

## Supporting Information

# Heavy-Element–Ligand Covalence: Ligand Noninnocence in Molybdenum and Tungsten Viking-Helmet Corroles

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Scalar-relativistic B3LYP/ZORA-STO-TZP coordinates (Å)

1. Mo[TPC]Cl<sub>2</sub>

Mo	-0.023226000	-0.010547000	-0.081087000
Cl	-0.004844000	1.525556000	1.728314000
Cl	-0.035438000	-1.566939000	1.711816000
C	-2.673107000	0.704196000	-1.202197000
C	-3.553300000	1.774296000	-1.490833000
C	-2.809352000	2.931371000	-1.446735000
C	-1.462340000	2.577854000	-1.139313000
C	-0.298837000	3.334188000	-1.176511000
C	0.974904000	2.740332000	-1.123546000
C	2.221078000	3.426046000	-1.224814000
C	3.217957000	2.498654000	-1.191785000
C	2.609059000	1.217583000	-1.072065000
C	3.262852000	-0.013304000	-1.065751000
C	2.604271000	-1.242042000	-1.071777000
C	3.206752000	-2.523298000	-1.214986000
C	2.205425000	-3.445703000	-1.261611000
C	0.962630000	-2.755914000	-1.150713000
C	-0.314635000	-3.340592000	-1.221689000
C	-1.473659000	-2.577781000	-1.178123000
C	-2.822033000	-2.920703000	-1.491754000
C	-3.560931000	-1.759994000	-1.517999000
C	-2.675876000	-0.698351000	-1.212939000
C	-1.088375000	6.965846000	-0.495634000
C	-1.136450000	-6.979339000	-0.617752000
C	-0.968479000	5.590673000	-0.339240000
C	-1.006992000	-5.608426000	-0.432737000
C	-0.659435000	7.576219000	-1.667514000
C	-0.703663000	-7.569314000	-1.798660000
C	-0.412174000	4.807942000	-1.352890000
C	-0.436954000	-4.809828000	-1.426145000
C	-0.109346000	6.804581000	-2.684172000
C	-0.140973000	-6.781469000	-2.795645000
C	7.550607000	-0.014596000	-1.154573000
C	6.831871000	0.171808000	-2.329278000
C	6.874315000	-0.204633000	0.043993000
C	5.484995000	-0.207252000	0.068966000
C	5.442329000	0.171457000	-2.304704000
C	4.756408000	-0.016948000	-1.105244000
C	-0.006665000	-5.411981000	-2.610440000
C	0.015177000	5.430599000	-2.527644000
N	1.227299000	1.379640000	-1.004907000
N	1.222029000	-1.398873000	-1.008547000
N	-1.431955000	-1.211144000	-0.973549000
N	-1.427197000	1.208314000	-0.954320000
H	0.220054000	7.271803000	-3.602922000
H	0.190930000	-7.232469000	-3.721643000
H	0.437429000	4.832368000	-3.324125000
H	0.424551000	-4.801085000	-3.392279000

H	2.327412000	4.492243000	-1.320293000
H	2.306801000	-4.510351000	-1.377911000
H	4.277595000	2.672263000	-1.257003000
H	4.265451000	-2.699755000	-1.291056000
H	4.959766000	-0.352884000	1.003628000
H	4.884232000	0.316047000	-3.220419000
H	7.352129000	0.316973000	-3.266831000
H	7.426994000	-0.349301000	0.962846000
H	8.632453000	-0.013042000	-1.173290000
H	-0.805409000	-8.636887000	-1.942417000
H	-0.753755000	8.647286000	-1.788746000
H	-1.336285000	-5.150627000	0.490235000
H	-1.293991000	5.116830000	0.576992000
H	-1.572870000	-7.586372000	0.164489000
H	-1.513901000	7.560300000	0.302127000
H	-3.169335000	-3.914535000	-1.716248000
H	-3.152324000	3.929986000	-1.656127000
H	-4.599192000	1.683837000	-1.732711000
H	-4.606428000	-1.661216000	-1.758314000

## 2. Mo[TPC] (O)

Mo	0.016796000	-0.002462000	-0.221183000
O	0.101075000	0.004495000	1.461906000
C	-2.687891000	0.706923000	-1.172786000
C	-3.564882000	1.769096000	-1.476439000
C	-2.818982000	2.934806000	-1.461392000
C	-1.469466000	2.596603000	-1.154176000
C	-0.291251000	3.365526000	-1.184291000
C	0.986331000	2.786800000	-1.128205000
C	2.244051000	3.458966000	-1.197602000
C	3.237927000	2.523619000	-1.173015000
C	2.631834000	1.234819000	-1.084050000
C	3.279049000	-0.010973000	-1.080571000
C	2.628735000	-1.255189000	-1.079606000
C	3.229022000	-2.542442000	-1.218082000
C	2.232085000	-3.474518000	-1.241990000
C	0.978177000	-2.800404000	-1.132971000
C	-0.302411000	-3.372047000	-1.192552000
C	-1.477384000	-2.598994000	-1.153105000
C	-2.828391000	-2.932943000	-1.458697000
C	-3.570857000	-1.765241000	-1.472428000
C	-2.690161000	-0.705606000	-1.170345000
C	-1.209816000	6.975743000	-0.523800000
C	-1.240814000	-6.989015000	-0.595690000
C	-1.080961000	5.600450000	-0.380417000
C	-1.096185000	-5.618585000	-0.423137000
C	-0.682731000	7.614953000	-1.639194000
C	-0.733842000	-7.607916000	-1.731584000
C	-0.417601000	4.839283000	-1.346862000
C	-0.437991000	-4.842450000	-1.381147000
C	-0.028312000	6.868536000	-2.611727000

C	-0.083492000	-6.846400000	-2.694984000
C	7.573600000	-0.020346000	-1.196217000
C	6.847273000	0.340775000	-2.324448000
C	6.902842000	-0.381055000	-0.034135000
C	5.513843000	-0.378794000	-0.000300000
C	5.458222000	0.342494000	-2.289665000
C	4.773570000	-0.015774000	-1.126852000
C	0.063033000	-5.476348000	-2.521470000
C	0.103324000	5.493540000	-2.466693000
N	1.256113000	1.419065000	-1.029099000
N	1.254344000	-1.437034000	-1.005756000
N	-1.442019000	-1.242103000	-0.943883000
N	-1.438502000	1.239763000	-0.946816000
H	0.375894000	7.355848000	-3.489429000
H	0.305682000	-7.317884000	-3.587965000
H	0.602026000	4.916328000	-3.233709000
H	0.557162000	-4.887007000	-3.282146000
H	2.366713000	4.525813000	-1.265502000
H	2.349324000	-4.539115000	-1.344848000
H	4.297712000	2.704283000	-1.216805000
H	4.286460000	-2.722327000	-1.304038000
H	4.994920000	-0.653752000	0.908523000
H	4.896234000	0.618911000	-3.172106000
H	7.361800000	0.618630000	-3.235074000
H	7.460277000	-0.660901000	0.850244000
H	8.655355000	-0.020820000	-1.222481000
H	-0.846840000	-8.675512000	-1.866665000
H	-0.783105000	8.686486000	-1.751186000
H	-1.485481000	-5.142502000	0.466899000
H	-1.485629000	5.108744000	0.494087000
H	-1.746998000	-7.573852000	0.161061000
H	-1.719230000	7.548497000	0.240072000
H	-3.186449000	-3.923066000	-1.684040000
H	-3.174081000	3.926078000	-1.686366000
H	-4.611987000	1.678614000	-1.713719000
H	-4.617726000	-1.671437000	-1.709404000

### 3. W[TPC]Cl<sub>2</sub>

W	-0.027106000	-0.013883000	-0.064810000
Cl	-0.004368000	1.505803000	1.756734000
Cl	-0.033881000	-1.561737000	1.733468000
C	-2.683032000	0.704184000	-1.175844000
C	-3.556846000	1.773806000	-1.468685000
C	-2.808329000	2.930553000	-1.431004000
C	-1.465074000	2.577577000	-1.119310000
C	-0.299046000	3.333824000	-1.158264000
C	0.969904000	2.740347000	-1.099945000
C	2.216323000	3.421306000	-1.207526000
C	3.213093000	2.493693000	-1.175318000
C	2.607032000	1.212939000	-1.051363000

C	3.262523000	-0.015770000	-1.052646000
C	2.601173000	-1.241528000	-1.064167000
C	3.198693000	-2.522085000	-1.221512000
C	2.196428000	-3.443372000	-1.268384000
C	0.954425000	-2.758118000	-1.141435000
C	-0.318512000	-3.341583000	-1.215309000
C	-1.479455000	-2.577853000	-1.168353000
C	-2.824102000	-2.916867000	-1.489904000
C	-3.565180000	-1.755106000	-1.509151000
C	-2.686343000	-0.696554000	-1.191668000
C	-1.068437000	6.979801000	-0.523397000
C	-1.114881000	-6.991908000	-0.639066000
C	-0.954664000	5.606249000	-0.347141000
C	-0.990583000	-5.621965000	-0.441510000
C	-0.646520000	7.570185000	-1.708243000
C	-0.693840000	-7.567562000	-1.831249000
C	-0.409856000	4.805389000	-1.352407000
C	-0.439078000	-4.809771000	-1.433774000
C	-0.110227000	6.780087000	-2.717678000
C	-0.149345000	-6.766064000	-2.827378000
C	7.551508000	-0.005196000	-1.148624000
C	6.830398000	0.155202000	-2.325646000
C	6.877537000	-0.173453000	0.054331000
C	5.488234000	-0.179243000	0.081125000
C	5.440802000	0.147855000	-2.299479000
C	4.756568000	-0.017735000	-1.095559000
C	-0.022282000	-5.397530000	-2.630043000
C	0.009123000	5.408192000	-2.540465000
N	1.223531000	1.373735000	-0.972790000
N	1.216826000	-1.396093000	-0.986344000
N	-1.437285000	-1.212762000	-0.950098000
N	-1.430805000	1.208708000	-0.925733000
H	0.213105000	7.231157000	-3.646672000
H	0.172384000	-7.205321000	-3.762627000
H	0.420383000	4.795288000	-3.331599000
H	0.394371000	-4.775681000	-3.411354000
H	2.323740000	4.486940000	-1.308425000
H	2.297040000	-4.506661000	-1.397366000
H	4.272421000	2.667205000	-1.245974000
H	4.256467000	-2.698982000	-1.308413000
H	4.964851000	-0.307002000	1.019443000
H	4.881022000	0.271524000	-3.217267000
H	7.348932000	0.284435000	-3.266512000
H	7.431950000	-0.297572000	0.975128000
H	8.633367000	0.000772000	-1.168709000
H	-0.791515000	-8.634123000	-1.984687000
H	-0.736154000	8.639782000	-1.845120000
H	-1.311721000	-5.175601000	0.489936000
H	-1.275739000	5.148480000	0.578773000
H	-1.538488000	-7.609393000	0.142013000
H	-1.484356000	7.588679000	0.268599000

H	-3.170180000	-3.908336000	-1.726490000
H	-3.149175000	3.928399000	-1.647614000
H	-4.602524000	1.686455000	-1.712440000
H	-4.609205000	-1.656551000	-1.755802000

#### 4. W[TPC] (O)

W	0.010169000	-0.002556000	-0.179361000
O	0.086854000	0.001101000	1.525679000
C	-2.693111000	0.710079000	-1.144592000
C	-3.561887000	1.771921000	-1.468519000
C	-2.813727000	2.936734000	-1.450228000
C	-1.470468000	2.598170000	-1.121329000
C	-0.289537000	3.362895000	-1.152771000
C	0.988365000	2.786224000	-1.087980000
C	2.244068000	3.457314000	-1.181865000
C	3.239641000	2.522927000	-1.158517000
C	2.636958000	1.235377000	-1.046113000
C	3.282902000	-0.010365000	-1.047506000
C	2.631829000	-1.253623000	-1.042753000
C	3.228384000	-2.539664000	-1.194142000
C	2.229535000	-3.470147000	-1.222276000
C	0.977535000	-2.796708000	-1.099719000
C	-0.303522000	-3.365803000	-1.172553000
C	-1.480549000	-2.595902000	-1.132595000
C	-2.825109000	-2.926837000	-1.465348000
C	-3.568289000	-1.759054000	-1.477716000
C	-2.695626000	-0.702691000	-1.146865000
C	-1.197662000	6.984992000	-0.544392000
C	-1.221143000	-6.997472000	-0.633044000
C	-1.061023000	5.613348000	-0.374754000
C	-1.080240000	-5.629738000	-0.435986000
C	-0.696900000	7.601540000	-1.684338000
C	-0.726976000	-7.592145000	-1.787250000
C	-0.416514000	4.834627000	-1.339533000
C	-0.437484000	-4.833460000	-1.387232000
C	-0.060034000	6.836976000	-2.654452000
C	-0.092675000	-6.809531000	-2.744423000
C	7.575263000	-0.034860000	-1.214463000
C	6.835872000	0.272022000	-2.350129000
C	6.918535000	-0.335089000	-0.027407000
C	5.529913000	-0.327680000	0.023456000
C	5.447273000	0.278751000	-2.298374000
C	4.777127000	-0.018564000	-1.110708000
C	0.050801000	-5.442794000	-2.546190000
C	0.079120000	5.465848000	-2.483415000
N	1.260194000	1.417830000	-0.970543000
N	1.256025000	-1.432674000	-0.956648000
N	-1.449298000	-1.241086000	-0.902220000
N	-1.444775000	1.242396000	-0.899246000
H	0.324539000	7.307080000	-3.550106000

H	0.286340000	-7.262060000	-3.651555000
H	0.563779000	4.873668000	-3.248081000
H	0.533602000	-4.836572000	-3.300990000
H	2.364700000	4.523128000	-1.267822000
H	2.345093000	-4.533690000	-1.337780000
H	4.298525000	2.703839000	-1.221404000
H	4.285076000	-2.720792000	-1.287852000
H	5.021420000	-0.557478000	0.950557000
H	4.874622000	0.513929000	-3.185976000
H	7.339580000	0.503863000	-3.279568000
H	7.486592000	-0.572044000	0.862610000
H	8.656631000	-0.039751000	-1.254268000
H	-0.837008000	-8.657519000	-1.941119000
H	-0.803882000	8.670063000	-1.816999000
H	-1.459949000	-5.172275000	0.467828000
H	-1.445500000	5.138499000	0.518043000
H	-1.714196000	-7.599122000	0.119256000
H	-1.692291000	7.572574000	0.217943000
H	-3.178831000	-3.913867000	-1.709759000
H	-3.163740000	3.926718000	-1.687992000
H	-4.604952000	1.682388000	-1.723323000
H	-4.610630000	-1.663535000	-1.733340000