Supporting Information

1,4-Shifts in a Dinuclear Ni(I) Biarylyl Complex: A Mechanistic Study of C-H Bond Activation by Monovalent Nickel

Alana L. Keen, Meghan Doster, and Samuel A. Johnson*

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Optimized coordinates and energies from DFT studies. S2-S9

(40) Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

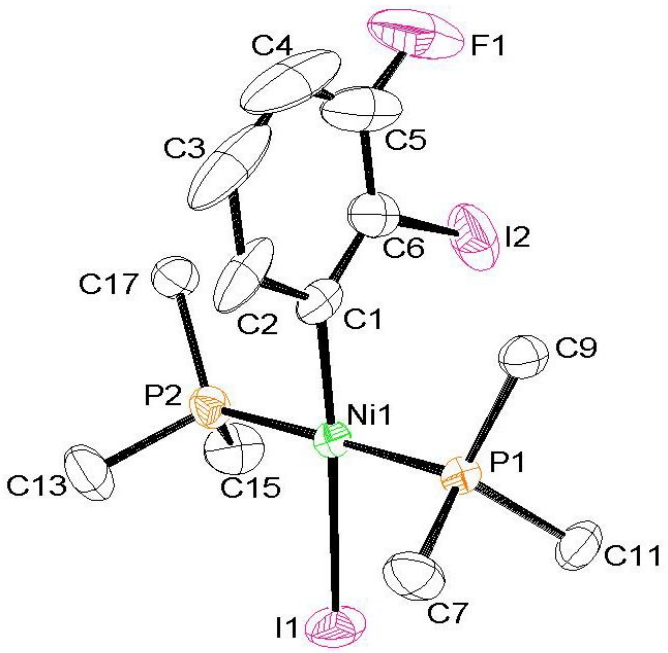
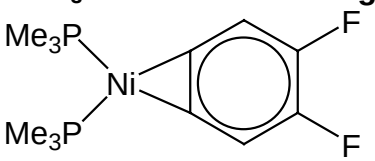


Figure 1. ORTEP depiction of **4**. Hydrogen atoms and CH_3 groups of the ethyl groups have been omitted for clarity.

DFT Calulations

PMe_3 substituted analogue of 1a in C_{2v} symmetry:



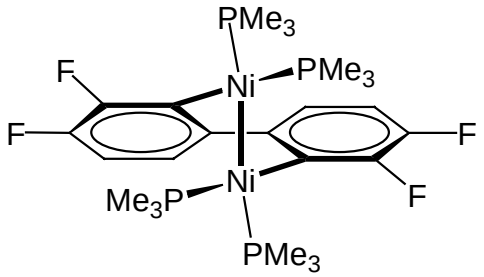
Item	Value	Threshold	Converged?
Maximum Force	0.000106	0.000450	YES
RMS Force	0.000013	0.000300	YES
Max. Displacement	0.000775	0.001800	YES
RMS Displacement	0.000251	0.001200	YES

Zero-point correction	0.291152
Thermal correction to Energy	0.314372
Thermal correction to Enthalpy	0.315316
Thermal correction to Gibbs Free Energy	0.238188
Sum of electronic and zero-point energies	-2859.97044
Sum of electronic and thermal energies	-2859.94722
Sum of electronic and thermal enthalpies	-2859.94628
Sum of electronic and thermal free energies	-2860.02341

Optimized XYZ coordinates:

37			
scf done:		-2860.2616	
C	0	-0.672807	1.246679
C	0	0.672807	1.246679
C	0	1.43493	2.411231
C	0	0.699784	3.593574
C	0	-0.699784	3.593574
C	0	-1.43493	2.411231
H	0	2.520863	2.463866
F	0	1.338313	4.790248
F	0	-1.338313	4.790248
H	0	-2.520863	2.463866
Ni	0	0	-0.510654
P	0	-1.857204	-1.698921
C	0	-1.884564	-3.55161
C	1.436976	-2.956917	-1.32918
C	-1.436976	-2.956917	-1.32918
P	0	1.857204	-1.698921
C	1.436976	2.956917	-1.32918
C	0	1.884564	-3.55161
C	-1.436976	2.956917	-1.32918
H	0	-2.907338	-3.939537
H	-0.883237	-1.36847	-3.933614
H	0.883237	-1.36847	-3.933614
H	1.366781	3.90992	-1.861491
H	1.479609	3.14446	-0.255581
H	2.365934	2.459719	-1.616178
H	0	2.907338	-3.939537
H	0.883237	1.36847	-3.933614
H	-0.883237	1.36847	-3.933614
H	-1.366781	-3.90992	-1.861491
H	-1.479609	-3.14446	-0.255581
H	-2.365934	-2.459719	-1.616178
H	1.366781	-3.90992	-1.861491
H	2.365934	-2.459719	-1.616178
H	1.479609	-3.14446	-0.255581
H	-1.366781	3.90992	-1.861491
H	-2.365934	2.459719	-1.616178
H	-1.479609	3.14446	-0.255581

$[(PMe_3)_2Ni]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}3,4\text{-}F_2C_6H_2\text{-}3',4'\text{-}F_2C_6H_2)$
PMe_3 substituted analogue of 2a in C_2 symmetry:



Item	Value	Threshold	Converged?
Maximum Force	0.000047	0.000450	YES
RMS Force	0.000005	0.000300	YES
Max. Displacement	0.000023	0.001800	YES
RMS Displacement	0.000006	0.001200	YES

Zero-point correction	0.585684
Thermal correction to Energy	0.632863
Thermal correction to Enthalpy	0.633807
Thermal correction to Gibbs Free Energy	0.508313
Sum of electronic and zero-point energies	-5720.010309
Sum of electronic and thermal energies	-5719.963131
Sum of electronic and thermal enthalpies	-5719.962187

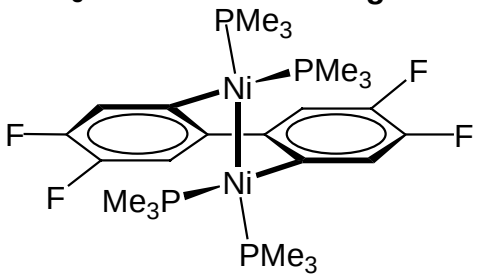
Sum of electronic and thermal free energies -5720.087681

Optimized XYZ coordinates:

scf done: -5720.595994

F	3.436268	-0.385295	0.25267
P	1.183663	1.716057	2.039984
F	4.833916	0.423732	-1.875451
C	2.732668	-0.089357	-0.893502
P	-1.183663	-1.716057	2.039984
C	3.484636	0.313908	-1.992768
Ni	0.215264	-1.160291	0.385357
P	1.009125	-3.189	-0.229395
Ni	-0.215264	1.160291	0.385357
C	1.354274	-0.238423	-0.918043
C	2.87225	0.592591	-3.201498
P	-1.009125	3.189	-0.229395
H	3.47167	0.913824	-4.045602
C	0.737923	0.061962	-2.169924
C	-1.354274	0.238423	-0.918043
C	1.482372	0.462478	-3.280808
F	-3.436268	0.385295	0.25267
C	-0.737923	-0.061962	-2.169924
C	-2.732668	0.089357	-0.893502
H	0.983587	0.701067	-4.215708
C	-1.482372	-0.462478	-3.280808
C	-3.484636	-0.313908	-1.992768
H	-0.983587	-0.701067	-4.215708
F	-4.833916	-0.423732	-1.875451
C	-2.87225	-0.592591	-3.201498
H	-3.47167	-0.913824	-4.045602
C	0.48221	2.833448	3.349883
H	0.146885	3.777325	2.917489
H	-0.380324	2.361368	3.824448
H	1.227083	3.052979	4.120293
C	2.685432	2.675442	1.533602
H	2.399297	3.552186	0.952775
H	3.257391	3.000821	2.407468
H	3.324071	2.048254	0.911897
C	1.977127	0.447498	3.132737
H	2.656156	0.917169	3.851653
H	1.212017	-0.100388	3.684037
H	2.533817	-0.259307	2.519557
C	-2.58275	3.692726	0.608653
H	-2.967859	4.634373	0.206085
H	-3.332643	2.9125	0.474595
H	-2.41265	3.813218	1.680803
C	-0.015934	4.751172	-0.060469
H	-0.58402	5.616857	-0.413517
H	0.270708	4.92973	0.977006
H	0.896463	4.672768	-0.655752
C	-1.482372	3.345866	-2.010026
H	-1.891221	4.338264	-2.220133
H	-0.603395	3.183592	-2.636731
H	-2.222685	2.590285	-2.271466
C	1.482372	-3.345866	-2.010026
H	0.603395	-3.183592	-2.636731
H	2.222685	-2.590285	-2.271466
H	1.891221	-4.338264	-2.220133
C	0.015934	-4.751172	-0.060469
H	-0.896463	-4.672768	-0.655752
H	0.58402	-5.616857	-0.413517
H	-0.270708	-4.92973	0.977006
C	-2.685432	-2.675442	1.533602
H	-3.324071	-2.048254	0.911897
H	-2.399297	-3.552186	0.952775
H	-3.257391	-3.000821	2.407468
C	-1.977127	-0.447498	3.132737
H	-2.533817	0.259307	2.519557
H	-2.656156	-0.917169	3.851653
H	-1.212017	0.100388	3.684037
C	2.58275	-3.692726	0.608653
H	2.967859	-4.634373	0.206085
H	3.332643	-2.9125	0.474595
H	2.41265	-3.813218	1.680803
C	-0.48221	-2.833448	3.349883
H	-1.227083	-3.052979	4.120293
H	-0.146885	-3.777325	2.917489
H	0.380324	-2.361368	3.824448

$[(PMe_3)_2Ni]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}4,5\text{-}F_2C_6H_2\text{-}4',5'\text{-}F_2C_6H_2)$
PMe_3 Substituted Analogue of 7a in C_2 symmetry:



Item	Value	Threshold	Converged?
Maximum Force	0.000131	0.000450	YES
RMS Force	0.000023	0.000300	YES
Max. Displacement	0.000148	0.001800	YES
RMS Displacement	0.000039	0.001200	YES

Zero-point correction	0.586328
Thermal correction to Energy	0.633516
Thermal correction to Enthalpy	0.634455
Thermal correction to Gibbs Free Energy	0.508808
Sum of electronic and zero-point energies	-5719.992422
Sum of electronic and thermal energies	-5719.945234
Sum of electronic and thermal enthalpies	-5719.944295
Sum of electronic and thermal free energies	-5720.069942

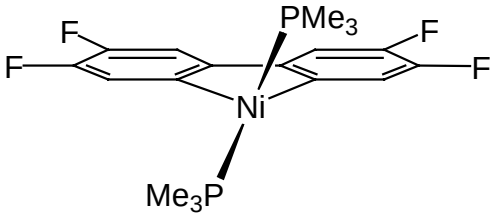
Optimized XYZ coordinates:

scf done: -5720.57875

H	3.083532	1.232961	-0.302024	C	-3.431795	-0.691167	1.71262
P	1.666522	-1.299755	-2.244357	H	-1.173026	0.372514	3.98247
F	4.761123	0.953682	1.618402	F	-4.761123	-0.953682	1.618402
C	2.610638	0.861465	0.603293	C	-2.909271	-0.262931	2.922308
P	-1.666522	1.299755	-2.244357	F	-3.728826	-0.093364	3.989431
C	3.431795	0.691167	1.71262	C	1.301123	-2.49266	-3.621442
Ni	-0.161032	1.167729	-0.598288	H	1.162251	-3.500189	-3.226168
P	0.032554	3.322735	0.052055	H	0.378488	-2.207425	-4.130585
Ni	0.161032	-1.167729	-0.598288	H	2.110926	-2.516639	-4.356472
C	1.229382	0.603012	0.662789	C	3.358038	-1.871277	-1.743522
C	2.909271	0.262931	2.922308	H	3.306919	-2.872206	-1.314199
P	-0.032554	-3.322735	0.052055	H	4.042526	-1.890551	-2.596588
F	3.728826	0.093364	3.989431	H	3.757936	-1.201756	-0.980905
C	0.723961	0.14894	1.918625	C	2.129232	0.184593	-3.256195
C	-1.229382	-0.603012	0.662789	H	2.93806	-0.044741	-3.957404
C	1.552703	-0.01248	3.030913	H	1.263026	0.529271	-3.822386
H	-3.083532	-1.232961	-0.302024	H	2.442618	0.997533	-2.600788
C	-0.723961	-0.14894	1.918625	C	-1.479042	-4.207858	-0.694648
C	-2.610638	-0.861465	0.603293	H	-1.583242	-5.220749	-0.29481
H	1.173026	-0.372514	3.98247	H	-2.393562	-3.652416	-0.481181
C	-1.552703	0.01248	3.030913	H	-1.362537	-4.268276	-1.779096
				C	1.301123	-4.592061	-0.204075

H	0.990524	-5.572066	0.169948
H	1.551026	-4.692705	-1.261707
H	2.203561	-4.289779	0.331523
C	-0.344181	-3.587341	1.854826
H	-0.488792	-4.64833	2.07767
H	0.506944	-3.216714	2.429174
H	-1.227522	-3.031002	2.166678
C	0.344181	3.587341	1.854826
H	-0.506944	3.216714	2.429174
H	1.227522	3.031002	2.166678
H	0.488792	4.64833	2.07767
C	-1.301123	4.592061	-0.204075
H	-2.203561	4.289779	0.331523
H	-0.990524	5.572066	0.169948
H	-1.551026	4.692705	-1.261707
C	-3.358038	1.871277	-1.743522
H	-3.757936	1.201756	-0.980905
H	-3.306919	2.872206	-1.314199
H	-4.042526	1.890551	-2.596588
C	-2.129232	-0.184593	-3.256195
H	-2.442618	-0.997533	-2.600788
H	-2.93806	0.044741	-3.957404
H	-1.263026	-0.529271	-3.822386
C	1.479042	4.207858	-0.694648
H	1.583242	5.220749	-0.29481
H	2.393562	3.652416	-0.481181
H	1.362537	4.268276	-1.779096
C	-1.301123	2.49266	-3.621442
H	-2.110926	2.516639	-4.356472
H	-1.162251	3.500189	-3.226168
H	-0.378488	2.207425	-4.130585

PMe_3 substituted analogue of the speculated structure of 9a in C_2 symmetry:



Item	Value	Threshold	Converged?
Maximum Force	0.000013	0.000450	YES
RMS Force	0.000004	0.000300	YES
Max. Displacement	0.001103	0.001800	YES
RMS Displacement	0.000253	0.001200	YES

Zero-point correction	0.355122
Thermal correction to Energy	0.384695
Thermal correction to Enthalpy	0.385639
Thermal correction to Gibbs Free Energy	0.293986
Sum of electronic and zero-point energies	-3289.54545
Sum of electronic and thermal energies	-3289.51588
Sum of electronic and thermal enthalpies	-3289.51493
Sum of electronic and thermal free energies	-3289.60658

Optimized XYZ coordinates:

scf done: -3289.90057

F	-2.35599	4.215363	1.514194
F	-1.947703	3.213272	4.010248
C	-1.679643	3.050164	1.664418
H	-0.965499	2.704071	-3.556224
C	-1.474019	2.540563	2.936296

H	-1.396437	2.830443	-0.421278	H	-1.957684	-2.974488	-0.615588
C	-1.192167	2.38063	0.545596	H	-1.991926	-3.719331	-2.233475
H	0.537911	3.818663	-1.219788	H	2.898498	1.617712	-3.477987
H	-2.990296	-0.598589	-2.025646	H	0.274527	-1.340303	-4.441527
H	0.618021	2.867863	-4.338639	H	0.696275	-0.947566	4.113933
H	-2.173422	0.003847	-3.468091	C	-1.37154	-3.180692	-1.511983
C	-0.034457	2.183046	-3.790093	C	2.358826	0.887922	-2.867896
C	-0.804777	1.33791	3.106922	C	0.485946	-1.183162	0.679909
H	-0.696275	0.947566	4.113933	H	-0.618021	-2.867863	-4.338639
C	1.37154	3.180692	-1.511983	C	0.804777	-1.33791	3.106922
C	-2.358826	-0.887922	-2.867896	C	0.034457	-2.183046	-3.790093
H	-2.898498	-1.617712	-3.477987	H	2.173422	-0.003847	-3.468091
H	1.991926	3.719331	-2.233475	H	-0.537911	-3.818663	-1.219788
H	-0.274527	1.340303	-4.441527	H	2.990296	0.598589	-2.025646
C	-0.485946	1.183162	0.679909	C	1.192167	-2.38063	0.545596
H	1.957684	2.974488	-0.615588	C	1.474019	-2.540563	2.936296
C	-0.326321	0.656429	1.986121	H	0.965499	-2.704071	-3.556224
P	0.769198	1.589143	-2.228272	H	1.396437	-2.830443	-0.421278
Ni	0	0	-0.762928	F	1.947703	-3.213272	4.010248
P	-0.769198	-1.589143	-2.228272	C	1.679643	-3.050164	1.664418
C	0.326321	-0.656429	1.986121	F	2.35599	-4.215363	1.514194

$Ni(PMe_3)_4$, T_d symmetry

Item	Value	Threshold	Converged?
Maximum	Force	0.000039	0.000450 YES
RMS	Force	0.000013	0.000300 YES
Maximum	Displacement	0.000641	0.001800 YES
RMS	Displacement	0.000273	0.001200 YES

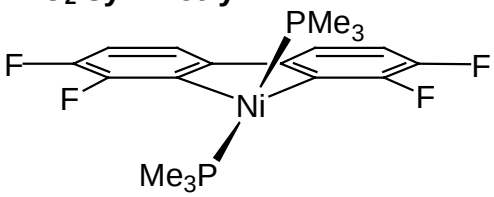
Zero-point correction	0.460709
Thermal correction to Energy	0.491087
Thermal correction to Enthalpy	0.492031
Thermal correction to Gibbs Free Energy	0.406301
Sum of electronic and zero-point energies	-3352.53621
Sum of electronic and thermal energies	-3352.50584
Sum of electronic and thermal enthalpies	-3352.50489
Sum of electronic and thermal free energies	-3352.59062

Optimized XYZ coordinates:

scf	done:	-3352.99692		C	0.47225	-2.464717	2.464717
Ni	0	0	0	C	2.464717	-2.464717	0.47225
P	-1.271962	1.271962	1.271962	C	2.464717	-0.47225	2.464717
C	-2.464717	0.47225	2.464717	P	1.271962	1.271962	-1.271962
C	-0.47225	2.464717	2.464717	C	2.464717	2.464717	-0.47225
C	-2.464717	2.464717	0.47225	C	2.464717	0.47225	-2.464717
P	1.271962	-1.271962	1.271962	C	0.47225	2.464717	-2.464717

P	-1.271962	-1.271962	-1.271962	H	3.035492	1.21263	-3.035492
C	-0.47225	-2.464717	-2.464717	H	1.919633	-0.163813	-3.165918
C	-2.464717	-2.464717	-0.47225	H	1.21263	3.035492	-3.035492
C	-2.464717	-0.47225	-2.464717	H	-0.163813	1.919633	-3.165918
H	-1.21263	3.035492	3.035492	H	-0.163813	3.165918	-1.919633
H	0.163813	1.919633	3.165918	H	-1.21263	-3.035492	-3.035492
H	0.163813	3.165918	1.919633	H	0.163813	-1.919633	-3.165918
H	-3.035492	1.21263	3.035492	H	0.163813	-3.165918	-1.919633
H	-1.919633	-0.163813	3.165918	H	-3.035492	-1.21263	-3.035492
H	-3.035492	3.035492	1.21263	H	-3.165918	0.163813	-1.919633
H	-1.919633	3.165918	-0.163813	H	-1.919633	0.163813	-3.165918
H	-3.165918	1.919633	-0.163813	H	-3.035492	-3.035492	-1.21263
H	3.035492	-1.21263	3.035492	H	-1.919633	-3.165918	0.163813
H	3.165918	0.163813	1.919633	H	1.21263	-3.035492	3.035492
H	1.919633	0.163813	3.165918	H	-0.163813	-1.919633	3.165918
H	3.035492	-3.035492	1.21263	H	-0.163813	-3.165918	1.919633
H	1.919633	-3.165918	-0.163813	H	-3.165918	-0.163813	1.919633
H	3.035492	3.035492	-1.21263	H	-3.165918	-1.919633	0.163813
H	1.919633	3.165918	0.163813	H	3.165918	-0.163813	-1.919633
H	3.165918	1.919633	0.163813	H	3.165918	-1.919633	-0.163813

In C_2 symmetry:



Item	Value	Threshold	Converged?
Maximum	Force	0.000376	0.000450 YES
RMS	Force	0.000114	0.000300 YES
Maximum	Displacement	0.001376	0.001800 YES
RMS	Displacement	0.000330	0.001200 YES

Zero-point correction	0.35563
Thermal correction to Energy	0.385056
Thermal correction to Enthalpy	0.386
Thermal correction to Gibbs Free Energy	0.296444
Sum of electronic and zero-point energies	-3289.55928
Sum of electronic and thermal energies	-3289.52985
Sum of electronic and thermal enthalpies	-3289.52891
Sum of electronic and thermal free energies	-3289.61847

Optimized XYZ coordinates:

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scf done: -3289.915138

F	0.592928	4.792698	-1.855418
H	0.553944	3.563927	-4.153107
C	0.410927	3.460068	-2.025469

H	-0.099236	3.179474	2.803753
C	0.406645	2.916606	-3.296097
F	0.273344	3.274745	0.312564
C	0.2297	2.647233	-0.907613
H	-2.144148	3.096227	0.592971
H	2.775268	0.67685	2.188628
H	-1.550967	2.828561	3.767876
H	1.713223	0.514948	3.587102
C	-0.700481	2.38403	3.243747
C	0.237442	1.537954	-3.431699
H	0.273103	1.101549	-4.424915
C	-2.581404	2.224509	1.076613
C	2.317776	-0.042299	2.870954
H	3.110936	-0.561837	3.415704
H	-3.33546	2.555093	1.796378
H	-0.088101	1.850362	3.972789
C	0.015045	1.284441	-0.998359
H	-3.063218	1.614828	0.310662
C	0.057093	0.732605	-2.305608
P	-1.270393	1.232991	1.914566
Ni	0	0	0.453845
P	1.270393	-1.232991	1.914566
C	-0.057093	-0.732605	-2.305608
H	3.063218	-1.614828	0.310662
H	3.33546	-2.555093	1.796378
H	-3.110936	0.561837	3.415704
H	0.088101	-1.850362	3.972789
H	-0.273103	-1.101549	-4.424915
C	2.581404	-2.224509	1.076613
C	-2.317776	0.042299	2.870954
C	-0.015045	-1.284441	-0.998359
H	1.550967	-2.828561	3.767876
C	-0.237442	-1.537954	-3.431699
C	0.700481	-2.38403	3.243747
H	-1.713223	-0.514948	3.587102
H	2.144148	-3.096227	0.592971
H	-2.775268	-0.67685	2.188628
C	-0.2297	-2.647233	-0.907613
C	-0.406645	-2.916606	-3.296097
H	0.099236	-3.179474	2.803753
F	-0.273344	-3.274745	0.312564
H	-0.553944	-3.563927	-4.153107
C	-0.410927	-3.460068	-2.025469
F	-0.592928	-4.792698	-1.855418