ELECTRONIC SUPPLEMENTARY INFORMATION

Solution Dynamics of Agostic Interactions in T-Shaped Pt(II) Complexes from Ab Initio Molecular Dynamics Simulations

Manuel A. Ortuño,[a] Pietro Vidossich,*[a] Gregori Ujaque,[a] Salvador Conejero[b] and Agustí Lledós*[a]

[a] *Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain.*
[b] *Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica, CSIC and Universidad de Sevilla, Avda. Américo Vespucio 49, 41092, Sevilla, Spain.*

I. Ab initio molecular dynamics basics

Ab initio molecular dynamics (AIMD) is a molecular simulation technique designed to investigate electronic and nuclear rearrangements in complex systems. Atomic positions, treated as classical coordinates, are evolved in time according to Newton's equations of motion. At variance with classical molecular dynamics, which is based on empirical potentials, the ab initio version computes interatomic forces from a quantum chemical method (here, Density Functional Theory). AIMD is free of empirical parameters and does not assume any connectivity among the atoms, thus being suitable to investigate chemical reactions where bonds break and new ones form. In this work, the Born-

Oppenheimer form of AIMD was used, in which the electronic ground state of the system is computed for each configuration visited during the dynamics. The Car-Parrinello form is an alternative approach to AIMD. A comprehensive account of AIMD and of its numerous successful applications can be found in the literature.1

II. Computational details

Ab initio molecular dynamics (AIMD) simulations were performed according to the Born-Oppenheimer approach using the CP2K program package.2 Simulations were carried out at the DFT level by means of the PBE exchange-correlation functional.3 Simulations of complexes **1**, **7** and **6** were run in explicit dichloromethane solvent. An additional simulation of **6** in explicit solvent was performed with the PBE functional supplemented by the dispersion correction of Grimme et al.4 AIMD were performed at constant volume and temperature (300 K) through a velocity rescaling thermostat which guarantees canonical sampling.5 The Quick-step algorithm6 was used to solve the electronic structure problem using a double-zeta plus polarization (DZVP) basis set7 to represent the orbitals and plane waves (up to 300 Ry) for the electron density. Core electrons were described using pseudopotentials.8 Wave function optimization was achieved through the orbital transformation method using electronic gradients of $5 \cdot 10^{-7}$ as convergence criterion.9

About 1000 dichloromethane molecules were included in a cubic box of 47.482 Å edge to reproduce the experimental density. The simulation cell was treated under periodic boundary conditions. The Poisson-solver developed by Martyna and Tuckerman was used to remove the periodicity intrinsic in the plane wave representation.[10] A counteranion $[SbF_6]^-$ was included in the model to neutralize the simulation cell. The organometallic complexes were treated quantum mechanically (QM) whereas the solvent molecules and the counteranion were described using molecular mechanics (MM). The QM box was cubic of 25 Å edge for each complex. Dichloromethane (DCM) was described by the fully flexible all-atom potential developed by Kollman and co-workers.[11] The force field was shown to reproduce the macroscopic properties of liquid DCM, including density, heat of vaporization and diffusion constant, in good agreement with experimental data. Suitable parameters were particularly calculated for the counteranion using the method developed by Seminario.[12]

Initially, each model underwent 1 ns classical MD simulation keeping the organometallic complex fixed and the final conformation was used to start the QM/MM MD simulation.[13] About 15 ps were simulated.

III. Conformation event on the cyclometalated ring of **7**

As shown in Fig. S1, a conformational event in the cyclometalated ring was detected by monitoring the C_{ItBu}–Pt–C*–C dihedral angle (where C* stands for the cyclometalated carbon atom). C_{ItBu}, Pt and C* atoms form a plane and the methylene CH_2 (red point) is located under it. After 10 ps, the latter group is found above such plane. The evolution of the dihedral angle from ca. −25 to +25 degrees indicates this conformational event.

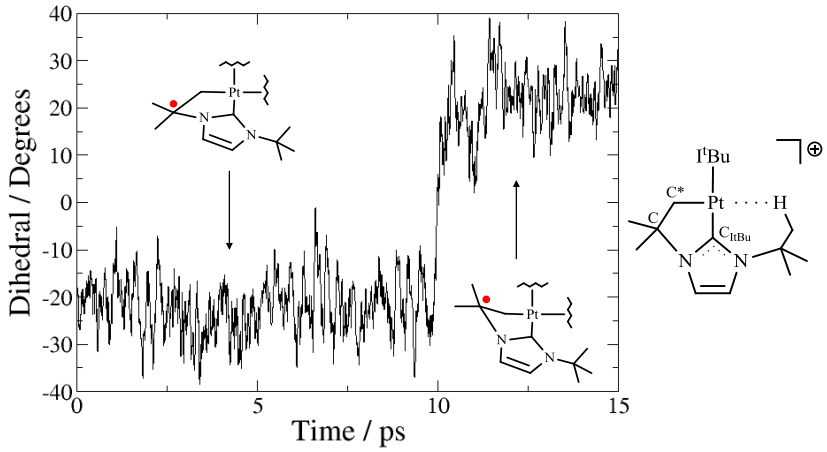

Fig. S1. C_{ItBu}–Pt–C*–C dihedral angle along the simulation of complex **7** in solution.

IV. Radial distribution functions of **7** and **6**

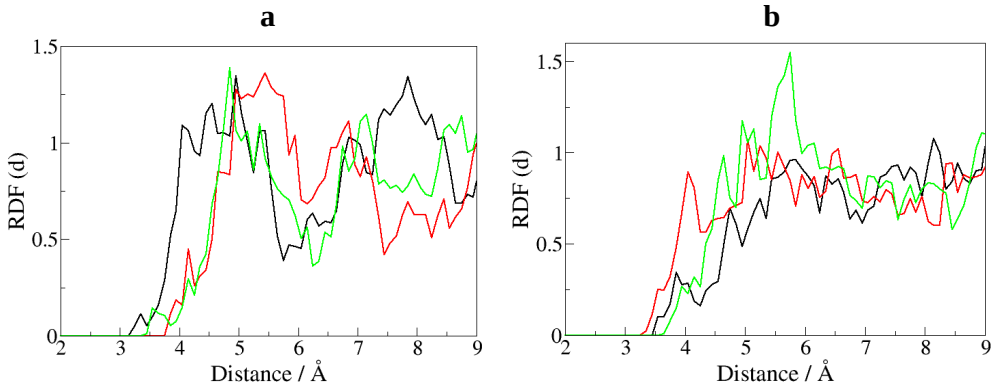

Fig. S2. C···C_{DCM} radial distribution functions (RDFs) of C54 (black line), C58 (red line) and C62 (green line) atoms in complex **7** during the first 6 ps (panel a) and the last 5 ps (panel b).

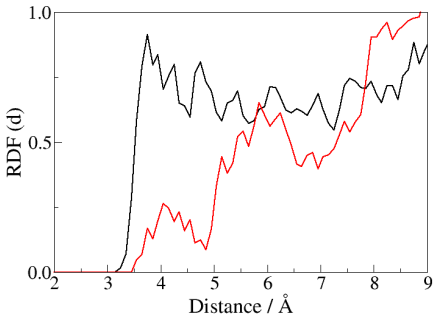

Fig. S3. C···C_{DCM} radial distribution functions (RDFs) of C83 (black line) and C87 (red line) atoms in complex **6** during the 8-15 ps interval using PBE-D3 functional.

V. Interaction energy between **6** and one dichloromethane molecule

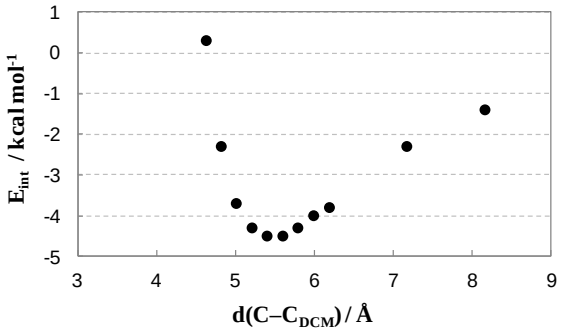

Figure S4. Interaction energy (kcal mol^{-1}) between complex **6** and one DCM molecule according to the C···C_{DCM} distance.

VI. Distance scatter plots of **1**, **7** and **6**

Figure S5 displays scatter plots representing Pt–L_{trans} versus Pt–$C_{agostic}$ distances for each model along the entire simulations in solution. For complex **1** (panel a), the graph does not provide additional information; since the geometry hardly changes during the simulation, only one maximum is observed at ca. 2.3 Å and 2.4 Å for d(Pt–P_{trans}) and d(Pt–C_{ago}), respectively. For complex **7** (panel b), two maxima can be distinguished describing the two possible situations of the methyl group (agostic at 3.1 Å and non-agostic at 5.0 Å). However, the average d(Pt–C*$_{ItBu}$), 2.0–2.1 Å, is not altered since the agostic interaction is always present (though it is formed through other methyl group). For complex **6** (panel c), one maximum is detected at 2.0–2.1 Å and 3.1 Å for d(Pt–C*$_{IPr}$) and d(Pt–C87), respectively. When the agostic interaction is lost, the Pt–C87 distance appears at 4.0–4.5 Å but the Pt–C*$_{IPr}$ bond distance is not significantly affected.

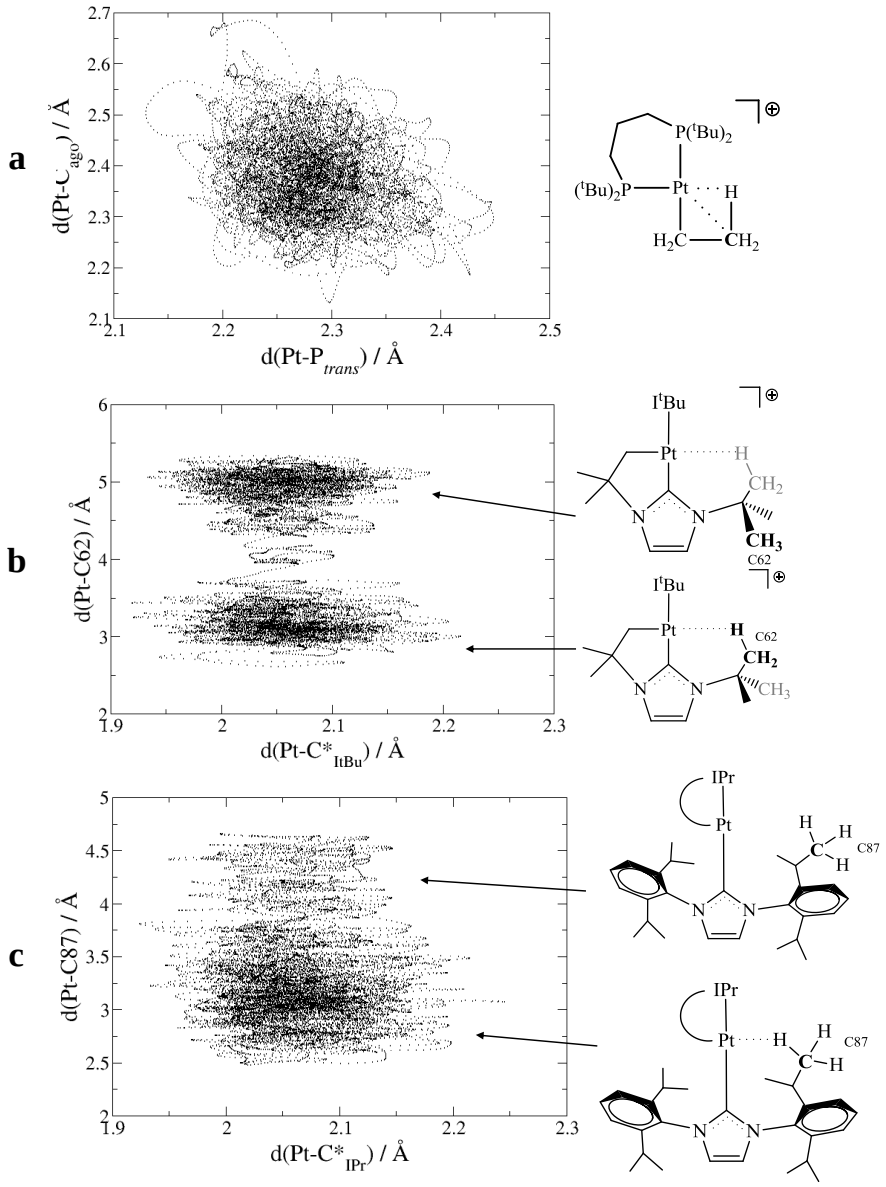

Figure S5. Correlation plots between Pt–L$_{trans}$ and Pt···C$_{agostic}$ distances for complexes **1** (panel a) and **6** (panel b) using PBE and **7** (panel c) using PBE-D3.

VII. Cartesian coordinates of gas-phase geometries of **1**, **7** and **6**

1

Pt	-0.0226196055	-0.1242525850	0.8999004588
C	-1.0598343928	-0.2409714772	2.7234700555
H	-1.6903568904	-1.1172193572	2.8698242660
H	-1.5738669899	0.6809997948	3.0014391893
C	0.3432840355	-0.3675838494	3.2248936093
H	0.5892769732	-1.3369604563	3.6726988004
H	1.1597081702	-0.3364423923	2.3394269713
H	0.7012762242	0.4682160152	3.8366144452
P	1.8262926428	0.0459036830	-0.5667537810
P	-1.7457407796	0.0545736615	-0.5731808260
C	-1.1724059639	0.1817341662	-2.3262243997
H	-2.0286674231	0.5240342122	-2.9208804534
H	-0.9620534626	-0.8419944786	-2.6584597080
C	1.3960957413	0.3482059152	-2.3424950193
H	2.2254845430	0.9028785034	-2.8038431912

H	1.3785556883	-0.6328465667	-2.8364557036
C	0.0587966408	1.0602638754	-2.6118790236
H	0.0366063546	1.3258498217	-3.6805624800
H	0.0038048790	2.0099680118	-2.0682979863
C	2.8193943615	-1.5807510543	-0.6359685571
C	-2.7540608422	1.6636862256	-0.2705258529
C	-2.8725520959	-1.4969860813	-0.6536057341
C	2.9472145078	1.5230232947	-0.1086517964
C	3.7908378292	-1.6771129135	-1.8307167809
H	4.2589523928	-2.6730661752	-1.8144946445
H	3.2837263772	-1.5802430902	-2.7984498971
H	4.5967498561	-0.9379533995	-1.7901214275
C	3.5979352565	-1.7924427560	0.6765940687
H	2.9491428527	-1.7173817446	1.5600493193
H	4.0262459128	-2.8062180230	0.6751220774
H	4.4296464447	-1.0875586354	0.7933418915
C	1.7709198943	-2.7064362077	-0.7614305214
H	1.1678270684	-2.6195763465	-1.6750255387
H	2.2882558947	-3.6767935416	-0.8022114785
H	1.0886768464	-2.7135234904	0.0995755549
C	4.3164229108	1.4907469966	-0.8133307892
H	4.8360361573	2.4397342372	-0.6109452380
H	4.9591255470	0.6840483081	-0.4416966886
H	4.2323706510	1.3956436681	-1.9038460283
C	2.2067113569	2.8115992822	-0.5262529476
H	1.2098748341	2.8729674527	-0.0701013436
H	2.7867081444	3.6779272467	-0.1738021569
H	2.1079640518	2.9096856204	-1.6142020576
C	3.1533104716	1.5785695619	1.4182374419
H	3.8057475841	2.4322760142	1.6568828305
H	2.2012347276	1.7374504668	1.9412996652
H	3.6306291694	0.6788264902	1.8231108103
C	-1.7784820850	2.7499505886	0.2337887848
H	-1.2524818325	2.4307939155	1.1429953581
H	-1.0294282757	3.0213555771	-0.5197831197
H	-2.3550698328	3.6580170808	0.4668566489
C	-3.8237413735	1.4472632658	0.8181038684
H	-4.2756648831	2.4222588310	1.0549932070
H	-4.6335043305	0.7847469949	0.4907851908
H	-3.3980034675	1.0486519820	1.7468078966
C	-3.4315620448	2.1816269922	-1.5570415306
H	-4.1081297271	1.4516811846	-2.0166251660
H	-4.0334539519	3.0651147745	-1.2947420230
H	-2.7018810827	2.5049700911	-2.3096978445
C	-4.0704837103	-1.2724343088	-1.6000053040
H	-3.7636705785	-0.9786864773	-2.6118707549
H	-4.6186245333	-2.2224694420	-1.6931761826
H	-4.7783790431	-0.5263303590	-1.2202499047
C	-2.0283311650	-2.6770313154	-1.1868775098
H	-2.6211305624	-3.5976396425	-1.0802447774
H	-1.7727639906	-2.5855223694	-2.2490123564
H	-1.1053994851	-2.8079399346	-0.6083416708
C	-3.3808089499	-1.9159220027	0.7397078885
H	-2.5528967108	-2.2592954668	1.3700085193
H	-3.9213328675	-1.1272385595	1.2712080540
H	-4.0717059781	-2.7625434336	0.6110630663

7

Pt	0.0811700168	-0.0097005306	0.0095585514
N	-2.8367844359	-0.7901300164	-0.7383408846
N	-2.8210130387	1.0949363241	0.3688460900
N	3.1001496022	0.4500199089	-0.6327463962
N	2.6451747617	-0.9041409998	1.0118555429
C	-1.9871063498	0.0944061041	-0.0976904967
C	-4.1484023262	-0.3545424018	-0.6487146493
C	-4.1387343427	0.8176880078	0.0400660938
C	2.0660525814	-0.1143179789	0.0627793124
C	4.0273277691	-0.8440653458	0.9282067325
C	4.3130386967	0.0116461076	-0.0966769131
H	-4.9812590719	-0.8887126253	-1.0770719643
H	-4.9638050980	1.4588321287	0.3049869270
H	4.6881594002	-1.3953641395	1.5830929305
H	5.2709135707	0.3300973254	-0.4816277649

C	1.7426239771	-1.7132922522	1.8642266542
C	0.3725799242	-0.9827138073	1.7922650482
H	-0.4504099636	-1.6829476677	1.9769061487
H	0.3451309471	-0.1840684279	2.5459432450
C	1.6744960323	-3.1403187732	1.2977828890
H	2.6621782624	-3.6195122956	1.3257431095
H	0.9864354177	-3.7502666411	1.8985284170
H	1.3234832474	-3.1322451005	0.2584366288
C	2.2432563817	-1.7299492357	3.3163770361
H	1.5118895269	-2.2510539271	3.9494542367
H	3.1966274486	-2.2684980344	3.4084414410
H	2.3735229678	-0.7117499169	3.7050052131
C	-2.4267529195	-2.0489772736	-1.4728241320
C	-2.4125469686	2.3196662668	1.1584480115
C	-1.2896233841	3.0560018730	0.4133031101
H	-1.0268411731	3.9684395204	0.9645606680
H	-0.3895680796	2.4217518309	0.3466849079
H	-1.6037717211	3.3424164900	-0.5983156012
C	-1.8503315474	-3.0520898656	-0.4637785500
H	-0.9467245940	-2.6490164204	0.0057622622
H	-2.5834532452	-3.2920382270	0.3167786180
H	-1.5863494220	-3.9827644831	-0.9833516547
C	-1.3929712560	-1.6834286879	-2.5493753387
H	-1.7929717062	-0.9375344063	-3.2475011672
H	-0.4767724488	-1.2861078627	-2.0806458026
H	-1.1240961520	-2.5825459911	-3.1193924436
C	-3.6553118288	-2.6740204334	-2.1507097853
H	-3.3234672665	-3.5694614053	-2.6927963099
H	-4.4127779356	-2.9975530052	-1.4247270749
H	-4.1176893653	-1.9998285784	-2.8834505262
C	-1.9591956066	1.8791187008	2.5580560244
H	-2.7567289259	1.3315634140	3.0760917378
H	-1.0737618972	1.2389584542	2.4972090416
H	-1.7064815794	2.7644185148	3.1564760196
C	-3.6167082175	3.2646277929	1.2942042478
H	-3.2807229680	4.1682746433	1.8197252080
H	-4.0123130501	3.5777960377	0.3191215669
H	-4.4277810495	2.8274611876	1.8911978740
C	2.9525659850	1.4876872159	-1.7025508513
C	4.0741184998	1.3069922188	-2.7388990942
H	5.0632266058	1.5284931447	-2.3175381195
H	4.0835893531	0.2886874618	-3.1484043191
H	3.9152356815	2.0097562693	-3.5677397113
C	3.0404877089	2.8736950846	-1.0409805776
H	2.9481120556	3.6607644043	-1.8014024901
H	2.2388232709	3.0058757230	-0.3027402814
H	4.0037127083	3.0050162033	-0.5313797458
C	1.5940150725	1.2977470913	-2.3944972409
H	1.5038642092	0.3052652381	-2.8506835255
H	0.7535108717	1.4529804869	-1.6819699485
H	1.4739360704	2.0560627823	-3.1793683069

6 PBE

Pt	0.0592961570	0.0024556109	-0.0312889490
N	-1.0262382914	-2.8514950113	0.6567667900
N	0.9408271214	-2.4935381115	1.4779431425
N	-0.7623546525	2.9514637636	-0.6383531328
N	1.2125533710	2.4656608937	-1.3798904521
C	-0.0271717251	-1.9047017750	0.6979071313
C	-0.6891020408	-3.9732107707	1.4089741053
C	0.5484388899	-3.7499994927	1.9241938974
C	-2.3399984714	-2.7118625401	0.0617591883
C	-3.3530848340	-2.0873520946	0.8198955921
C	-4.6379869839	-2.0417100525	0.2587919437
C	-4.9037383981	-2.6076787673	-0.9867172584
C	-3.8867941504	-3.2414694930	-1.6998604605
C	-2.5809906078	-3.3141364732	-1.1928887830
C	2.2205616957	-1.9009341639	1.7921061862
C	3.3708828128	-2.3787079382	1.1311945122
C	4.5960177260	-1.7829147034	1.4705455073
C	4.6661958033	-0.7653056922	2.4193767885
C	3.5126861006	-0.3345517568	3.0755394555
C	2.2641567225	-0.9002626617	2.7851454686

C	0.1574241663	1.9245284549	-0.6846823725
C	0.9468487408	3.7707258547	-1.7808296706
C	-0.2912206537	4.0742214657	-1.3139807372
C	-2.1172786557	2.9131964581	-0.1154808736
C	-2.3838493265	3.4999619012	1.1437917918
C	-3.7231055099	3.5618287223	1.5547809710
C	-4.7495703359	3.0655569624	0.7528046932
C	-4.4570478510	2.4943569811	-0.4826636349
C	-3.1380548342	2.4116014189	-0.9526834744
C	2.3919408774	1.7401364006	-1.7788094087
C	2.2128469426	0.6446230397	-2.6532052185
C	3.3624067650	-0.0029685399	-3.1182323710
C	4.6341804220	0.4182152093	-2.7194737048
C	4.7763469023	1.4871795964	-1.8388219782
C	3.6571684782	2.1766734596	-1.3421975116
C	-3.1255070410	-1.5353789766	2.2207730112
C	-3.8154536662	-2.4229536979	3.2786103642
C	-3.5933916628	-0.0746952118	2.3482222773
C	-1.5044428653	-4.0877796616	-1.9443106080
C	-1.5035451188	-3.8086720057	-3.4582305546
C	-1.6599754787	-5.6023661105	-1.6834431569
C	3.3292756948	-3.5211653929	0.1248256132
C	4.0654003946	-3.1816367847	-1.1843331154
C	3.9041707270	-4.8126618008	0.7456295862
C	1.0119473746	-0.4496408355	3.5264576720
H	-0.2630893003	0.4378060855	1.9256742959
C	1.2808610384	-0.0972648182	5.0042413531
H	1.8177867250	-0.9046593733	5.5192135589
H	0.3301892549	0.0685913383	5.5293461362
H	1.8718484884	0.8216627542	5.1109257611
C	0.3396489053	0.7494814007	2.8293047110
H	1.0678618392	1.5118537452	2.5322981755
H	-0.4120576291	1.2176283659	3.4794113837
C	-2.8709581515	1.8658610654	-2.3492212047
C	-3.3376475382	2.8705257430	-3.4252798215
H	-4.4225964201	3.0323812948	-3.3691812933
H	-3.1104184267	2.4895663372	-4.4306529374
H	-2.8504275561	3.8483482126	-3.3147110016
C	-3.5187626305	0.4874618228	-2.5739171228
C	-1.2911315815	4.0909955439	2.0273405554
C	-1.5575830737	3.8855895811	3.5314805505
C	-1.1003391605	5.5987985361	1.7500922596
C	0.8152503304	0.1907533575	-3.0404779999
H	0.1934038526	1.0906765320	-3.1438473412
H	1.2409612648	-1.5344324841	-4.3458412932
C	0.1849369331	-0.7113207964	-1.9593288298
H	0.7629984418	-1.6420470879	-1.8907633184
H	-0.8507743833	-0.9601617705	-2.2309214708
C	0.7562722032	-0.5501820860	-4.3924811209
H	1.2420879342	0.0306921501	-5.1885242879
H	-0.2888362492	-0.7181434651	-4.6852562016
C	3.8494597189	3.3311356772	-0.3670582614
C	4.6129183907	2.8827251069	0.8963201430
C	4.5589819501	4.5257348270	-1.0359698115
H	-1.3681529257	-4.8074129503	1.5150071745
H	1.1788868761	-4.3541820252	2.5613924702
H	-5.4429557430	-1.5656185355	0.8147625103
H	-5.9095135735	-2.5644100154	-1.3998448270
H	-4.1110221095	-3.6951376792	-2.6628422756
H	5.5066335114	-2.1237865656	0.9823045036
H	5.6266865097	-0.3151030318	2.6627060358
H	3.5886559155	0.4402701859	3.8349189820
H	1.6497032414	4.3433398390	-2.3691408152
H	-0.8912701015	4.9669645214	-1.4155423675
H	-3.9661043379	4.0078805586	2.5161910687
H	-5.7815952237	3.1293586570	1.0920732386
H	-5.2656165409	2.1180527856	-1.1058198183
H	3.2676275856	-0.8383448559	-3.8077751147
H	5.5163170181	-0.0946362417	-3.0985477494
H	5.7720620833	1.7968770339	-1.5273239301
H	-2.0473742693	-1.5555664028	2.4209328115
H	-3.6205605767	-2.0377489359	4.2892633469
H	-3.4646986967	-3.4627497995	3.2372602732
H	-4.9041348528	-2.4349022673	3.1338990309
H	-3.1061704260	0.5728795384	1.6075885197
H	-3.3668608063	0.3110067946	3.3521871466

H	-4.6782011457	0.0171701062	2.2079601958
H	-0.5308104468	-3.7732828942	-1.5470025710
H	-2.4021256040	-4.2069830946	-3.9471074780
H	-0.6402412061	-4.2966253470	-3.9310193199
H	-1.4503112411	-2.7344375460	-3.6760886296
H	-1.5995324937	-5.8458924524	-0.6150587259
H	-0.8787242590	-6.1767288760	-2.2016064540
H	-2.6314904815	-5.9632446271	-2.0470883605
H	2.2780159682	-3.7083271143	-0.1273793113
H	3.6822254214	-2.2569926135	-1.6336921728
H	3.9446051226	-4.0002951295	-1.9068128043
H	5.1434260854	-3.0529354276	-1.0219742300
H	3.8378747585	-5.6455591763	0.0324154705
H	3.3733512638	-5.1057789224	1.6611994119
H	4.9626662505	-4.6827083783	1.0089157939
H	0.3010516846	-1.2868194031	3.5176609883
H	-1.7877571717	1.7381654746	-2.4566274115
H	-3.2059393748	-0.2354912238	-1.8097783953
H	-3.2396540275	0.0947691373	-3.5614281907
H	-4.6148350346	0.5437612202	-2.5510454316
H	-0.3524780848	3.5797661847	1.7741960557
H	-2.3636176861	4.5378307484	3.8927786577
H	-0.6601932011	4.1417075417	4.1110902158
H	-1.8393794573	2.8512149942	3.7673746042
H	-0.8155181224	5.7988032483	0.7103183584
H	-0.3140787308	6.0146963742	2.3957122288
H	-2.0241709278	6.1574249341	1.9550691754
H	2.8569476961	3.6675680285	-0.0440806141
H	4.1118963956	2.0405006108	1.3914611854
H	4.6861453685	3.7154674246	1.6092841060
H	5.6370366453	2.5674689327	0.6578572206
H	5.5700494210	4.2516172296	-1.3656442873
H	4.6563134472	5.3610725772	-0.3293591825
H	4.0162320394	4.8872244374	-1.9199901964

6 PBE-D3

Pt	0.0541503243	-0.0335634616	-0.0266169682
N	-1.0258672385	-2.8706802316	0.6496615995
N	0.9312870301	-2.5025372250	1.4843571621
N	-0.7603819753	2.8881484672	-0.6387281400
N	1.2093358759	2.4048059521	-1.3839419516
C	-0.0310855301	-1.9275276022	0.6957180801
C	-0.6937605705	-3.9888603918	1.4112519188
C	0.5409660440	-3.7592585802	1.9353553005
C	-2.3284611953	-2.6949641862	0.0455615149
C	-3.3184772655	-2.0335828821	0.7986324547
C	-4.5990040355	-1.9398475920	0.2338858094
C	-4.8751196015	-2.4915668152	-1.0165048012
C	-3.8721867062	-3.1410322057	-1.7371055798
C	-2.5728883123	-3.2596401428	-1.2226257292
C	2.1926906734	-1.8733668789	1.7883613850
C	3.3394235399	-2.3066765352	1.0996596190
C	4.5486977706	-1.6654859953	1.4047465563
C	4.6039859554	-0.6518447967	2.3595822232
C	3.4487179249	-0.2577652128	3.0388114497
C	2.2145624737	-0.8623383116	2.7688868301
C	0.1615720763	1.8698910370	-0.6797809829
C	0.9375386157	3.7043063771	-1.7996712898
C	-0.3006779776	4.0070702691	-1.3302422805
C	-2.1088538231	2.8332856802	-0.1122167509
C	-2.3772108482	3.3996942484	1.1526710660
C	-3.7169557022	3.4485348545	1.5611396820
C	-4.7380794582	2.9511738358	0.7513204901
C	-4.4397689925	2.3835180824	-0.4846273112
C	-3.1183168054	2.3194720358	-0.9493610648
C	2.3842218476	1.6720573433	-1.7722698560
C	2.2069605995	0.5861880886	-2.6558081273
C	3.3568002695	-0.0637734061	-3.1136642434
C	4.6253254700	0.3426214685	-2.6869211965
C	4.7623697175	1.3976856852	-1.7889900350
C	3.6407801001	2.0960856670	-1.3125627458
C	-3.0530149062	-1.4839709918	2.1914346086
C	-3.7796963373	-2.3311931970	3.2550171990

C	-3.4266861015	0.0030764476	2.2987877519
C	-1.5018625656	-4.0308998093	-1.9803137165
C	-1.5010652874	-3.7443031804	-3.4928294717
C	-1.6652823688	-5.5436149009	-1.7253728750
C	3.2997788188	-3.4512575693	0.1009665616
C	3.9963646819	-3.1021989491	-1.2239484933
C	3.9043677355	-4.7232817888	0.7310001271
C	0.9487231360	-0.4288650113	3.4939027971
H	-0.3365761043	0.4294158872	1.8794070044
C	1.1965200355	-0.0659676871	4.9712226325
H	1.7324311237	-0.8689240915	5.4938840784
H	0.2385421090	0.0976825742	5.4828672326
H	1.7819017534	0.8568216727	5.0792274118
C	0.2744155800	0.7552175127	2.7759132344
H	0.9981357089	1.5180352648	2.4687612837
H	-0.4862846002	1.2275357417	3.4112962367
C	-2.8252785814	1.7654958174	-2.3328066542
C	-3.3195751943	2.7389221467	-3.4226364657
H	-4.4082807781	2.8735551889	-3.3705367124
H	-3.0761102429	2.3537128893	-4.4221674073
H	-2.8571801290	3.7300251510	-3.3196334539
C	-3.4135958662	0.3575647767	-2.5158610720
C	-1.2771826814	3.9585987348	2.0431687114
C	-1.5759803535	3.7778794251	3.5434431793
C	-1.0166538324	5.4515634239	1.7535970063
C	0.8082999504	0.1459104631	-3.0445031723
H	0.1923964682	1.0503354652	-3.1468184992
H	1.2162680977	-1.5861496472	-4.3432269732
C	0.1809970742	-0.7511138672	-1.9555996223
H	0.7611604554	-1.6816787852	-1.8893545502
H	-0.8547029547	-1.0028349047	-2.2239385992
C	0.7437275678	-0.5961069159	-4.3931003689
H	1.2386536819	-0.0216389994	-5.1874777250
H	-0.3022952988	-0.7508702860	-4.6883866030
C	3.8145033692	3.2547194661	-0.3443979002
C	4.5343689252	2.8056358004	0.9418583744
C	4.5493654956	4.4328184248	-1.0155567833
H	-1.3710762419	-4.8242874631	1.5200412865
H	1.1700295112	-4.3592174885	2.5782045680
H	-5.3882705419	-1.4349930214	0.7871996886
H	-5.8760878378	-2.4117823897	-1.4360448326
H	-4.0994906665	-3.5663455461	-2.7119011330
H	5.4565256652	-1.9699662694	0.8886804525
H	5.5527998432	-0.1660872308	2.5800990529
H	3.5119081302	0.5251801186	3.7910311429
H	1.6416988354	4.2745878155	-2.3890845746
H	-0.9090320784	4.8936075974	-1.4385229809
H	-3.9645057034	3.8812244338	2.5271374438
H	-5.7709623293	3.0031276993	1.0902212427
H	-5.2408910625	1.9960832759	-1.1106741588
H	3.2655953636	-0.8895507570	-3.8149316475
H	5.5093532905	-0.1744147931	-3.0551769000
H	5.7542415781	1.6963794105	-1.4560666264
H	-1.9769295322	-1.5609021997	2.3857900644
H	-3.5586161069	-1.9565815910	4.2638577824
H	-3.4736493666	-3.3852799765	3.2098979124
H	-4.8682927319	-2.2955459638	3.1150613278
H	-2.9126263789	0.5978946592	1.5320944258
H	-3.1505500335	0.3967453028	3.2867437240
H	-4.5049374122	0.1646651193	2.1748655517
H	-0.5264148019	-3.7216031832	-1.5829377518
H	-2.3947075462	-4.1491670054	-3.9856568701
H	-0.6314077869	-4.2214209201	-3.9647311002
H	-1.4551492591	-2.6685981167	-3.7044179087
H	-1.6092740702	-5.7878708792	-0.6569042990
H	-0.8841130090	-6.1169976525	-2.2426788802
H	-2.6392820655	-5.8938068151	-2.0925578462
H	2.2481059493	-3.6584148410	-0.1324431391
H	3.5812860474	-2.1840165860	-1.6572026690
H	3.8685162715	-3.9195570116	-1.9465279149
H	5.0762230454	-2.9517024187	-1.0944169691
H	3.8436046731	-5.5690965949	0.0330355926
H	3.3863210286	-5.0068724720	1.6568412111
H	4.9623636734	-4.5693892340	0.9832087818
H	0.2468685280	-1.2732669347	3.4789678564
H	-1.7385599617	1.6745619136	-2.4355013173

H	-3.0749822045	-0.3178047481	-1.7199890845
H	-3.1057213264	-0.0637783730	-3.4828929076
H	-4.5108529424	0.3659639769	-2.5015759517
H	-0.3570341918	3.4056658060	1.8089409550
H	-2.3499974815	4.4766584228	3.8886012735
H	-0.6739098917	3.9824470164	4.1353301958
H	-1.9210614369	2.7621297634	3.7781236433
H	-0.6984921038	5.6250812457	0.7193142843
H	-0.2260725624	5.8362987290	2.4120595175
H	-1.9220283136	6.0475336730	1.9318710587
H	2.8176917205	3.6035260253	-0.0491903010
H	4.0003752730	1.9764531881	1.4241974549
H	4.6010420298	3.6403643829	1.6531817416
H	5.5588258738	2.4680336813	0.7362606819
H	5.5654262702	4.1448415410	-1.3180625614
H	4.6346036181	5.2818469928	-0.3237685728
H	4.0276857029	4.7781316488	-1.9188079876

VIII. References

1. D. Marx and J. Hutter, *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods*, Cambridge University Press, Cambridge, 2009.
2. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, **167**, 103.
3. *(a)* J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; *(b)* J. P. Perdew, M. Ernzerhof and K. Burke, *J. Chem. Phys.*, 1996, **105**, 9982.
4. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
5. G. Bussi, D. Donadio and M. Parrinello, *J. Chem. Phys.*, 2007, **126**, 014101.
6. G. Lippert, J. Hutter and M. Parrinello, *Mol. Phys.*, 1997, **92**, 477.
7. J. VandeVondele and J. Hutter, *J. Chem. Phys.*, 2007, **127**, 114105.
8. *(a)* S. Goedecker, M. Teter and J. Hutter, *Phys. Rev. B*, 1996, **54**, 1703; *(b)* M. Krack, *Theor. Chem. Acc.*, 2005, **114**, 145.
9. J. VandeVondele and J. Hutter, *J. Chem. Phys.*, 2003, **118**, 4365.
10. G. J. Martyna and M. E. Tuckerman, *J. Chem. Phys.*, 1999, **110**, 2810.
11. T. Fox and P. Kollman, *J. Phys. Chem. B*, 1998, **102**, 8070.
12. J. M. Seminario, *Int. J. Quantum Chem.*, 1996, **60**, 1271.
13. T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Theory Comput.*, 2005, **1**, 1176.