Orbital control over the metal *vs* ligand reduction in a series of neutral and cationic bis(cyclopentadienyl) Ti(IV) complexes

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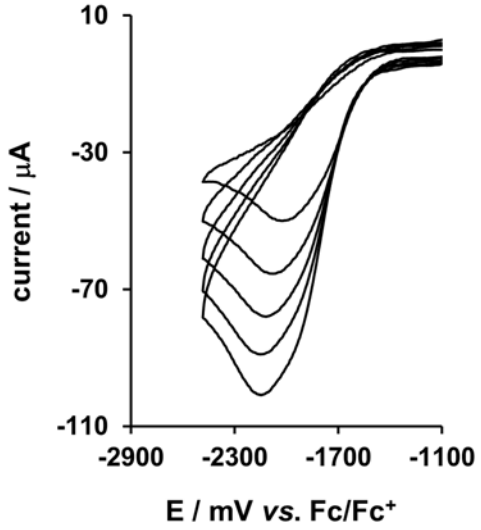
Supporting information

Table of Contents

Electrochemical data



Cyclic voltammograms (*vs* Fc/Fc^+) for 2,2'-biphenol at scan rates 100, 200, 300, 400 and 500 mV s^{-1}.
Measured in 0.1 mol dm^{-3} $[NBu_4][PF_6]$ / CH_3CN on a glassy carbon working electrode at 25 °C. [2,2'-biphenol] = 3 mmol dm^{-3}.

ν mV s^{-1}	**E_{pc}** mV	**i_{pc}** μA
100	-1934	51
200	-1942	75
300	-1952	94
500	-1967	124
1000	-1992	176
2000	-2027	244

Cyclic voltammetric data (*vs*. Fc/Fc^+) for 2,2'-biphenol at indicated scan rates. Measured in 0.1 mol dm^{-3} $[NBu_4][PF_6]$ / CH_3CN on a glassy carbon working electrode at 25 °C. [2,2'-biphenol] = 3 mmol dm^{-3}.

DFT calculated energies (Table S1)

Table S1. Cyclic voltammetric data (*vs*. Fc/Fc^{+}) and DFT calculated data of the indicated complexes.

Complex **A: Neutral Complexes**	**Reduction 1** **$E^{o'}$ / V Ti^{IV}/Ti^{III}**	**E_{LUMO}** **/ eV**	**EA** **/ eV**	**ω** **/ eV**	**χ** **/ eV**
A1	-1.31	-3.696	1.503	1.73	4.69
A2	-1.40	-3.532	1.412	1.65	4.54
A3	-1.48	-3.478	1.416	1.63	4.45
A4	-1.59	-3.351	1.335	1.56	4.32
A5	-1.62	-3.242	1.251	1.49	4.15
A6	-1.28	-3.691	1.599	1.76	4.60
A7	-1.62	-3.306	1.384	1.56	4.15
B: Cationic Complexes	**$E^{o'}$ / V Ti^{IV}/Ti^{III}**				
B1 $[Cp_2Ti(acac)]^{+}$	-0.85	-7.174	5.32	5.79	8.278
B2	-0.84	-6.983	5.23	5.76	8.017
B3	-0.82	-6.826	5.15	5.75	7.798
B4	-0.63	-7.625	5.70	6.34	8.646
B5	-0.62	-7.325	5.54	6.23	8.316
B6	-0.62	-7.295	5.51	6.16	8.303
B7	-0.62	-7.367	5.56	6.25	8.351
	Reduction 2 **E_{pc} / V** ligand				
B1 [Cp2Ti(acac)]+	-2.80	-1.993	0.33	0.80	2.825
B2	-2.31	-2.490	0.99	1.14	3.111
B3	-2.11	-2.727	1.34	1.38	3.247
B4	-2.16	-2.759	1.01	1.20	3.355
B5	-1.89	-3.092	1.49	1.53	3.516
B6	-1.92	-2.980	1.37	1.43	3.439
B7	-1.92	-3.048	1.48	1.52	3.520

Optimized Cartesian coordinates (Å)

All compounds were optimized using the PW91/TZP (Triple ζ polarized) functional [i] and basis sets as implemented in the Amsterdam Density Functional (ADF2013) [ii].

1. $[Cp_2TiCl_2]$ (complex A1)

Ti	0.000000000	0.000000000	-0.017575000
Cl	-0.077760000	1.744087000	-1.558360000
Cl	0.077760000	-1.744087000	-1.558360000
C	-1.536138000	-0.970696000	1.531770000
C	-1.442171000	0.412490000	1.856609000
C	-1.970575000	1.148519000	0.777970000
C	-2.412963000	0.226511000	-0.208680000
C	-2.165563000	-1.074621000	0.268569000
C	1.442171000	-0.412490000	1.856609000
C	1.536138000	0.970696000	1.531770000
C	2.165563000	1.074621000	0.268569000
C	2.412963000	-0.226511000	-0.208680000
C	1.970575000	-1.148519000	0.777970000
H	-1.214170000	-1.799472000	2.150654000
H	-1.031041000	0.825862000	2.768866000
H	-2.000883000	2.227958000	0.693501000
H	-2.819132000	0.483747000	-1.178869000
H	-2.359530000	-1.995167000	-0.266187000
H	1.031041000	-0.825862000	2.768866000
H	1.214170000	1.799472000	2.150654000
H	2.359530000	1.995167000	-0.266187000
H	2.819132000	-0.483747000	-1.178869000
H	2.000883000	-2.227958000	0.693501000

2. Complex A2

Ti	0.000000000	0.000000000	-0.091682000
Cl	0.121949000	-1.732029000	-1.631112000
C	2.200488000	1.156830000	0.230736000
C	1.525361000	1.008384000	1.471143000
C	1.433998000	-0.379730000	1.771426000
H	1.015073000	-0.811349000	2.671947000
C	1.985274000	-1.090941000	0.688548000
C	2.434862000	-0.144224000	-0.269523000
H	2.864998000	-0.379400000	-1.235829000
C	2.653211000	2.436891000	-0.379358000
H	3.657448000	2.680301000	-0.003961000

H	1.985557000	3.265460000	-0.124698000
H	2.704069000	2.364900000	-1.469298000
Cl	-0.121949000	1.732029000	-1.631112000
C	-2.200488000	-1.156830000	0.230736000
C	-1.525361000	-1.008384000	1.471143000
C	-1.433998000	0.379730000	1.771426000
H	-1.015073000	0.811349000	2.671947000
C	-1.985274000	1.090941000	0.688548000
C	-2.434862000	0.144224000	-0.269523000
C	-2.653211000	-2.436891000	-0.379358000
H	-3.657448000	-2.680301000	-0.003961000
H	-1.985557000	-3.265460000	-0.124698000
H	-2.704069000	-2.364900000	-1.469298000
H	-2.864998000	0.379400000	-1.235829000
H	-1.198596000	-1.824482000	2.106144000
H	-2.027985000	2.167748000	0.582708000
H	1.198596000	1.824482000	2.106144000
H	2.027985000	-2.167748000	0.582708000

3. Complex A3

Ti	0.000000000	0.000000000	-0.021670000
Cl	0.185179000	-1.735912000	-1.574387000
C	2.131719000	1.139804000	0.158677000
C	1.525310000	1.153259000	1.441956000
C	1.477433000	-0.203601000	1.879061000
H	1.109556000	-0.539648000	2.841718000
C	2.038027000	-1.040000000	0.886438000
C	2.422601000	-0.190252000	-0.191504000
H	2.837186000	-0.522590000	-1.135552000
C	1.198222000	2.376010000	2.235605000
H	0.451094000	2.181193000	3.012039000
H	0.829173000	3.183790000	1.593617000
H	2.100902000	2.745654000	2.742089000
C	2.288967000	-2.508613000	0.978084000
H	3.352389000	-2.689932000	1.184660000
H	2.040730000	-3.010293000	0.036157000
H	1.711763000	-2.970893000	1.784796000
Cl	-0.185179000	1.735912000	-1.574387000
C	-2.131719000	-1.139804000	0.158677000
C	-1.525310000	-1.153259000	1.441956000
C	-1.477433000	0.203601000	1.879061000
C	-1.198222000	-2.376010000	2.235605000
H	-0.451094000	-2.181193000	3.012039000
H	-0.829173000	-3.183790000	1.593617000
H	-2.100902000	-2.745654000	2.742089000
H	-1.109556000	0.539648000	2.841718000
C	-2.038027000	1.040000000	0.886438000
C	-2.422601000	0.190252000	-0.191504000
C	-2.288967000	2.508613000	0.978084000

H	-3.352389000	2.689932000	1.184660000
H	-2.040730000	3.010293000	0.036157000
H	-1.711763000	2.970893000	1.784796000
H	-2.837186000	0.522590000	-1.135552000
H	-2.296947000	-2.008946000	-0.463997000
H	2.296947000	2.008946000	-0.463997000

4. Complex A4

Ti	0.000000000	0.000000000	-0.048749000
Cl	0.172155000	-1.722993000	-1.602812000
C	2.221079000	1.142384000	0.145731000
C	1.560314000	1.157346000	1.411044000
C	1.457400000	-0.196291000	1.845514000
H	1.066600000	-0.520442000	2.803743000
C	2.005295000	-1.048531000	0.860355000
C	2.441283000	-0.207218000	-0.202222000
H	2.874450000	-0.550012000	-1.135588000
C	2.706082000	2.330662000	-0.608619000
H	3.663879000	2.667830000	-0.184699000
H	2.001828000	3.167269000	-0.559199000
H	2.866164000	2.091596000	-1.663782000
C	1.252549000	2.381892000	2.210487000
H	0.547785000	2.174970000	3.022661000
H	0.835334000	3.183061000	1.589444000
H	2.170286000	2.776223000	2.671395000
C	2.223855000	-2.522547000	0.960701000
H	3.279271000	-2.726114000	1.188158000
H	1.982480000	-3.024897000	0.017358000
H	1.623356000	-2.969197000	1.759549000
Cl	-0.172155000	1.722993000	-1.602812000
C	-2.221079000	-1.142384000	0.145731000
C	-1.560314000	-1.157346000	1.411044000
C	-1.457400000	0.196291000	1.845514000
C	-1.252549000	-2.381892000	2.210487000
H	-0.547785000	-2.174970000	3.022661000
H	-0.835334000	-3.183061000	1.589444000
H	-2.170286000	-2.776223000	2.671395000
H	-1.066600000	0.520442000	2.803743000
C	-2.005295000	1.048531000	0.860355000
C	-2.441283000	0.207218000	-0.202222000
C	-2.706082000	-2.330662000	-0.608619000
H	-3.663879000	-2.667830000	-0.184699000
H	-2.001828000	-3.167269000	-0.559199000
H	-2.866164000	-2.091596000	-1.663782000
C	-2.223855000	2.522547000	0.960701000
H	-3.279271000	2.726114000	1.188158000
H	-1.982480000	3.024897000	0.017358000
H	-1.623356000	2.969197000	1.759549000
H	-2.874450000	0.550012000	-1.135588000

5. Complex A5

Ti	0.000000000	0.000000000	0.022569000
Cl	0.416556000	-1.674202000	1.584549000
C	1.302276000	0.703739000	-1.839470000
H	0.812515000	0.919167000	-2.781930000
C	1.595078000	1.656255000	-0.838246000
C	2.304057000	0.974493000	0.200543000
C	2.468271000	-0.379768000	-0.192140000
C	1.819334000	-0.564373000	-1.447582000
C	1.346429000	3.127541000	-0.906301000
H	0.899833000	3.506163000	0.020334000
H	0.683929000	3.382644000	-1.739524000
H	2.294467000	3.661749000	-1.061127000
C	2.873057000	1.602294000	1.426724000
H	2.868665000	0.906634000	2.272617000
H	2.300591000	2.486399000	1.721619000
H	3.914475000	1.912215000	1.254323000
C	3.308216000	-1.391850000	0.507721000
H	4.348398000	-1.310901000	0.158015000
H	2.965708000	-2.412517000	0.313665000
H	3.305211000	-1.243101000	1.591204000
C	1.899671000	-1.800440000	-2.284502000
H	1.203236000	-1.767715000	-3.128596000
H	1.693220000	-2.707949000	-1.705613000
H	2.910608000	-1.908996000	-2.703741000
Cl	-0.416556000	1.674202000	1.584549000
C	-1.302276000	-0.703739000	-1.839470000
H	-0.812515000	-0.919167000	-2.781930000
C	-1.595078000	-1.656255000	-0.838246000
C	-2.304057000	-0.974493000	0.200543000
C	-2.468271000	0.379768000	-0.192140000
C	-1.819334000	0.564373000	-1.447582000
C	-1.346429000	-3.127541000	-0.906301000
H	-0.899833000	-3.506163000	0.020334000
H	-0.683929000	-3.382644000	-1.739524000
H	-2.294467000	-3.661749000	-1.061127000
C	-2.873057000	-1.602294000	1.426724000
H	-2.868665000	-0.906634000	2.272617000
H	-2.300591000	-2.486399000	1.721619000
H	-3.914475000	-1.912215000	1.254323000
C	-3.308216000	1.391850000	0.507721000
H	-4.348398000	1.310901000	0.158015000
H	-2.965708000	2.412517000	0.313665000
H	-3.305211000	1.243101000	1.591204000
C	-1.899671000	1.800440000	-2.284502000
H	-1.203236000	1.767715000	-3.128596000
H	-1.693220000	2.707949000	-1.705613000
H	-2.910608000	1.908996000	-2.703741000

6. Complex A6

Ti	0.000000000	0.000000000	-0.023754000
Cl	0.358674000	-1.727045000	-1.528250000
Si	0.000000000	0.000000000	3.275718000
C	1.311547000	0.268883000	1.968801000
C	1.913034000	-0.767775000	1.195527000
C	2.465645000	-0.201675000	0.017409000
C	2.178654000	1.171017000	0.020049000
C	1.445897000	1.463150000	1.199657000
C	0.307885000	-1.521292000	4.316960000
H	1.942948000	-1.820775000	1.454302000
H	2.965364000	-0.747148000	-0.773150000
H	2.417108000	1.873227000	-0.768274000
H	1.050530000	2.438825000	1.462078000
H	-0.554842000	-1.727213000	4.962443000
H	0.485464000	-2.411303000	3.702502000
H	1.184335000	-1.378064000	4.960523000
Cl	-0.358674000	1.727045000	-1.528250000
C	-1.311547000	-0.268883000	1.968801000
C	-1.913034000	0.767775000	1.195527000
C	-2.465645000	0.201675000	0.017409000
C	-2.178654000	-1.171017000	0.020049000
C	-1.445897000	-1.463150000	1.199657000
C	-0.307885000	1.521292000	4.316960000
H	-1.942948000	1.820775000	1.454302000
H	-2.965364000	0.747148000	-0.773150000
H	-2.417108000	-1.873227000	-0.768274000
H	-1.050530000	-2.438825000	1.462078000
H	0.554842000	1.727213000	4.962443000
H	-0.485464000	2.411303000	3.702502000
H	-1.184335000	1.378064000	4.960523000

7. Complex A7

Ti	0.000000000	0.000000000	0.017859000
Cl	0.295991000	1.723721000	1.539402000
Cl	-0.295991000	-1.723721000	1.539402000
C	-1.346453000	0.227495000	-1.935606000
C	-1.946722000	-0.836742000	-1.175683000
C	-2.544174000	-0.279407000	-0.005151000
C	-2.303839000	1.110895000	-0.007116000
C	-1.553713000	1.432273000	-1.177357000
C	-2.149953000	-2.271260000	-1.555784000
H	-3.215933000	-2.448513000	-1.756940000
H	-1.857443000	-2.949619000	-0.745290000
H	-1.601302000	-2.552228000	-2.453818000
C	-3.389813000	-1.030418000	0.962976000

H	-3.478487000	-0.504521000	1.917943000
H	-2.977868000	-2.023594000	1.167869000
H	-4.403630000	-1.162561000	0.556110000
C	-2.850234000	2.107211000	0.955973000
H	-3.739413000	2.594345000	0.529708000
H	-2.116242000	2.887023000	1.183763000
H	-3.144019000	1.640892000	1.900648000
C	-1.263177000	2.850654000	-1.560678000
H	-2.209049000	3.381764000	-1.740177000
H	-0.672424000	2.928295000	-2.472662000
H	-0.739598000	3.387698000	-0.760481000
C	1.346453000	-0.227495000	-1.935606000
C	1.946722000	0.836742000	-1.175683000
C	2.544174000	0.279407000	-0.005151000
C	2.303839000	-1.110895000	-0.007116000
C	1.553713000	-1.432273000	-1.177357000
C	2.149953000	2.271260000	-1.555784000
H	1.857443000	2.949619000	-0.745290000
H	1.601302000	2.552228000	-2.453818000
H	3.215933000	2.448513000	-1.756940000
C	3.389813000	1.030418000	0.962976000
H	3.478487000	0.504521000	1.917943000
H	2.977868000	2.023594000	1.167869000
H	4.403630000	1.162561000	0.556110000
C	2.850234000	-2.107211000	0.955973000
H	3.739413000	-2.594345000	0.529708000
H	2.116242000	-2.887023000	1.183763000
H	3.144019000	-1.640892000	1.900648000
C	1.263177000	-2.850654000	-1.560678000
H	2.209049000	-3.381764000	-1.740177000
H	0.672424000	-2.928295000	-2.472662000
H	0.739598000	-3.387698000	-0.760481000
Si	0.000000000	0.000000000	-3.234863000
C	-0.236812000	-1.427219000	-4.444818000
H	-0.442036000	-2.416344000	-4.032416000
H	0.667088000	-1.506594000	-5.063238000
H	-1.068179000	-1.170018000	-5.114709000
C	0.236812000	1.427219000	-4.444818000
H	-0.667088000	1.506594000	-5.063238000
H	0.442036000	2.416344000	-4.032416000
H	1.068179000	1.170018000	-5.114709000

8. [Cp_2Ti(biphen)] (complex A8)

Ti	0.000000000	0.000000000	1.326179000
O	-1.118281000	-0.797950000	0.003676000
O	1.118281000	0.797950000	0.003676000
C	2.010389000	-1.151006000	2.025760000
C	1.351362000	-2.031138000	1.133318000
C	0.139665000	-2.433218000	1.736683000

C	0.032212000	-1.794279000	2.988121000
C	1.199160000	-1.001690000	3.173647000
C	-0.032212000	1.794279000	2.988121000
C	-0.139665000	2.433218000	1.736683000
C	-1.351362000	2.031138000	1.133318000
C	-2.010389000	1.151006000	2.025760000
C	-1.199160000	1.001690000	3.173647000
C	-1.594868000	-0.212130000	-1.109426000
C	-0.728007000	0.139601000	-2.176033000
C	-1.304810000	0.715564000	-3.318611000
C	-2.674599000	0.927528000	-3.435129000
C	-3.516942000	0.542693000	-2.394204000
C	-2.979346000	-0.024480000	-1.245058000
C	1.594868000	0.212130000	-1.109426000
C	0.728007000	-0.139601000	-2.176033000
C	1.304810000	-0.715564000	-3.318611000
C	2.674599000	-0.927528000	-3.435129000
C	3.516942000	-0.542693000	-2.394204000
C	2.979346000	0.024480000	-1.245058000
H	3.622293000	0.345382000	-0.427417000
H	0.644627000	-1.014973000	-4.131147000
H	3.080515000	-1.385225000	-4.334901000
H	0.616180000	3.058207000	1.276954000
H	4.593050000	-0.685333000	-2.474245000
H	-0.644627000	1.014973000	-4.131147000
H	-2.956152000	0.653844000	1.845711000
H	-3.622293000	-0.345382000	-0.427417000
H	-1.431645000	0.404741000	4.045969000
H	0.786465000	1.903594000	3.689064000
H	1.693363000	-2.307159000	0.143391000
H	2.956152000	-0.653844000	1.845711000
H	-4.593050000	0.685333000	-2.474245000
H	-0.616180000	-3.058207000	1.276954000
H	-0.786465000	-1.903594000	3.689064000
H	-1.693363000	2.307159000	0.143391000
H	1.431645000	-0.404741000	4.045969000
H	-3.080515000	1.385225000	-4.334901000

9. $[Cp_2Ti(acac)]^+$ (complex B1)

Ti	-0.025339000	-0.000342000	0.001099000
O	0.255019000	1.353423000	-1.426509000
O	0.290870000	-1.381605000	-1.399173000
C	0.086248000	2.486063000	-3.498051000
H	-0.768002000	3.099711000	-3.180278000
H	0.017556000	2.302546000	-4.573338000
H	0.991760000	3.068944000	-3.283379000
C	0.110047000	1.213215000	-2.707004000
C	0.024725000	-0.036454000	-3.337974000
H	-0.039394000	-0.048053000	-4.423469000

C	0.159246000	-1.270152000	-2.682377000
C	-2.327202000	-0.194751000	-0.738950000
H	-2.552023000	-0.343248000	-1.790130000
C	-2.206234000	1.052662000	-0.083849000
H	-2.315130000	2.030329000	-0.542153000
C	-1.874403000	0.811613000	1.273501000
H	-1.742821000	1.568215000	2.039228000
C	-1.818249000	-0.601350000	1.463806000
H	-1.624960000	-1.111173000	2.401178000
C	-2.091797000	-1.217663000	0.219822000
H	-2.101946000	-2.286386000	0.028651000
C	2.081211000	-0.970867000	0.675426000
H	2.412046000	-1.888284000	0.200514000
C	1.243529000	-0.884800000	1.819750000
H	0.875343000	-1.722364000	2.403047000
C	1.026809000	0.493991000	2.097596000
H	0.461426000	0.894556000	2.931420000
C	1.700856000	1.248965000	1.106586000
H	1.704100000	2.331409000	1.019718000
C	2.355545000	0.341088000	0.229846000
H	2.935287000	0.609957000	-0.646566000
C	0.201164000	-2.556156000	-3.451502000
H	-0.621119000	-3.206878000	-3.123748000
H	0.126912000	-2.395019000	-4.529960000
H	1.135070000	-3.088045000	-3.225819000

10. [$Cp_2Ti(ba)]^+$ (complex B2)

Ti	-0.034177000	0.000821000	-0.011933000
O	0.120476000	1.332545000	-1.463874000
O	0.287068000	-1.380361000	-1.398402000
C	-0.094576000	1.193253000	-2.740287000
C	-0.175284000	-0.081853000	-3.337723000
H	-0.330095000	-0.137906000	-4.409863000
C	0.049103000	-1.290618000	-2.673121000
C	-2.357524000	-0.329025000	-0.636003000
H	-2.622248000	-0.518996000	-1.670894000
C	-2.269879000	0.942882000	-0.024426000
H	-2.450094000	1.897012000	-0.509600000
C	-1.864368000	0.761253000	1.322210000
H	-1.733853000	1.546232000	2.059157000
C	-1.728618000	-0.640840000	1.550914000
H	-1.466058000	-1.110947000	2.492362000
C	-2.026531000	-1.308633000	0.339541000
H	-1.990757000	-2.381970000	0.180500000
C	2.154639000	-0.846930000	0.573807000
H	2.513434000	-1.748009000	0.088130000
C	1.365877000	-0.798855000	1.754607000
H	1.069901000	-1.651270000	2.357437000
C	1.084978000	0.567586000	2.034840000

H	0.535241000	0.942288000	2.890909000
C	1.670502000	1.351030000	1.010030000
H	1.612694000	2.431523000	0.918571000
C	2.335484000	0.474128000	0.109262000
H	2.856160000	0.768268000	-0.795554000
C	0.071450000	-2.592362000	-3.418038000
H	-0.682945000	-3.271022000	-2.997603000
H	-0.115883000	-2.460938000	-4.486830000
H	1.046989000	-3.077198000	-3.278389000
C	-0.205531000	2.440223000	-3.518771000
C	-0.225688000	2.448713000	-4.927386000
C	-0.285418000	3.666754000	-2.831511000
H	-0.143433000	1.521907000	-5.490824000
H	-0.263249000	3.664570000	-1.743789000
C	-0.325938000	3.648639000	-5.622158000
C	-0.391333000	4.863594000	-3.529947000
H	-0.331983000	3.643367000	-6.710483000
H	-0.456789000	5.805361000	-2.987602000
C	-0.411440000	4.857622000	-4.927318000
H	-0.490373000	5.795397000	-5.475395000

11. [$Cp_2Ti(dbm)]^+$ (complex B3)

Ti	-0.027828000	-0.002335000	-0.063172000
O	0.206012000	1.345746000	-1.472582000
O	0.318839000	-1.355227000	-1.463910000
C	-0.049848000	1.230542000	-2.749384000
C	-0.094110000	-0.020825000	-3.382997000
H	-0.220111000	-0.030796000	-4.458077000
C	0.145686000	-1.254853000	-2.751453000
C	-2.330816000	-0.291193000	-0.772905000
H	-2.560560000	-0.459424000	-1.819703000
C	-2.250088000	0.965548000	-0.131288000
H	-2.398307000	1.933163000	-0.600596000
C	-1.892694000	0.749448000	1.224262000
H	-1.776282000	1.517452000	1.981571000
C	-1.784327000	-0.659249000	1.427797000
H	-1.558596000	-1.152302000	2.367109000
C	-2.046297000	-1.296187000	0.192830000
H	-2.022012000	-2.365882000	0.009055000
C	2.142873000	-0.878092000	0.557758000
H	2.517807000	-1.755334000	0.041381000
C	1.312026000	-0.882708000	1.710835000
H	0.993153000	-1.760851000	2.263010000
C	1.022532000	0.470076000	2.044418000
H	0.442629000	0.806095000	2.896496000
C	1.642641000	1.298327000	1.077281000
H	1.587976000	2.382016000	1.035109000
C	2.339721000	0.462136000	0.161339000
H	2.890210000	0.795005000	-0.711738000

C	-0.220847000	2.496456000	-3.487620000
C	-0.677846000	2.533043000	-4.819519000
C	0.076026000	3.710388000	-2.839046000
H	-0.940970000	1.615381000	-5.341728000
H	0.429038000	3.686863000	-1.810554000
C	-0.824235000	3.747439000	-5.480706000
C	-0.064498000	4.921687000	-3.506595000
H	-1.184079000	3.763392000	-6.507692000
H	0.178433000	5.853117000	-2.997484000
C	-0.513609000	4.943810000	-4.829155000
H	-0.624275000	5.892698000	-5.351941000
C	0.242665000	-2.517135000	-3.510497000
C	0.200751000	-3.737353000	-2.809269000
C	0.390278000	-2.544165000	-4.910692000
H	0.093805000	-3.720337000	-1.726893000
H	0.461320000	-1.618771000	-5.478726000
C	0.289970000	-4.947258000	-3.488136000
C	0.486707000	-3.756659000	-5.585004000
H	0.248846000	-5.884477000	-2.935305000
H	0.612157000	-3.764735000	-6.666168000
C	0.433178000	-4.960177000	-4.877650000
H	0.507162000	-5.907620000	-5.409544000

12. $[Cp_2Ti(tfaa)]^+$ (complex B4)

Ti	-0.063831000	0.006503000	0.008635000
O	0.177066000	1.395424000	-1.413922000
O	0.296355000	-1.351967000	-1.428667000
C	0.184897000	2.579106000	-3.465284000
H	-0.588349000	3.259262000	-3.086234000
H	0.048759000	2.421639000	-4.538192000
H	1.152380000	3.074280000	-3.297993000
C	0.151820000	1.294423000	-2.697149000
C	0.138102000	0.047570000	-3.364599000
H	0.137880000	0.040825000	-4.450848000
C	0.234811000	-1.166386000	-2.698762000
C	-2.358890000	0.094180000	-0.744873000
H	-2.588451000	0.258695000	-1.792883000
C	-2.187263000	1.102676000	0.243190000
H	-2.257530000	2.174292000	0.081352000
C	-1.889409000	0.468040000	1.473167000
H	-1.736063000	0.961802000	2.426351000
C	-1.864213000	-0.939847000	1.243525000
H	-1.697338000	-1.709018000	1.989739000
C	-2.173939000	-1.162528000	-0.123585000
H	-2.222615000	-2.131053000	-0.611790000
C	1.755786000	-1.146603000	1.062675000
H	1.848002000	-2.220754000	0.930887000
C	1.020082000	-0.489949000	2.079533000
H	0.490594000	-0.968864000	2.895377000

C	1.124042000	0.912985000	1.858607000
H	0.695187000	1.693781000	2.478060000
C	1.953626000	1.113061000	0.721771000
H	2.213940000	2.073732000	0.289560000
C	2.333763000	-0.153548000	0.224533000
H	2.938336000	-0.340622000	-0.656914000
C	0.314118000	-2.483902000	-3.496245000
F	-0.734026000	-3.280816000	-3.162590000
F	0.277080000	-2.280190000	-4.831261000
F	1.454658000	-3.145611000	-3.197104000

13. $[Cp_2Ti(tfth)]^+$ (complex B5)

Ti	-0.170447000	-0.005155000	-0.085943000
O	-0.169845000	1.302822000	-1.593902000
O	0.374447000	-1.378176000	-1.433368000
C	-0.296112000	1.103661000	-2.870494000
C	-0.161898000	-0.192610000	-3.446241000
H	-0.241655000	-0.300211000	-4.522528000
C	0.178756000	-1.308383000	-2.709528000
C	-2.473134000	-0.308527000	-0.767419000
H	-2.750387000	-0.246172000	-1.814837000
C	-2.432810000	0.776235000	0.152467000
H	-2.667938000	1.812370000	-0.072977000
C	-2.015188000	0.273330000	1.407129000
H	-1.913122000	0.844931000	2.323210000
C	-1.781001000	-1.126761000	1.261436000
H	-1.479874000	-1.812242000	2.046251000
C	-2.085969000	-1.480651000	-0.078603000
H	-1.997692000	-2.474763000	-0.505937000
C	1.805533000	-0.793213000	1.023410000
H	2.043350000	-1.852128000	0.984224000
C	0.999283000	-0.153402000	1.996547000
H	0.549757000	-0.624263000	2.863590000
C	0.904206000	1.224243000	1.649248000
H	0.374534000	1.990891000	2.205308000
C	1.683730000	1.431841000	0.479151000
H	1.800708000	2.374217000	-0.046054000
C	2.229801000	0.189396000	0.086716000
H	2.839513000	0.007369000	-0.791937000
C	0.405574000	-2.656546000	-3.414167000
F	-0.470494000	-3.579466000	-2.935057000
F	0.230029000	-2.575403000	-4.754327000
F	1.656967000	-3.111517000	-3.178706000
C	-0.536841000	2.261248000	-3.690043000
S	-0.690572000	3.831412000	-2.933151000
C	-0.936483000	4.580247000	-4.455478000
C	-0.902958000	3.681078000	-5.503836000
C	-0.675569000	2.364019000	-5.072827000
H	-1.093194000	5.653467000	-4.505332000

H	-1.036876000	3.970208000	-6.542187000
H	-0.611649000	1.516181000	-5.749128000

14. $[Cp_2Ti(tffu)]^+$ (complex B6)

Ti	-0.142382000	0.017183000	-0.082626000
O	-0.106478000	1.331460000	-1.577263000
O	0.346945000	-1.369616000	-1.440158000
C	-0.218323000	1.143228000	-2.852033000
C	-0.121173000	-0.147663000	-3.447547000
H	-0.193854000	-0.236427000	-4.526409000
C	0.168092000	-1.282349000	-2.718029000
C	-2.452776000	-0.221258000	-0.760858000
H	-2.725909000	-0.163764000	-1.809698000
C	-2.378470000	0.873071000	0.144648000
H	-2.575053000	1.913693000	-0.095798000
C	-1.975593000	0.373706000	1.405598000
H	-1.854457000	0.954163000	2.313761000
C	-1.787693000	-1.035455000	1.278548000
H	-1.508876000	-1.719969000	2.072324000
C	-2.103129000	-1.396545000	-0.056848000
H	-2.046032000	-2.397973000	-0.472133000
C	1.802982000	-0.840335000	1.028315000
H	1.998044000	-1.908265000	0.998720000
C	1.027774000	-0.159335000	1.998368000
H	0.562791000	-0.603360000	2.871253000
C	0.986236000	1.217427000	1.637831000
H	0.488255000	2.009799000	2.186946000
C	1.769633000	1.382892000	0.463398000
H	1.918277000	2.314413000	-0.072837000
C	2.263663000	0.115819000	0.081163000
H	2.862419000	-0.099046000	-0.797555000
C	0.348353000	-2.631995000	-3.432019000
F	-0.568976000	-3.523458000	-2.971432000
F	0.191518000	-2.531756000	-4.773498000
F	1.577972000	-3.139187000	-3.187507000
C	-0.407063000	2.303724000	-3.676212000
O	-0.500055000	3.522346000	-3.034575000
C	-0.666620000	4.455220000	-4.005285000
C	-0.684763000	3.879503000	-5.251098000
C	-0.517786000	2.493536000	-5.044816000
H	-0.758011000	5.479744000	-3.664692000
H	-0.802335000	4.397174000	-6.195605000
H	-0.478591000	1.726260000	-5.809270000

15. $[Cp_2Ti(tfba)]^+$ (complex B7)

Ti	-0.063367000	-0.007251000	-0.024349000
O	0.061912000	1.349929000	-1.469770000

O	0.338631000	-1.367107000	-1.435924000
C	-0.064034000	1.248964000	-2.754795000
C	-0.047383000	-0.025300000	-3.387518000
H	-0.120857000	-0.082766000	-4.466760000
C	0.170311000	-1.207408000	-2.705994000
C	-2.382455000	-0.089729000	-0.715187000
H	-2.649184000	0.015885000	-1.761840000
C	-2.247517000	0.969805000	0.223385000
H	-2.389889000	2.026039000	0.015682000
C	-1.876708000	0.410301000	1.469468000
H	-1.723890000	0.954753000	2.395097000
C	-1.772841000	-1.003006000	1.299935000
H	-1.537306000	-1.726569000	2.072811000
C	-2.103616000	-1.304218000	-0.046417000
H	-2.104401000	-2.294420000	-0.491568000
C	1.787741000	-1.048279000	1.090650000
H	1.888179000	-2.129024000	1.052141000
C	1.071441000	-0.309586000	2.063858000
H	0.562189000	-0.718218000	2.929334000
C	1.155099000	1.068105000	1.716996000
H	0.725325000	1.895677000	2.272325000
C	1.961801000	1.173972000	0.550233000
H	2.205246000	2.093279000	0.027708000
C	2.342598000	-0.127294000	0.158278000
H	2.928291000	-0.386336000	-0.717353000
C	0.271622000	-2.534769000	-3.479256000
F	-0.698543000	-3.387524000	-3.055552000
F	0.123954000	-2.369028000	-4.814558000
F	1.468338000	-3.123407000	-3.255862000
C	-0.182956000	2.501447000	-3.511973000
C	-0.285959000	2.522344000	-4.918277000
C	-0.194857000	3.724261000	-2.809580000
H	-0.276088000	1.599520000	-5.493694000
H	-0.113974000	3.712306000	-1.724767000
C	-0.398175000	3.730829000	-5.595452000
C	-0.305553000	4.928491000	-3.491701000
H	-0.475727000	3.736511000	-6.680844000
H	-0.312425000	5.867249000	-2.940387000
C	-0.407461000	4.934608000	-4.886197000
H	-0.493352000	5.879315000	-5.421180000

16. [Cp_2Ti(indolato)]$^+$ (complex B8)

Ti	-0.160855000	-0.042755000	-0.052162000
O	-0.380706000	1.263581000	-1.510926000
O	-0.258860000	-1.470061000	-1.445250000
C	0.064417000	2.492511000	-3.494593000
H	-0.394801000	3.283115000	-2.896742000
H	-0.462444000	2.400130000	-4.451886000
H	1.100429000	2.778020000	-3.723134000

C	0.037114000	1.201347000	-2.743215000
C	0.390063000	-0.015672000	-3.321374000
C	0.190459000	-1.274692000	-2.639529000
C	-2.440501000	-0.838420000	0.102759000
H	-2.826906000	-1.485704000	-0.675003000
C	-2.491853000	0.568505000	0.111011000
H	-2.925609000	1.195458000	-0.658337000
C	-1.820876000	1.027558000	1.274674000
H	-1.687730000	2.063817000	1.566521000
C	-1.381727000	-0.108227000	1.999372000
H	-0.872259000	-0.095596000	2.954523000
C	-1.736268000	-1.263011000	1.259736000
H	-1.525585000	-2.290623000	1.536993000
C	2.007297000	-1.051172000	0.263484000
H	2.172568000	-2.076527000	-0.047019000
C	1.521342000	-0.640599000	1.523612000
H	1.287310000	-1.291084000	2.358121000
C	1.431135000	0.782775000	1.514017000
H	1.113924000	1.409201000	2.339352000
C	1.858454000	1.234363000	0.247249000
H	1.888630000	2.267651000	-0.079236000
C	2.208124000	0.102897000	-0.530467000
H	2.566682000	0.118937000	-1.552678000
N	0.475268000	-2.293204000	-3.487087000
C	0.827870000	-0.352851000	-4.664309000
C	0.876240000	-1.767280000	-4.729954000
C	1.196363000	0.390586000	-5.780107000
H	1.193036000	1.476176000	-5.793678000
C	1.603198000	-0.280759000	-6.942546000
C	1.276567000	-2.439120000	-5.870802000
H	1.294353000	-3.524665000	-5.917857000
C	1.643251000	-1.683936000	-6.984878000
H	1.955962000	-2.198821000	-7.887866000
O	1.943927000	0.523291000	-7.982117000
C	2.367774000	-0.091916000	-9.199764000
H	3.276063000	-0.690880000	-9.046997000
H	1.574048000	-0.722266000	-9.623618000
H	2.584881000	0.729061000	-9.885521000
C	0.359078000	-3.711987000	-3.168046000
H	0.134627000	-3.765825000	-2.095986000
H	1.338653000	-4.182880000	-3.326680000
C	-0.695977000	-4.438231000	-3.973929000
C	-0.397157000	-5.676058000	-4.545720000
C	-1.980305000	-3.909223000	-4.127891000
C	-1.367702000	-6.380442000	-5.256337000
C	-2.948287000	-4.607893000	-4.842633000
C	-2.644917000	-5.846729000	-5.406784000
H	0.602138000	-6.097347000	-4.433642000
H	-2.226390000	-2.940482000	-3.693260000
H	-1.122221000	-7.344911000	-5.696433000
H	-3.944405000	-4.185707000	-4.960560000

H	-3.402762000	-6.392401000	-5.965054000

[i] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Physical Review B: Condensed Matter 46 (1992) 6671-6687. DOI: 10.1103/PhysRevB.46.6671

[ii] The ADF program system was obtained from Scientific Computing and Modeling, Amsterdam (http://www.scm.com/). For a description of the methods used in ADF, see: G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C.F. Guerra, S.J.A. van Gisbergen, J.G. Snijders, T.J. Ziegler, Chemistry with ADF, Journal of Computational Chemistry 22 (2001) 931-967. DOI: 10.1002/jcc.1056.