O	0.741587000	4.925356000	12.618549000
O	2.660417000	5.617870000	13.635975000
O	1.012219000	4.686183000	15.816787000
O	0.523246000	6.083526000	17.535410000

10 Cp<sub>2</sub>Ti<sup>IV</sup>(Se,Se'-BID) complex: Cp<sub>2</sub>Ti<sup>IV</sup>(1,2-bis(methoxycarbonyl)ethylene-1,2-diselenolato-Se,Se')

Se	1.789115000	2.886524000	3.882402000
Se	4.409472000	5.148461000	3.997125000
Ti	4.296345000	2.676358000	3.297119000
S	0.208079000	5.210338000	2.403237000
S	-0.213665000	7.994254000	1.299653000
S	2.425748000	7.115511000	2.484446000
C	1.695313000	4.629051000	3.146441000
C	0.738385000	6.856106000	2.015829000
C	2.744106000	5.530297000	3.183215000
C	4.044754000	1.262891000	5.214910000
H	3.073047000	0.909253000	5.547033000
C	4.692454000	2.446181000	5.661568000
H	4.283092000	3.168347000	6.359467000
C	5.955510000	2.528644000	5.009923000
H	6.692019000	3.316298000	5.144606000
C	6.088468000	1.392618000	4.170718000
H	6.947565000	1.157192000	3.550823000
C	4.903255000	0.614196000	4.289436000
H	4.695662000	-0.322691000	3.781823000
C	4.818420000	3.701166000	1.163184000
H	5.099114000	4.746604000	1.096599000
C	3.506480000	3.181966000	1.058978000
H	2.604726000	3.758236000	0.888432000
C	3.574871000	1.764654000	1.196641000

H	2.732126000	1.081808000	1.158175000
C	4.934104000	1.413888000	1.372678000
H	5.323763000	0.407006000	1.485864000
C	5.705022000	2.614535000	1.384285000
H	6.782650000	2.685307000	1.498390000

11 Cp<sub>2</sub>Ti<sup>IV</sup>(Se,Se'-BID) complex: Cp<sub>2</sub>Ti<sup>IV</sup>(5,6-dihydro-1,4-dithiine-2,3-diselenolato-Se,Se')

Ti	3.199735000	3.606035000	18.796463000
Se	4.434432000	2.383189000	16.923011000
Se	1.221436000	3.400830000	17.159803000
C	3.616851000	3.438768000	15.558652000
C	2.288343000	3.798469000	15.637604000
S	1.397740000	4.638716000	14.354622000
S	4.779709000	3.817235000	14.274190000
C	2.350514000	4.106134000	12.878380000
C	3.790843000	4.588303000	12.915976000
C	3.511199000	5.762953000	17.733133000
C	2.687928000	5.949759000	18.880960000
C	4.786506000	5.325921000	18.167439000
C	4.755680000	5.223864000	19.582272000
C	3.461257000	5.634835000	20.023186000
C	3.602142000	2.766504000	20.976639000
H	4.266201000	3.297685000	21.650698000
C	2.808705000	1.300622000	19.394959000
C	3.981152000	1.741474000	20.071037000
C	2.200012000	2.973178000	20.849954000
H	1.602059000	3.686825000	21.408690000
C	1.710689000	2.063016000	19.877250000
H	2.758650000	0.534010000	18.629689000
H	0.676267000	1.945837000	19.568136000
H	5.581701000	4.916373000	20.216971000
H	1.653651000	6.278297000	18.872726000
H	3.212624000	5.929298000	16.704695000
H	3.127600000	5.688598000	21.055025000
H	5.633044000	5.094947000	17.530089000
H	2.289767000	3.013181000	12.796799000
H	1.818949000	4.552672000	12.025987000
H	4.322953000	4.298500000	11.997301000
H	4.985251000	1.352638000	19.925684000
H	3.830413000	5.679335000	13.016980000