Theoretical predictions of a highly reactive non-heme Fe(IV)=O complex with a high-spin ground state

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I. Methods

Note about free energy calculations involving complexation

Due to loss of translational and rotational degrees of freedom upon complexation of the constituent reactants, free energies cannot reliably be calculated by just adding the separately calculated free energies of the constituent reactants. Therefore, we estimated the thermal contributions for the complexation by putting the metal-oxo compound and the substrate in the same system, but placing them approximately 20 Å from each other, which allows the program to keep the same number of degrees of freedom as in the complex.

However, calculating free energies including solvent effects with PCM models needs to take into account the change of standard-state concentration from ideal gas to 1 M in solution phase. The conversion factor can be expressed as

$$\Delta G^{\bullet} = \Delta G^{\circ} + RT \ln\left(\frac{Q^{\bullet}}{Q^{\circ}}\right)$$

where the open ring symbolizes the gas phase concentration and the closed ring the solution phase concentration[S1,S2]. In a simple chemical model A + B → C (as in our study), evaluation of this equation yields a correction factor of -1.89 kcal/mol that has been added to the complexation free energies. In case of one of the reactants being a solvent molecule (i.e. in our case acetonitrile), the solution phase concentration is not 1 M, but 19.17 M, which gives a correction factor of -1.75 kcal/mol. Further details can be found in references S1 and S2.

Optimization in solvent

The usual way of doing calculations is to optimize the system in gas-phase, and then do a single-point solvent calculations as this saves time and optimization in solvent usually does not change the geometry or energy beyond the existing error margins. However, in few cases, such as when the system in question is highly charged, the gas-phase optimized structure can show very different results from the one optimized in solvent due to self-interaction errors in DFT.[S3,S4] We did indeed encounter artificial results where a net hydride transfer occured from the substrate (instead of a net hydrogen atom transfer) during optimization in gas-phase, which did not occur when we optimized in solvent using the CPCM model. Consequently, we optimized all the structures in solvent. Since we were studying H-transfer reaction, we used the UFF cavity since it puts a cavity around H atoms as well and not just around the heavy atoms.

II. (Me_6TREN)Fe(IV)=O

Intra-molecular transition state imaginary frequency: 1671 cm^{-1}.

Mulliken Spin distribution.

	Fe	O	4xN	Rest
Triplet (δ, δ', π^*, -π^*'(↓))	2.77	-0.82	-0.01	0.05
Triplet (π*, π*')	1.49	0.73	-0.22	0.00
Quintet (δ, δ', π*, π*')	3.12	0.73	0.09	0.07
Quintet intra-TS[a]	3.13	0.48	-0.11	0.50

[a] Transition state for intra-molecular H-abstraction.

Key geometries in Å.

	D(Fe-O)	D(Fe-N1)	D(Fe-N2)	D(Fe-N3)	D(Fe-N4)	D(O-H)[b]	D(C-H)[c]
Triplet (δ, δ', π*, π*'(↓))	1.73	2.06	2.08	2.13	2.10	2.52	1.09
Triplet (π*, π*')	1.63	2.09	2.09	2.01	2.10	2.60	1.09
Quintet (δ, δ', π*, π*')	1.65	2.08	2.10	2.13	2.10	2.55	1.09
Quintet intra-TS[a]	1.77	2.06	2.10	2.14	2.14	1.21	1.38

[a] Transition state for intra-molecular H-abstraction. [b] The closest H to the oxygen. [c] The C-H distance for the proton in question in *b*.

Absolute energies.

	LACVP (H)[a]	LACV3P^{*+} (H)[a]	Z_0 (kcal/mol)	E(thermal) (kcal/mol)	S (cal/mol/K)
Triplet (δ, δ', π*, π*'(↓))	-892.449970	-892.837309	278.696950	290.919000	136.502000
Triplet (π*, π*')	-892.453124	-892.841778	279.837070	292.259000	138.382000
Quintet (δ, δ', π*, π*')	-892.472876	-892.864413	278.825240	291.521000	141.561000
Quintet intra-TS[b]	-892.427891	-892.814359	274.322640	286.794000	140.113000

[a] Total free energy in solution with all non electrostatic terms. [b] Transition state for intra-molecular H-abstraction.

Relative energies (in kcal/mol).

	LACVP	LACV3P^{*+}	Z_0	E(thermal)	-TS	**Total**[a]
Triplet (δ, δ', π*,π*'(↓))	14.37	+2.63	-0.13	-0.47	+1.51	**17.91**
Triplet (π*, π*')	12.39	+1.81	+1.01	-0.27	+0.95	**15.89**
Quintet (δ, δ', π*, π*')	0.00	+0.00	+0.00	+0.00	+0.00	**0.00**
Quintet intra-TS[b]	28.23	+3.18	-4.5	-0.22	+0.43	**27.11**

[a] The total column is calculated by simpliy adding the values in each row. [b] Transition state for intra-molecular H-abstraction.

III. (Me_6TREN)Ru(IV)=O

Mulliken Spin distribution.

	Ru	O	4xN	Rest
Triplet (π^*, $\pi^{*'}$)	1.08	0.96	-0.08	0.04
Quintet (δ, σ^*_{xy}, π^*, $\pi^{*'}$)	2.56	0.97	0.32	0.15

Key geometries in Å.

	D(Ru-O)	D(Ru-N1)	D(Ru-N2)	D(Ru-N3)	D(Ru-N4)
Triplet (π^*, $\pi^{*'}$)	1.80	2.21	2.22	2.12	2.21
Quintet (δ, σ^*_{xy}, π^*, $\pi^{*'}$)	1.81	2.20	2.24	2.27	2.22

Absolute energies.

	LACVP (H)[a]	LACV3P^{*+} (H)[a]	Z_0 (kcal/mol)	E(thermal) (kcal/mol)	S (cal/mol/K)
Triplet (π^*, $\pi^{*'}$)	-862.899880	-863.267295	278.342590	291.227000	142.405000
Quintet (δ, σ^*_{xy}, π^*, $\pi^{*'}$)	-862.879211	-863.247014	277.147560	290.442000	147.559000

[a] Total free energy in solution with all non electrostatic terms.

Relative energies (in kcal/mol).

	LACVP	LACV3P^{*+}	Z_0	E(thermal)	-TS	**Total**[a]
Triplet (π^*, $\pi^{*'}$)	0.00	+0.00	+0.00	+0.00	+0.00	**0.00**
Quintet (δ, σ^*_{xy}, π^*, $\pi^{*'}$)	12.97	-0.24	-1.2	0.41	-1.51	**10.43**

[a] The total column is calculated by simpliy adding the values in each row.

IV. $(Me_6TREN)Fe(IV)=O + C_6H_{12}$

Transition state imaginary frequency: 885 cm^{-1}.

Mulliken Spin distribution.

	Fe	O	Cyclohexane	Rest
Reactant Complex	3.12	0.75	0.00	0.13
Transition state	3.81	0.17	-0.40	0.42
Intermediate	4.05	0.28	-0.91	0.58

Key geometries in Å or •.

	D(Fe-O)	D(O-H)	D(Fe-N1)	D(Fe-N2)	D(Fe-N3)	D(Fe-N4)	A(Fe-O-H)
Reactant Complex	1.65	2.58	2.08	2.10	2.13	2.10	178.04
Transition state	1.72	1.33	2.21	2.15	2.16	2.16	178.77
Intermediate	1.77	1.01	2.23	2.17	2.17	2.18	177.15

Absolute energies.

	LACVP (H)[a]	LACV3P^{*+} (H)[a]	Z_0 (kcal/mol)	E(thermal) (kcal/mol)	S (cal/mol/K)
Reactants, separated[b]	-1128.280796	-1128.779474	386.760580	404.001000	194.161000
Reactant complex	-1128.275824	-1128.774675	387.020900	404.738000	190.436000
Transition state	-1128.257743	-1128.753686	382.179780	399.826000	183.616000
Intermediate	-1128.265195	-1128.765004	383.429450	401.761000	193.458000

[a] Total free energy in solution with all non electrostatic terms. [b] The reactants were separated about 20 Å and then optimized.

Relative energies (in kcal/mol).

	LACVP	LACV3P^{*+}	Z_0	E(thermal)	-TS	Corr[b]	**Total**[c]
Reactants, separated[a]	0.00	+0.00	+0.00	+0.00	+0.00	+0.00	**0.00**
Reactant complex	3.12	-0.11	+0.26	+0.48	+1.09	-1.89	**2.95**
Transition state	14.47	+1.72	-4.58	+0.41	+3.09	-1.89	**13.21**
Intermediate	9.79	-0.71	-3.33	+1.09	+0.21	-1.89	**5.16**

[a] The reactants were separated about 20 Å and then optimized. [b] Correction factor -RTln(24.45) for standart state concentration change upon complexation, see text above. [c] The total column is calculated by simpliy adding the values in each row.

V. $(Me_6TREN)Ru(IV)=O + C_6H_{12}$

Transition state imaginary frequency: triplet 1491 cm^{-1}, quintet 1503 cm^{-1}.

Mulliken Spin distribution.

	Ru	O	Cyclohexane	Rest
Reactant Complex	1.05	0.98	0.00	-0.03
^{3}Transition state	0.82	0.61	0.58	-0.01
^{5}Transition state	2.38	0.66	0.60	0.37
Intermediate	0.79	0.24	0.97	0.00

Key geometries in Å or •.

	D(Ru-O)	D(O-H)	D(Ru-N1)	D(Ru-N2)	D(Ru-N3)	D(Ru-N4)	A(Ru-O-H)
Reactant Complex	1.80	2.70	2.21	2.22	2.12	2.21	142.71
^{3}Transition state	1.90	1.18	2.19	2.21	2.13	2.22	130.13
^{5}Transition state	1.91	1.18	2.19	2.22	2.31	2.23	127.76
Intermediate	1.95	0.99	2.18	2.20	2.13	2.21	123.93

Absolute energies.

	LACVP (H)[a]	LACV3P^{*+} (H)[a]	Z_0 (kcal/mol)	E(thermal) (kcal/mol)	S (cal/mol/K)
Reactants, separated[b]	-1098.707723	-1099.182220	386.168570	403.047000	185.077000
Reactant complex	-1098.702802	-1099.176668	386.389690	403.745000	183.087000
^{3}Transition state	-1098.671683	-1099.143259	382.352910	399.748000	179.387000
^{5}Transition state	-1098.649378	-1099.121995	380.946400	398.874000	186.041000
Intermediate	-1098.676564	-1099.154142	384.533420	402.586000	186.970000

[a] Total free energy in solution with all non electrostatic terms. [b] The reactants were separated about 20 Å and then optimized.

Relative energies (in kcal/mol).

	LACVP	LACV3P^{*+}	Z_0	E(thermal)	-TS	Corr[b]	**Total**[c]
Reactants, separated[a]	0.00	+0.00	+0.00	+0.00	+0.00	+0.00	**0.00**
Reactant complex	3.09	+0.4	+0.22	+0.48	+0.58	-1.89	**2.88**
^{3}Transition state	22.62	+1.83	-3.82	+0.52	+1.67	-1.89	**20.93**
^{5}Transition state	36.61	+1.18	-5.22	+1.05	-0.28	-1.89	**31.45**
Intermediate	19.55	-1.93	-1.64	+1.17	-0.55	-1.89	**14.71**

[a] The reactants were separated about 20 Å and then optimized. [b] Correction factor -RTln(24.45) for standart state concentration change upon complexation, see text above. [c] The total column is calculated by simpliy adding the values in each row.

VI. $(Me_6TREN)Fe(IV)=O + CH_3CN$

Transition state imaginary frequency: 1739 cm^{-1}.

Mulliken Spin distribution.

	Fe	O	Acetonitrile	Rest
Reactant Complex	3.10	0.75	0.00	0.15
Transition state	3.85	0.12	-0.43	0.45
Intermediate	4.02	0.45	-1.00	0.52

Key geometries in Å or •.

	D(Fe-O)	D(O-H)	D(Fe-N1)	D(Fe-N2)	D(Fe-N3)	D(Fe-N4)	A(Fe-O-H)
Reactant Complex	1.65	2.68	2.07	2.11	2.13	2.10	179.84
Transition state	1.73	1.19	2.18	2.15	2.15	2.15	178.59
Intermediate	1.76	2.68	2.23	2.17	2.18	2.19	178.16

Absolute energies.

	LACVP (H)[a]	LACV3P^{*+} (H)[a]	Z_0 (kcal/mol)	E(thermal) (kcal/mol)	S (cal/mol/K)
Reactants, separated[b]	-1025.189766	-1025.658537	307.314880	321.688000	165.285000
Reactant complex	-1025.191329	-1025.656845	307.748930	324.116000	177.782000
Transition state	-1025.157060	-1025.621500	303.147550	319.044000	169.652000
Intermediate	-1025.186448	-1025.651956	304.578740	320.925000	176.079000

[a] Total free energy in solution with all non electrostatic terms. [b] The reactants were separated about 20 Å and then optimized.

Relative energies (in kcal/mol).

	LACVP	LACV3P^{*+}	Z_0	E(thermal)	-TS	Corr[b]	**Total**[c]
Reactants, separated[a]	0.00	+0.00	+0.00	+0.00	+0.00	+0.00	**0.00**
Reactant complex	-0.98	+2.04	+0.43	+1.99	-3.73	-1.75	**-1.99**
Transition state	20.52	+2.72	-4.17	+1.52	-1.3	-1.75	**17.55**
Intermediate	2.08	+2.05	-2.74	+1.97	-3.22	-1.75	**-1.6**

[a] The reactants were separated about 20 Å and then optimized. [b] Correction factor -RTln(19.17) for standart state concentration change upon complexation, see text above. [c] The total column is calculated by simpliy adding the values in each row.

VII. References

Full reference for reference 14.

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S4. A. J. Johansson, M. R. A. Blomberg, and P. E. M. Siegbahn, *J. Phys. Chem. C,* 2007, **111**, 12397.

VIII. Coordinates

Acetonitrile

```
 6
 Energy: -132.724641675
 C 0.000612 0.000001 -0.026460
 C 0.000104 -0.000007 1.429878
 N 0.001621 0.000003 -1.199029
 H -0.512714 0.887912 1.811392
 H -0.512727 -0.887918 1.811401
 H 1.025285 0.000009 1.811819
```

Cyclohexane

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  18
Energy: -235.822867500
 C 30.948726 19.472865 -0.491723
 C 31.308628 20.918418 -0.090852
 H 31.392885 18.776067 0.236006
 C 32.825767 21.174198 -0.204551
 H 30.774698 21.619170 -0.751246
 H 30.964658 21.124039 0.931693
 C 33.350465 20.832982 -1.615179
 H 33.053064 22.219898 0.042451
 H 33.352659 20.552646 0.536061
 C 32.990566 19.387501 -2.016164
 H 32.906308 21.529864 -2.342832
 H 34.437893 20.979881 -1.660582
 C 31.473450 19.131505 -1.902272
 H 33.334266 19.181992 -3.038831
 H 33.524686 18.686663 -1.356017
 H 30.946404 19.752787 -2.642976
 H 31.246412 18.085689 -2.149032
 H 29.861278 19.325900 -0.446182
```

^{3}[(Me$_6$TREN)Fe^{IV}O]$^{2+}$ (δ, δ', π, π*'(↓))*

```
 48
Energy: -892.481566309
 H -4.747766 -1.997391 -3.162789
 H -2.586529 -1.926679 -2.734015
 H -5.348731 0.373061 -2.949875
 H -3.257489 0.442386 -3.085134
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 H -6.004599 2.268812 -1.722237
 H -3.988142 2.449172 -2.294467
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 C -5.919774 -0.361298 -2.379508
 C -2.682590 -1.262769 -1.869265
 H -5.813964 -2.459476 -1.846435
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 C -6.740979 1.661943 -1.199756
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 C -2.553137 0.191017 -2.291059
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 H -8.212753 -0.513700 -0.869442
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 H -0.808135 1.650058 -0.734664
Fe -4.406130 0.155260 -0.028096
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 H -6.975264 -1.582419 -0.186346
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 H -2.203803 -2.014059 0.889031
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 H -3.591004 0.519831 2.988662
 H -4.997145 -2.044041 3.207104
 H -2.878347 -1.046116 3.467027
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^{3}[(Me$_6$TREN)Fe^{IV}O]$^{2+}$ (π, π*')*

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 48
Energy: -892.483070340
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 H -3.532706 0.691707 -2.887610
 H -7.534947 1.687663 -2.178235
 H -5.850262 2.071189 -2.555887
 H -4.180233 2.632204 -1.739463
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 H -1.955996 -1.509713 -1.433127
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 H -2.916871 -3.014546 1.734302
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 O -4.946505 1.341820 1.009166
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 H -1.891899 -0.185870 2.288737
 C -5.021068 -1.482446 2.227213
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^{5}[(Me$_6$TREN)Fe^{IV}O]$^{2+}$

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 H -3.252245 0.447824 -3.078433
 H -7.700514 1.633511 -1.767763
 H -6.034210 2.258374 -1.748946
 H -3.993621 2.450568 -2.270808
 C -5.154422 -1.668128 -2.201597
 H -2.303072 2.939176 -2.039689
 C -5.927920 -0.364687 -2.379145
 C -2.682439 -1.263888 -1.868753
 H -5.811960 -2.462987 -1.847078
 H -6.858531 -0.549858 -2.929512
 C -6.760657 1.657373 -1.205970
 H -1.893246 -1.541265 -1.167786
 C -2.547950 0.191566 -2.285218
 C -3.173875 2.485693 -1.554236
 H -1.540041 0.387747 -2.667863
 H -6.927497 2.093580 -0.222326
 N -4.023287 -1.508028 -1.190135
 N -6.247843 0.252390 -1.035745
 H -3.463753 3.079612 -0.688144
 H -8.227648 -0.520397 -0.867318
 N -2.826371 1.094205 -1.100426
 H -4.940397 -3.062554 -0.062599
 H -3.375128 -3.513257 -0.729939
 C -3.928531 -2.699932 -0.249607
 C -7.292384 -0.543802 -0.297719
 H -0.804646 1.664970 -0.725543
Fe -4.407126 0.166141 -0.020734
 C -1.627393 1.177873 -0.191527
 H -7.459634 -0.092210 0.679962
 H -6.986324 -1.582564 -0.182710
 H -1.886146 1.770094 0.685784
 C -3.253425 -2.278722 1.047265
 H -1.298148 0.183061 0.109101
 H -3.277360 -3.096706 1.775970
 H -2.204536 -2.016260 0.891041
 O -4.723738 1.477780 0.931441
 N -3.949191 -1.060861 1.624071
 H -5.879304 -2.018665 1.649957
 H -2.121793 -0.094890 2.182607
 C -5.238483 -1.440471 2.312405
 C -3.070593 -0.372813 2.636388
 H -5.751539 -0.533201 2.631495
 H -3.581621 0.518902 2.997241
 H -5.004781 -2.050616 3.190935
 H -2.882066 -1.055842 3.471280
```

^{5}[(Me$_6$TREN)Fe^{IV}O]$^{2+}$ intra-TS

```
 48
Energy: -892.459891099
 C -0.007327 -0.046987 -0.001964
 N -0.009568 -0.024613 1.501696
Fe 1.930919 0.009105 2.304415
 N 2.599195 1.334185 3.843515
 C 3.847759 1.819872 3.287950
 C -0.620322 -1.288066 2.063204
 C -0.297928 -1.422912 3.549917
 N 1.179892 -1.168534 3.821121
 C 1.408147 -0.424762 5.131057
 C 2.681517 0.412419 5.047820
 C 2.009750 -2.449648 3.821372
 C 2.439541 -2.847853 2.418460
 N 3.107923 -1.678478 1.733585
 C 4.525850 -1.501176 2.208080
 C -0.771321 1.195841 1.948295
 C 3.137647 -1.869640 0.242459
 O 2.756221 1.141573 1.215027
 C 1.641736 2.478141 4.061666
 H -0.576151 -2.418894 3.905845
 H 1.429087 -3.250606 4.289043
 H -0.226051 -2.127578 1.487653
 H 1.588280 -3.155567 1.808655
 H -1.039067 -0.052377 -0.370900
 H 0.499429 -0.939420 -0.364588
 H 2.139685 -2.110034 -0.121088
 H 3.810745 -2.696376 -0.010006
 H -0.871839 -0.700678 4.133910
 H -1.707529 -1.275962 1.917779
 H 2.883259 -2.275129 4.452494
 H 3.129337 -3.698830 2.465909
 H 0.508962 0.840709 -0.367366
 H 3.491704 -0.950382 -0.223617
 H -1.783512 1.165404 1.529877
 H 0.538957 0.205789 5.321195
 H 1.477205 -1.136949 5.959229
 H 5.116405 -2.380041 1.926696
 H -0.261897 2.088450 1.584060
 H -0.847966 1.229315 3.034045
 H 4.950817 -0.618916 1.729554
 H 4.568384 -1.393372 3.292359
 H 2.808457 1.010241 5.956593
 H 3.574109 -0.206692 4.935678
 H 0.668634 2.115031 4.382880
```

```
 H 4.706694 1.179995 3.470069
 H 1.540095 3.037372 3.131964
 H 3.544238 1.688449 1.951223
 H 2.046945 3.133060 4.838989
 H 4.022497 2.889890 3.388156
```

$^{3}[(Me_6TREN)Ru^{IV}O]^{2+}$

```
 48
Energy: -862.932808172
 H -0.883093 0.251845 0.321847
 H 0.060493 -0.001527 2.392476
 H 1.418529 -0.547548 -0.085634
 H 2.384479 -0.270043 1.608348
 H 3.190523 -0.070052 -2.367494
 H 3.605213 -0.324002 -0.665095
 H 4.464213 0.596567 0.902534
 C -0.127608 0.981611 0.010525
 H 4.852357 0.516034 2.635991
 C 1.020365 0.266510 -0.691927
 C 0.704450 0.883909 2.395849
 H -0.616897 1.685376 -0.667162
 H 0.658585 -0.178161 -1.626246
 C 3.381841 0.434194 -1.414156
 H 0.474155 1.440312 3.305598
 C 2.167238 0.450934 2.394374
 C 4.486721 1.158427 1.829505
 H 2.415952 -0.021735 3.350498
 H 4.225186 1.115415 -1.526396
 N 0.364790 1.769281 1.207492
 N 2.164762 1.215642 -1.007206
 H 5.136316 2.024969 1.719625
 H 1.492789 1.539992 -3.021389
 N 3.097385 1.637790 2.189938
 H -1.085030 3.226667 0.687068
 H -1.412568 2.443909 2.227710
 C -0.615841 2.858582 1.600920
 C 1.791299 2.133100 -2.150288
 H 3.696954 1.788619 4.222218
Ru 2.243646 2.751121 0.598004
 C 3.227362 2.427529 3.467568
 H 2.652452 2.748736 -2.409396
 H 0.946289 2.774188 -1.879518
 H 3.862089 3.293060 3.287082
 C 0.093368 3.986857 2.344968
 H 2.252084 2.735701 3.833859
 H -0.601283 4.821210 2.498251
 H 0.428528 3.665207 3.332922
 O 3.754636 3.587671 0.080034
 N 1.312836 4.486346 1.591108
 H 0.359854 4.597090 -0.347926
 H 2.361410 4.941634 3.400055
 C 0.902360 5.243758 0.347929
 C 2.123279 5.415524 2.451399
 H 1.794234 5.641257 -0.136895
 H 3.042144 5.670528 1.923377
 H 0.238497 6.072154 0.617763
 H 1.545901 6.325882 2.645561
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$^{5}[(Me_6TREN)Ru^{IV}O]^{2+}$

```
 48
Energy: -862.915227681
 H -4.808024 -2.104380 -3.136429
 H -2.615240 -1.890261 -2.809827
 H -5.399999 0.278618 -3.004524
 H -3.284266 0.490767 -3.077629
 H -7.761829 1.600972 -1.980241
 H -6.089848 2.208339 -1.931215
 H -3.917612 2.532372 -2.239275
 C -5.177856 -1.730591 -2.177050
 H -2.189603 2.940059 -2.160745
 C -5.968804 -0.441588 -2.413225
 C -2.694130 -1.256336 -1.920663
 H -5.826846 -2.504943 -1.764717
 H -6.879478 -0.674877 -2.978578
 C -6.844376 1.644444 -1.383299
 H -1.886117 -1.550020 -1.247322
 C -2.548627 0.209426 -2.321718
 C -3.038175 2.539184 -1.595340
 H -1.557080 0.369478 -2.761956
 H -7.046858 2.135337 -0.431756
 N -4.011708 -1.539977 -1.213356
 N -6.352459 0.248001 -1.117504
 H -3.224512 3.165340 -0.722889
 H -8.333776 -0.532662 -0.963819
 N -2.726189 1.141996 -1.138633
 H -4.867123 -3.113070 -0.068082
 H -3.288568 -3.517630 -0.732568
 C -3.868303 -2.718259 -0.259388
 C -7.414267 -0.510629 -0.367962
 H -0.663828 1.598214 -0.823148
Ru -4.437422 0.222125 0.035264
 C -1.503888 1.172519 -0.262897
 H -7.613861 -0.004817 0.577374
 H -7.100103 -1.537120 -0.180139
 H -1.704927 1.797117 0.608324
 C -3.198640 -2.295782 1.045275
 H -1.231408 0.166016 0.055647
 H -3.163729 -3.146756 1.735040
 H -2.167407 -1.972571 0.881117
 O -4.790319 1.664625 1.073481
 N -3.933320 -1.145528 1.713683
 H -5.846351 -2.126761 1.670423
 H -2.133053 -0.135199 2.276388
 C -5.203713 -1.607200 2.380261
 C -3.058551 -0.475891 2.740263
 H -5.726903 -0.741898 2.789393
 H -3.595373 0.375405 3.158893
 H -4.953583 -2.295389 3.195265
 H -2.819204 -1.189586 3.536047
```

$^{5}[(Me_6TREN)Fe^{IV}O]^{2+}$ + C_6H_{12}, separated reactants

```
 66
Energy: -1128.32755956
 H -0.050793 -0.097687 -0.019807
 H -0.144428 -0.092254 2.189487
 H 2.344734 0.047928 -0.488205
 H 2.220023 -0.557281 1.559588
 H 3.822218 1.581063 -2.458549
 H 4.354892 1.211542 -0.800577
 H 4.314623 0.179664 1.041160
 C 0.355138 0.899979 -0.206354
 H 4.744517 -0.014960 2.752536
 C 1.685021 0.786590 -0.947570
 C 0.606468 0.696122 2.298708
 H -0.380244 1.436233 -0.807963
 H 1.511810 0.466240 -1.981936
 C 3.833797 1.936253 -1.422888
 H 0.357104 1.256166 3.201736
 C 2.002148 0.103436 2.400238
 C 4.385446 0.694235 1.998962
 H 2.098058 -0.491198 3.315576
 H 4.345242 2.895927 -1.364373
 N 0.515095 1.646269 1.114149
 N 2.417736 2.110614 -0.942865
 H 5.079139 1.531278 1.921866
 H 1.778213 2.762423 -2.869886
 N 3.034033 1.214113 2.404035
 H -0.860301 3.083234 0.359550
 H -1.493188 2.153311 1.713580
 C -0.599752 2.656575 1.329744
 C 1.739029 3.117759 -1.834550
 H 3.543933 1.089226 4.472341
Fe 2.300354 2.703475 1.073098
 C 3.153195 1.834952 3.772247
 H 2.265622 4.069479 -1.765310
 H 0.694653 3.248274 -1.554781
 H 3.841808 2.678114 3.723007
 C -0.133550 3.737837 2.292328
 H 2.178729 2.166168 4.131609
 H -0.881474 4.534615 2.366312
 H 0.020438 3.345187 3.300092
 O 3.703533 3.572228 1.038718
 N 1.185778 4.321376 1.821397
 H 0.386461 4.873677 -0.100110
 H 2.036937 4.358228 3.785974
 C 0.977850 5.311652 0.701165
 C 1.884625 5.036148 2.948547
 H 1.950028 5.625321 0.320779
 H 2.846218 5.401086 2.589814
 H 0.444137 6.183763 1.092483
 H 1.266697 5.878222 3.277582
 H 20.910204 13.720840 1.157181
 C 21.873822 14.242407 1.089243
 C 22.095627 14.765207 -0.345550
 H 21.822099 15.099116 1.779900
 C 23.471306 15.447800 -0.492623
 H 22.035498 13.920413 -1.049845
 H 21.294631 15.464168 -0.622169
 C 24.615437 14.511628 -0.050917
 H 23.625641 15.771339 -1.530857
 H 23.490153 16.357158 0.128152
 C 24.394800 13.989219 1.384049
 H 24.668685 13.655811 -0.742006
 H 25.579623 15.033029 -0.120212
 C 23.018758 13.307028 1.530567
 H 25.195995 13.290542 1.660207
 H 24.454863 14.833907 2.088086
 H 23.000155 12.397384 0.909748
 H 22.865268 12.983483 2.568982
```

$^{5}[(Me_6TREN)Fe^{IV}O]^{2+}$ + C_6H_{12}, complexed reactants

```
 66
Energy: -1128.32675937
 H -0.057102 -0.100086 -0.020701
 H -0.150754 -0.095502 2.188574
 H 2.338550 0.044659 -0.488493
 H 2.214042 -0.560697 1.559388
 H 3.817634 1.577212 -2.457921
 H 4.350025 1.207459 -0.800003
 H 4.309814 0.176520 1.042321
 C 0.349227 0.897525 -0.206850
 H 4.739581 -0.016979 2.754134
 C 1.679316 0.783754 -0.947883
 C 0.600215 0.692789 2.298059
 H -0.385887 1.434170 -0.808495
 H 1.506136 0.463635 -1.982328
 C 3.829023 1.932412 -1.422307
 H 0.350624 1.252613 3.201168
 C 1.995910 0.099925 2.400057
 C 4.379753 0.691483 2.000100
 H 2.091380 -0.494860 3.315375
 H 4.340642 2.892075 -1.363566
 N 0.509153 1.643311 1.113852
 N 2.412781 2.107418 -0.942794
 H 5.072508 1.529534 1.922883
 H 1.774031 2.759945 -2.870231
 N 3.027871 1.210622 2.404497
 H -0.865478 3.081228 0.359605
 H -1.498850 2.151507 1.713604
 C -0.605090 2.654218 1.329693
 C 1.734702 3.114859 -1.834739
 H 3.536687 1.085757 4.473252
Fe 2.294929 2.699967 1.073272
 C 3.146195 1.831314 3.772881
 H 2.261292 4.066590 -1.765297
 H 0.690287 3.245749 -1.555205
 H 3.834575 2.674673 3.723897
 C -0.138220 3.735215 2.292455
 H 2.171609 2.162584 4.131832
 H -0.885806 4.532275 2.366786
 H 0.015710 3.342239 3.300104
 O 3.698063 3.568161 1.038816
 N 1.181423 4.318247 1.821667
 H 0.382788 4.871800 -0.099813
 H 2.033787 4.353930 3.785625
 C 0.974189 5.309034 0.701842
 C 1.880890 5.032360 2.948800
 H 1.946739 5.622162 0.321871
 H 2.842347 5.397273 2.589664
 H 0.441029 6.181516 1.093185
 H 1.263197 5.874178 3.278765
 H 5.919073 4.878376 1.054114
 C 6.882494 5.399937 0.986244
 C 7.104724 5.922763 -0.448576
 H 6.832190 6.257256 1.676724
 C 8.480994 6.604112 -0.596866
 H 7.043662 5.077806 -1.152908
 H 6.304208 6.622482 -0.725140
 C 9.624484 5.666922 -0.155519
 H 8.635245 6.927369 -1.635296
 H 8.500962 7.513602 0.023760
 C 9.404236 5.145057 1.279769
 H 9.676640 4.810817 -0.846466
 H 10.589120 6.187418 -0.225530
 C 8.027468 4.464349 1.427143
 H 10.205104 4.445784 1.555627
 H 9.465360 5.989931 1.983607
 H 8.008084 3.554440 0.806421
 H 7.874473 4.141078 2.465810
```

$^{5}[(Me_6TREN)Fe^{IV}O]^{2+}$ + C_6H_{12}, transition state

```
 66
```

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Energy: -1128.30856337
 H 0.146127 0.041636 -0.076967
 H 0.083517 0.000806 2.139632
 H 2.547924 0.147919 -0.514449
 H 2.448037 -0.438281 1.525209
 H 4.042086 1.579500 -2.513080
 H 4.586388 1.254674 -0.849129
 H 4.575257 0.285044 1.069692
 C 0.573156 1.036691 -0.237642
 H 4.924104 -0.005111 2.787661
 C 1.904674 0.898270 -0.979595
 C 0.821317 0.803188 2.253528
 H -0.143449 1.592167 -0.845334
 H 1.718539 0.568735 -2.009746
 C 4.073280 1.970776 -1.490050
 H 0.559413 1.350068 3.161831
 C 2.219784 0.208978 2.374012
 C 4.618672 0.750051 2.054848
 H 2.288733 -0.407424 3.278294
 H 4.610280 2.917849 -1.473110
 N 0.728169 1.757427 1.085021
 N 2.671766 2.197374 -0.994579
 H 5.342937 1.563952 2.044882
 H 2.024543 2.862500 -2.919236
 N 3.268761 1.297437 2.422275
 H -0.615121 3.216709 0.339673
 H -1.267587 2.303384 1.694962
 C -0.360226 2.781476 1.307897
 C 2.012658 3.216817 -1.882063
 H 3.712406 1.155020 4.508113
Fe 2.644072 2.850311 1.058048
 C 3.353094 1.906224 3.796021
 H 2.565924 4.154597 -1.820933
 H 0.976808 3.380592 -1.587044
 H 4.050889 2.743830 3.775080
 C 0.111305 3.863974 2.272504
 H 2.371541 2.249676 4.124326
 H -0.648260 4.650889 2.352711
 H 0.264885 3.463218 3.277805
 O 4.101583 3.765711 1.023007
 N 1.421336 4.465215 1.816609
 H 0.641348 5.001817 -0.113239
 H 2.270319 4.494507 3.780729
 C 1.212379 5.451013 0.697470
 C 2.097329 5.181920 2.953701
 H 2.184539 5.778055 0.327098
 H 3.049881 5.576399 2.603458
 H 0.659954 6.318816 1.074672
 H 1.460253 6.003507 3.300393
 H 5.234595 4.456780 1.018654
 C 6.293774 5.097068 1.007193
 C 6.466604 5.646559 -0.401081
 H 6.094521 5.883263 1.748325
 C 7.847159 6.358143 -0.519150
 H 6.434628 4.824732 -1.131196
 H 5.661427 6.345894 -0.653919
 C 8.994115 5.420480 -0.097937
 H 7.985133 6.702057 -1.551839
 H 7.846488 7.251507 0.121278
 C 8.779452 4.861338 1.321004
 H 9.063813 4.586093 -0.811654
 H 9.950438 5.957877 -0.145151
 C 7.400164 4.147428 1.442268
 H 9.573717 4.151426 1.583542
 H 8.824493 5.681330 2.051544
 H 7.407973 3.258850 0.794661
 H 7.246169 3.806537 2.472801
```

$^{5}[(Me_6TREN)Fe^{IV}O]^{2+} + C_6H_{12}$, intermediate

```
 66
Energy: -1128.31695056
 H 0.150492 -0.008813 -0.073473
 H 0.084704 -0.044745 2.136088
 H 2.548389 0.141418 -0.519951
 H 2.456560 -0.449432 1.520271
 H 4.009541 1.593266 -2.528787
 H 4.564122 1.287319 -0.865493
 H 4.575691 0.315382 1.065721
 C 0.559071 0.993443 -0.238465
 H 4.922918 0.013109 2.781558
 C 1.889242 0.877107 -0.986236
 C 0.811907 0.767414 2.249706
 H -0.169828 1.534100 -0.845109
 H 1.703612 0.537975 -2.013575
 C 4.033612 1.990157 -1.507552
 H 0.542584 1.309785 3.158471
 C 2.218265 0.192229 2.370733
 C 4.608028 0.771391 2.055781
 H 2.293658 -0.426027 3.273223
 H 4.550525 2.948530 -1.496623
 N 0.704322 1.719783 1.081867
 N 2.629284 2.188457 -1.009084
 H 5.320515 1.595852 2.056469
 H 1.957571 2.841322 -2.930563
 N 3.248958 1.294718 2.423846
 H -0.665734 3.152184 0.334569
 H -1.305468 2.218040 1.682170
 C -0.406988 2.718771 1.302658
 C 1.946136 3.194188 -1.892639
 H 3.690261 1.158679 4.511162
Fe 2.621139 2.861577 1.056562
 C 3.321108 1.903891 3.797614
 H 2.480791 4.143230 -1.835138
 H 0.909108 3.338109 -1.590663
 H 4.005897 2.752494 3.780085
 C 0.031612 3.809028 2.273885
 H 2.333906 2.232926 4.123899
 H -0.750125 4.574412 2.353419
 H 0.190118 3.407945 3.278203
 O 4.096915 3.834159 1.017456
 N 1.325503 4.442431 1.826759
 H 0.547551 4.958164 -0.108600
 H 2.171734 4.483856 3.791700
 C 1.099002 5.422812 0.707332
 C 1.980556 5.170634 2.967645
 H 2.064673 5.776877 0.344153
 H 2.922073 5.593180 2.620401
 H 0.519360 6.275423 1.078952
 H 1.322915 5.973846 3.319877
 H 4.936943 4.388017 1.045299
 C 6.504503 5.331759 1.095276
 C 6.616062 5.828088 -0.320370
 H 6.140731 6.029606 1.852024
 C 8.062963 6.367302 -0.569981
 H 6.442711 5.003669 -1.030385
 H 5.879906 6.609874 -0.535443
 C 9.119414 5.312556 -0.186822
 H 8.163677 6.653498 -1.624192
 H 8.212707 7.275590 0.029696
 C 8.954183 4.837026 1.269861
 H 9.033148 4.449116 -0.863538
 H 10.125927 5.726594 -0.330120
 C 7.508153 4.296717 1.522993
 H 9.679496 4.048723 1.506083
 H 9.147210 5.673143 1.955868
 H 7.388279 3.378784 0.925981
 H 7.387095 4.025914 2.577306
```

$^{3}[(Me_6TREN)Ru^{IV}O]^{2+} + C_6H_{12}$, separated reactants

```
 66
Energy: -1098.75567243
 H -0.915716 0.325333 0.337345
 H 0.043920 0.049605 2.401388
 H 1.356477 -0.540937 -0.088953
 H 2.358190 -0.275565 1.618121
 H 3.140589 -0.133131 -2.353950
 H 3.548332 -0.376091 -0.648251
 H 4.450670 0.542357 0.885512
 C -0.142666 1.033085 0.018540
 H 4.839228 0.444704 2.618200
 C 0.980045 0.285947 -0.691513
 C 0.705845 0.921672 2.399294
 H -0.617380 1.748777 -0.656812
 H 0.600543 -0.146167 -1.624749
 C 3.346162 0.378226 -1.407381
 H 0.488859 1.485873 3.307514
 C 2.159379 0.457265 2.398036
 C 4.490934 1.100256 1.814615
 H 2.399367 -0.013377 3.357614
 H 4.208525 1.033405 -1.529448
 N 0.379735 1.810543 1.209359
 N 2.152173 1.199320 -1.010482
 H 5.166795 1.946971 1.705833
 H 1.485147 1.531184 -3.024929
 N 3.117104 1.619584 2.179352
 H -1.036808 3.302413 0.695010
 H -1.371643 2.533287 2.240862
 C -0.569566 2.925400 1.606386
 C 1.810431 2.120028 -2.160578
 H 3.737080 1.776445 4.205574
Ru 2.278633 2.742329 0.585683
 C 3.273417 2.416751 3.449154
 H 2.694462 2.698390 -2.428478
 H 0.992854 2.796434 -1.892634
 H 3.922751 3.268562 3.256941
 C 0.173295 4.037251 2.342071
 H 2.307655 2.747571 3.820726
 H -0.499993 4.887836 2.500804
 H 0.510880 3.709254 3.327089
 O 3.800983 3.544323 0.047747
 N 1.396165 4.506435 1.574690
 H 0.429563 4.620212 -0.356859
 H 2.478910 4.946224 3.366637
 C 0.990708 5.261888 0.328834
 C 2.233210 5.424412 2.421826
 H 1.885936 5.637791 -0.166971
 H 3.145169 5.669892 1.876925
 H 0.345457 6.105334 0.596647
 H 1.672147 6.342382 2.627064
 H 13.959936 18.641151 -4.841776
 C 14.888877 19.125671 -4.511674
 C 14.652946 20.640829 -4.341571
 H 15.153259 18.689799 -3.535415
 C 15.951735 21.375710 -3.949893
 H 14.276787 21.053804 -5.290145
 H 13.874694 20.821032 -3.587822
 C 17.085168 21.090713 -4.957068
 H 15.769553 22.456212 -3.880238
 H 16.266779 21.042630 -2.948987
 C 17.324535 19.575807 -5.122968
 H 16.816346 21.522346 -5.933635
 H 18.010529 21.587512 -4.636573
 C 16.026200 18.839666 -5.514412
 H 18.103866 19.395346 -5.875487
 H 17.700619 19.164296 -4.173435
 H 15.713657 19.169975 -6.517197
 H 16.209225 17.758584 -5.581568
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$^{3}[(Me_6TREN)Ru^{IV}O]^{2+} + C_6H_{12}$, complexed reactants

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 66
Energy: -1098.754508
 H -0.911437 0.307489 0.339024
 H 0.039781 0.043222 2.406830
 H 1.366576 -0.545787 -0.084280
 H 2.354452 -0.281654 1.621690
 H 3.144214 -0.123621 -2.360562
 H 3.555277 -0.372862 -0.656575
 H 4.445019 0.536017 0.888397
 C -0.142276 1.019213 0.019657
 H 4.836437 0.442124 2.620666
 C 0.984964 0.277324 -0.688747
 C 0.701611 0.915351 2.402143
 H -0.620713 1.731380 -0.656794
 H 0.608276 -0.159185 -1.621078
 C 3.348505 0.384154 -1.411789
 H 0.485022 1.482015 3.308924
 C 2.155221 0.451433 2.401259
 C 4.486140 1.095730 1.816367
 H 2.395313 -0.018569 3.361126
 H 4.207554 1.044055 -1.531772
 N 0.375206 1.800909 1.209925
 N 2.151061 1.197595 -1.009520
 H 5.160868 1.942997 1.704869
 H 1.484454 1.529585 -3.024085
 N 3.112306 1.614226 2.182239
 H -1.041999 3.290460 0.690220
 H -1.381896 2.519715 2.234250
 C -0.577939 2.913682 1.603315
 C 1.800446 2.118798 -2.156546
 H 3.735380 1.771128 4.207483
Ru 2.272816 2.737797 0.589478
 C 3.269316 2.411017 3.452188
 H 2.677798 2.709234 -2.420018
 H 0.973904 2.783840 -1.887662
 H 3.916825 3.264076 3.259347
 C 0.160208 4.026139 2.342873
 H 2.303586 2.739897 3.825560
 H -0.515224 4.875341 2.499906
 H 0.494852 3.697867 3.328802
 O 3.794531 3.543372 0.054736
 N 1.384867 4.498300 1.580111
 H 0.420055 4.615953 -0.352359
 H 2.461419 4.938893 3.376192
 C 0.981903 5.255656 0.334600
 C 2.218474 5.416415 2.430331
 H 1.878468 5.630490 -0.159596
 H 3.132572 5.661613 1.888990
 H 0.338232 6.100170 0.602846
```

H 1.656617 6.334406 2.633263
H 6.312845 4.128182 0.848357
C 7.242660 4.611740 1.177535
C 7.008561 6.126738 1.351400
H 7.509088 4.173550 2.152202
C 8.308896 6.859497 1.742055
H 6.630871 6.542171 0.404511
H 6.232002 6.306040 2.107108
C 9.440485 6.575023 0.732590
H 8.128014 7.940079 1.813801
H 8.625214 6.524470 2.741906
C 9.677436 5.060156 0.562740
H 9.170944 7.009355 -0.242581
H 10.367048 7.069686 1.052913
C 8.377392 4.326941 0.171598
H 10.455304 4.880332 -0.191442
H 10.054402 4.645843 1.510703
H 8.063319 4.660777 -0.829540
H 8.558688 3.245797 0.100833

$^{3}[(Me_6TREN)Ru^{IV}O]^{2+}$ + C_6H_{12}, transition state

66
Energy: -1098.72065892
H -0.524813 0.459658 0.154870
H 0.281561 0.092919 2.242270
H 1.783384 -0.351571 -0.207831
H 2.640807 -0.192671 1.595484
H 3.694992 0.242587 -2.346740
H 3.989883 -0.114333 -0.637511
H 4.752436 0.672899 1.019198
C 0.253821 1.191415 -0.087629
H 5.042734 0.485058 2.762135
C 1.420566 0.501702 -0.781305
C 0.943554 0.960405 2.331289
H -0.193967 1.938028 -0.746902
H 1.095006 0.117448 -1.755325
C 3.820152 0.688478 -1.353731
H 0.667195 1.478504 3.251004
C 2.393513 0.501563 2.396918
C 4.734246 1.182128 1.976548
H 2.581612 -0.013857 3.345417
H 4.670143 1.370701 -1.367112
N 0.703251 1.910648 1.169162
N 2.582100 1.455881 -0.984460
H 5.418499 2.027554 1.957027
H 2.081329 1.865948 -3.032016
N 3.342293 1.682805 2.280411
H -0.706311 3.404349 0.635739
H -1.133043 2.538548 2.107998
C -0.298094 2.984919 1.556700
C 2.284354 2.421598 -2.109814
H 3.846109 1.732636 4.349965
Ru 2.597001 2.899058 0.693400
C 3.421065 2.406925 3.599533
H 3.148702 3.069802 -2.251689
H 1.405920 3.029478 -1.877690
H 4.070117 3.274424 3.494571
C 0.364835 4.068252 2.399237
H 2.432407 2.713228 3.930243
H -0.341188 4.891660 2.563130
H 0.649919 3.691382 3.383760
O 4.081731 3.904338 0.063238
N 1.615267 4.600583 1.732479
H 0.728062 4.848425 -0.219931
H 2.596789 4.932345 3.605052
C 1.262447 5.441434 0.526113
C 2.383687 5.471862 2.685827
H 2.182541 5.828923 0.089389
H 3.314856 5.779214 2.210493
H 0.617477 6.274156 0.827796
H 1.791024 6.361356 2.927443
H 5.110680 4.152436 0.587287
C 6.323263 4.553499 1.110911
C 6.318716 6.062947 0.956507
H 6.258701 4.215911 2.153416
C 7.726103 6.631859 1.309871
H 6.084577 6.329968 -0.083886
H 5.559440 6.528777 1.595600
C 8.827566 5.943267 0.481786
H 7.729295 7.715143 1.135710
H 7.917665 6.476380 2.380960
C 8.790224 4.411962 0.645922
H 8.697507 6.198952 -0.580202
H 9.812194 6.325720 0.781010
C 7.383124 3.841773 0.291404
H 9.542593 3.934358 0.005931
H 9.033576 4.146383 1.684411
H 7.199066 4.008917 -0.779561
H 7.366055 2.759061 0.463160

$^{5}[(Me_6TREN)Ru^{IV}O]^{2+}$ + C_6H_{12}, transition state

66
Energy: -1098.70164684
H -0.095975 -0.001563 0.522094
H 0.330898 0.250127 2.677421
H 2.214396 -0.210105 -0.292223
H 2.572382 -0.368517 1.792579
H 3.497119 0.738055 -2.730355
H 4.209745 0.598595 -1.106044
H 4.649358 0.166359 0.982854
C 0.381523 0.898552 0.123528
H 5.205600 0.114011 2.670232
C 1.545917 0.500308 -0.782532
C 1.091127 1.028714 2.551289
H -0.376661 1.433636 -0.450170
H 1.155349 0.007643 -1.682221
C 3.683964 1.266421 -1.788613
H 0.981774 1.721629 3.387978
C 2.480073 0.402776 2.559845
C 4.830062 0.767773 1.873869
H 2.654743 -0.083836 3.527840
H 4.291583 2.152240 -1.970442
N 0.816386 1.803330 1.272764
N 2.378526 1.697416 -1.181051
H 5.579897 1.527599 1.653273
H 1.487027 2.032352 -3.094423
N 3.558534 1.434568 2.310319
H -0.644511 3.174387 0.563389
H -1.041341 2.483230 2.133739
C -0.222639 2.887216 1.527895
C 1.658023 2.582095 -2.161317
H 4.236605 1.586728 4.334157
Ru 2.663874 2.839037 0.707277
C 3.832878 2.238758 3.549919
H 2.275325 3.457129 -2.368286
H 0.694290 2.896448 -1.761372
H 4.567981 3.012254 3.323472
C 0.392654 4.095693 2.220827
H 2.917425 2.699513 3.922176
H -0.364507 4.881016 2.333050
H 0.748753 3.847535 3.223991
O 4.140736 3.843253 0.021698
N 1.572156 4.644126 1.442115
H 0.464975 4.851929 -0.383805
H 2.789255 4.946137 3.174067
C 1.126519 5.444777 0.246980
C 2.420320 5.518450 2.322732
H 2.006670 5.741847 -0.324399
H 3.258132 5.896509 1.738028
H 0.589539 6.338962 0.583310
H 1.824462 6.361521 2.690596
H 5.093990 4.218825 0.608098
C 6.265004 4.727776 1.147589
C 6.270363 6.193479 0.756157
H 6.124750 4.552597 2.221976
C 7.652374 6.825165 1.104778
H 6.105777 6.290621 -0.326299
H 5.471535 6.747426 1.262819
C 8.805081 6.027164 0.466645
H 7.665956 7.867816 0.763596
H 7.774486 6.840657 2.196952
C 8.759066 4.541443 0.870233
H 8.741980 6.108859 -0.628630
H 9.768271 6.463437 0.761805
C 7.377617 3.907383 0.522650
H 9.550415 3.975928 0.362537
H 8.935811 4.446291 1.950804
H 7.263880 3.897498 -0.570797
H 7.352711 2.866268 0.865351

$^{3}[(Me_6TREN)Ru^{IV}O]^{2+}$ + C_6H_{12}, intermediate

66
Energy: -1098.72691065
H -0.619442 0.450143 0.195548
H 0.203615 0.123363 2.277552
H 1.673621 -0.388128 -0.198554
H 2.552790 -0.206762 1.604580
H 3.563691 0.172045 -2.359200
H 3.878808 -0.165190 -0.649642
H 4.675574 0.631217 0.989846
C 0.159826 1.170075 -0.076469
H 4.975192 0.466309 2.733595
C 1.309189 0.461114 -0.776825
C 0.879264 0.982450 2.339135
H -0.293940 1.908051 -0.740697
H 0.970770 0.069879 -1.744047
C 3.704815 0.629304 -1.373843
H 0.622256 1.524624 3.250472
C 2.323283 0.505481 2.395903
C 4.668654 1.154570 1.939668
H 2.516548 0.005725 3.351564
H 4.556966 1.307679 -1.407159
N 0.638330 1.911341 1.159079
N 2.473495 1.406110 -0.999482
H 5.363445 1.993024 1.903785
H 1.975369 1.820481 -3.047015
N 3.282891 1.673956 2.246255
H -0.771408 3.402251 0.609028
H -1.181366 2.573861 2.106979
C -0.352121 3.002704 1.534202
C 2.176256 2.373241 -2.122942
H 3.809243 1.761623 4.309275
Ru 2.530285 2.862076 0.650687
C 3.383168 2.424515 3.549468
H 3.042283 3.020043 -2.264879
H 1.295315 2.978603 -1.893021
H 4.040733 3.282256 3.418440
C 0.331001 4.099173 2.341672
H 2.402012 2.749176 3.884852
H -0.359556 4.939115 2.484779
H 0.617838 3.746890 3.334839
O 4.123865 3.795890 0.040723
N 1.585296 4.588409 1.649005
H 0.676138 4.803740 -0.298070
H 2.589992 4.956104 3.504095
C 1.244930 5.400310 0.419147
C 2.385215 5.470171 2.568389
H 2.171952 5.742969 -0.041279
H 3.319540 5.737691 2.074648
H 0.636027 6.265447 0.702217
H 1.816789 6.381720 2.783298
H 4.956759 3.868325 0.568199
C 6.916067 4.504848 1.533913
C 6.645956 5.982735 1.433946
H 6.822831 4.026704 2.510666
C 7.990835 6.775644 1.483705
H 6.157390 6.217074 0.473515
H 5.977409 6.325976 2.233386
C 8.988747 6.242032 0.434479
H 7.789930 7.842292 1.319880
H 8.425887 6.676656 2.488464
C 9.239674 4.729500 0.598671
H 8.593510 6.438182 -0.574478
H 9.939180 6.786482 0.511752
C 7.897768 3.930864 0.546574
H 9.915070 4.362193 -0.186033
H 9.730993 4.539738 1.564043
H 7.500860 4.018599 -0.478465
H 8.085689 2.867649 0.734272

$^{5}[(Me_6TREN)Fe^{IV}O]^{2+}$ + CH_3CN, separated reactants

54
Energy: -1025.22914295
H 0.223637 0.057956 -0.153208
H -0.024108 0.045513 2.047202
H 2.642526 0.153926 -0.486750
H 2.354005 -0.491359 1.539629
H 4.266011 1.672719 -2.329286
H 4.694900 1.282415 -0.646004
H 4.507463 0.207269 1.141445
C 0.659992 1.049163 -0.300907
H 4.800354 -0.092704 2.866513
C 2.027503 0.917966 -0.966405
C 0.746469 0.805138 2.211123
H -0.028715 1.608856 -0.935240
H 1.907388 0.623768 -2.015920
C 4.226185 2.021460 -1.292036
H 0.465345 1.361035 3.107461
C 2.112050 0.161487 2.379838
C 4.531339 0.669721 2.127374
H 2.135911 -0.452433 3.287039
H 4.755677 2.968145 -1.197845
N 0.757979 1.773014 1.038133
N 2.789760 2.223746 -0.891400
H 5.268473 1.471788 2.144285

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 H 2.285816 2.925102 -2.840013
 N 3.179669 1.234346 2.462696
 H -0.518189 3.265465 0.220160
 H -1.270987 2.331121 1.508673
 C -0.338740 2.813498 1.197233
 C 2.189947 3.263075 -1.802606
 H 3.573568 1.062952 4.553713
Fe 2.571218 2.775351 1.128935
 C 3.239859 1.829397 3.846164
 H 2.731279 4.201290 -1.682182
 H 1.133057 3.413050 -1.586393
 H 3.949947 2.656030 3.848184
 C 0.091720 3.862086 2.210882
 H 2.255378 2.179191 4.157302
 H -0.633454 4.682458 2.245421
 H 0.158963 3.447411 3.219364
 O 4.003039 3.594769 1.201328
 N 1.459752 4.409037 1.848003
 H 0.813456 5.029194 -0.109701
 H 2.156257 4.374143 3.872760
 C 1.365335 5.429245 0.738771
 C 2.097734 5.073055 3.040307
 H 2.372293 5.712472 0.431958
 H 3.098886 5.405007 2.767774
 H 0.838048 6.312622 1.113242
 H 1.489920 5.933310 3.339965
 H 21.387540 12.971710 3.014278
 C 21.736674 13.679883 2.257080
 C 20.773667 13.777813 1.169122
 H 21.876331 14.655421 2.732352
 N 19.998711 13.857536 0.292754
 H 22.704701 13.336174 1.880481
```

$^5[(Me_6TREN)Fe^{IV}O]^{2+}$ + CH_3CN, complexed reactants

```
 54
Energy: -1025.23086977
 H 0.197127 0.079934 -0.193948
 H -0.096238 0.056301 2.002924
 H 2.625422 0.152923 -0.484245
 H 2.278717 -0.523085 1.528664
 H 4.280660 1.582401 -2.270627
 H 4.728443 1.348647 -0.560996
 H 4.438826 0.141245 1.155157
 C 0.647900 1.066979 -0.325806
 H 4.728524 -0.159407 2.881200
 C 2.025157 0.925532 -0.969458
 C 0.685716 0.800260 2.184430
 H -0.023148 1.640587 -0.966854
 H 1.918840 0.636940 -2.022123
 C 4.237846 2.016194 -1.265756
 H 0.401073 1.354040 3.081029
 C 2.036636 0.130314 2.368704
 C 4.467178 0.604376 2.140920
 H 2.036328 -0.488438 3.272877
 H 4.729916 2.986898 -1.261278
 N 0.732918 1.777677 1.020842
 N 2.797081 2.223321 -0.877856
 H 5.210539 1.400763 2.156088
 H 2.305994 2.926445 -2.828756
 N 3.120927 1.184569 2.472855
 H -0.505766 3.297110 0.196863
 H -1.292252 2.366557 1.468274
 C -0.347943 2.835044 1.172684
 C 2.218701 3.273066 -1.792872
 H 3.489166 0.980640 4.565576
Fe 2.559899 2.750446 1.147390
 C 3.178651 1.761963 3.863711
 H 2.787290 4.195973 -1.677491
 H 1.165646 3.446181 -1.576486
 H 3.904903 2.574185 3.882918
 C 0.086339 3.869742 2.200080
 H 2.198261 2.128138 4.169248
 H -0.628274 4.699118 2.234769
 H 0.137801 3.445837 3.205788
 O 4.005137 3.537611 1.282703
 N 1.465290 4.400202 1.855839
 H 0.839781 5.046147 -0.099494
 H 2.160946 4.334714 3.879995
 C 1.399034 5.428706 0.752045
 C 2.101686 5.046295 3.058525
 H 2.412312 5.690622 0.445962
 H 3.102839 5.380459 2.789537
 H 0.891092 6.322237 1.129430
 H 1.494610 5.902960 3.370187
 H 6.349294 4.816776 1.509451
 C 6.719078 5.530584 0.766677
 C 5.765531 5.628071 -0.329081
 H 6.853764 6.503722 1.247917
 N 4.980266 5.686349 -1.198299
 H 7.691320 5.187276 0.401027
```

$^5[(Me_6TREN)Fe^{IV}O]^{2+}$ + CH_3CN, transition state

```
 54
Energy: -1025.19846661
 H 0.224281 0.067481 -0.127291
 H 0.094443 0.008660 2.083909
 H 2.630665 0.218596 -0.528497
 H 2.470286 -0.424250 1.498699
 H 4.121341 1.680745 -2.473567
 H 4.664981 1.386473 -0.804256
 H 4.596963 0.337687 1.062798
 C 0.636914 1.070557 -0.271379
 H 4.922033 -0.007135 2.774344
 C 1.981363 0.964662 -0.991793
 C 0.833093 0.805309 2.223966
 H -0.080982 1.621981 -0.880843
 H 1.820376 0.650265 -2.030442
 C 4.137886 2.082889 -1.454784
 H 0.556895 1.339328 3.135642
 C 2.228429 0.210587 2.353025
 C 4.627509 0.771420 2.062217
 H 2.289953 -0.416590 3.249894
 H 4.653041 3.042344 -1.450176
 N 0.762326 1.777368 1.065052
 N 2.725978 2.278967 -0.973308
 H 5.351359 1.584619 2.089424
 H 2.104117 2.970251 -2.895276
 N 3.271207 1.304840 2.430085
 H -0.576792 3.239542 0.311756
 H -1.252511 2.294194 1.633072
 C -0.341918 2.789592 1.278017
 C 2.061433 3.303792 -1.852401
 H 3.697671 1.128063 4.515279
Fe 2.649030 2.872684 1.090942
 C 3.339699 1.891087 3.815650
 H 2.591595 4.252345 -1.761175
 H 1.016083 3.436731 -1.577156
 H 4.033040 2.732266 3.816159
 C 0.100786 3.854036 2.273029
 H 2.353142 2.221315 4.142441
 H -0.661324 4.638149 2.350635
 H 0.235281 3.436845 3.274038
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 N 1.418803 4.468993 1.853901
 H 0.672713 5.040489 -0.080300
 H 2.235882 4.458840 3.832223
 C 1.224560 5.476901 0.750144
 C 2.066961 5.165202 3.020892
 H 2.199495 5.823743 0.405847
 H 3.017781 5.585681 2.698501
 H 0.655639 6.329120 1.137467
 H 1.410131 5.966806 3.376564
 H 5.128093 4.410366 1.116208
 C 6.273785 5.104562 1.060950
 C 6.625607 5.161037 -0.313624
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 N 6.861100 5.170020 -1.468582
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$^5[(Me_6TREN)Fe^{IV}O]^{2+}$ + CH_3CN, intermediate

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 H 2.433576 -0.522943 1.487601
 H 3.824791 1.600239 -2.597010
 H 4.433142 1.291258 -0.951253
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 C 0.459995 0.903187 -0.200171
 H 4.939493 -0.019151 2.665303
 C 1.765875 0.820767 -0.994034
 C 0.795763 0.664036 2.277797
 H -0.300764 1.432174 -0.777441
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 C 3.868488 1.986867 -1.572444
 H 0.548124 1.196686 3.198392
 C 2.213822 0.110128 2.349503
 C 4.580462 0.732908 1.953291
 H 2.327798 -0.512619 3.244998
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 H -1.363601 2.076815 1.787918
 C -0.487374 2.598510 1.385283
 C 1.741596 3.142852 -1.886260
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Fe 2.526179 2.800899 1.042578
 C 3.338142 1.830264 3.748827
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 H 0.711794 3.262788 -1.550859
 H 4.013943 2.685445 3.712089
 C -0.039310 3.689529 2.351174
 H 2.358921 2.147950 4.109106
 H -0.834326 4.437022 2.464125
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 N 1.225357 4.351755 1.867802
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 H 2.130211 4.389686 3.805673
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 H 2.836552 5.511010 2.619332
 H 0.372370 6.181291 1.165546
 H 1.255046 5.875668 3.368622
 H 4.812261 4.335104 0.905920
 C 8.457002 6.614350 0.585195
 C 7.283025 5.893429 0.689271
 H 9.248766 6.471973 1.310784
 N 6.278177 5.275757 0.778585
 H 8.592752 7.325528 -0.220777
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