Formation of Mn hydrides from bis(trimethylsilylmethyl) Mn(II): a DFT study

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Supporting Information Placeholder

ABSTRACT: We recently reported the synthesis and characterization of KMH-1 (Kubas Manganese Hydride – 1 [*Energy Environ. Sci.*, 2019, DOI: 10.1039/C8EE02499E]), a manganese hydride molecular sieve which, if incorporated into a hydrogen storage system, has sufficient performance to realise the DOE system targets for H_2 storage and delivery. KMH-1 is amorphous and paramagnetic, making its characterization challenging, and how it is formed from its simple Mn(II) organometallic precursors is not fully understood. In this contribution, we explore computationally several series of reactions that could occur in the production of KMH-1 from bis(trimethylsilylmethyl) manganese (II) ($Mn(TMSM)_2$), including the formation of hydrides, ways to generate the extended structure and reactions to produce species with Mn(I) centres (KMH-1 is believed to contain a substantial proportion of Mn(I)). We show that the most likely route to the formation of Mn hydrides is via elimination of tetramethylsilane (TMS) by reaction of $Mn(TMSM)_2$ with H_2. These hydrides could then react to grow the extended KMH-1 structure via Mn hydride condensation reactions. Alternatively, multimetallic TMS-containing products could be formed via condensation reactions involving $Mn(TMSM)_2$ and/or MnTMSM, after which the TMS ligand could be removed via elimination reactions with H_2. The formation of Mn(I) centres from Mn(II) hydrides is most likely via H_2 elimination from Mn(II) hydrides.

INTRODUCTION

The current use of fossil fuels to power vehicles places a heavy burden on the environment and so an alternative fuel source is highly desirable, for example the hydrogen fuel cell.[1] To realise efficient and commercially attractive hydrogen powered vehicles requires innovation in the storage of the gas to allow for longer driving ranges, as current approaches, carbon fibre based high pressure cylinders, require frequent refuelling.[2-4] We have turned towards materials-based solutions to try to store a greater amount of hydrogen. Multiple classes of materials have shown some promise in this field, with the majority of research focussed on either metal hydrides or metal organic frameworks (MOFs). Metal hydrides generally perform well in storing the gas however removing the dihydrogen can be difficult as it binds strongly to the material.[5,6] MOFs generally suffer from different problems as they require cryogenic temperatures to store the dihydrogen due to weaker overall binding, although they do show good kinetic properties.[7,8] Both metal hydrides and MOFs have issues with the heat management required for cooling/boil off which causes problems in practical implementation.[9,10]

We have recently proposed a new material with the potential to resolve these problems. "KMH-1" (Kubas Manganese Hydride-1) is an amorphous manganese hydride molecular sieve that has a thermodynamically neutral H_2 adsorption process.[11] KMH-1 stores enough H_2 to meet or surpass the gravimetric and volumetric storage capacity targets set by the US Department of Energy for a viable hydrogen storage solution,[12] whilst also requiring only pressure changes to release the stored gas. In addition to its characterisation by many experimental techniques, we provided quantum chemical computational analysis, concluding that a mixture of Kubas-like[13-16] interaction and physisorption accounts for its binding H_2 in a manner in between chemisorption - metal hydride like - and physisorption, MOF like.[17] Our model suggested that KMH-1 contains a large percentage of Mn(I) centres, unexpected given that it is synthesised from bis(neopentyl) manganese (II), yet best agreeing with the dihydrogen binding properties, including H_2 rotational barriers provided by inelastic neutron scattering data.

We have subsequently refined our synthetic procedure, such that we now prepare KMH-1 from bis(trimethylsilylmethyl) manganese (II), which we also employ in the production of other proposed hydrogen storage solutions.[18,19] In the present computational study we have explored potential steps in the generation of KMH-1 from this precursor. These proposed reactions broadly fall into three categories: loss of ligand for the introduction of hydrides, chain growth to produce the networked structure, and the re-

duction of Mn(II) to Mn(I). We find that the loss of the precursor ligand likely proceeds *via* elimination facilitated by the H_2 present in the reaction with little contribution through other routes such as involving the solvent. Growth of the material from monomers to larger networks is shown to be plausible, starting from either the trimethylsilyl-containing precursor or from the hydrides formed after elimination of ligand; manganese hydrides react very exothermically. We provide possible routes for the reduction of Mn(II) including homolytic cleavage, a molecular rearrangement releasing H_2 from the extended structure, and a multi-step process generating a metal atom and the subsequent reaction with a hydride.

METHODOLOGY

We have previously used density functional theory (DFT) calculations to investigate the properties of KMH-1, as well as other hydrogen storage materials,[20,21] and the same technique has been employed in the present study. The PBE functional[22,23] was used in conjunction with Grimme's D3 dispersion corrections[24] and the 6-311++G** basis set; this approach has been shown to provide reasonable geometry, IR and electronic data for optimised geometries in our previous work as well as in benchmarking against ab initio techniques.[25-28] Gaussian 09 revision D.01[29] and Gaussian 16 revision A.03[30] have been used to perform all the calculations presented herein.

All structures were optimised with spin unrestricted DFT with no constraints on the geometry. Unless otherwise stated all of the optimisations were performed with the UltraFine integration grid and VeryTight geometry convergence criteria as defined in Gaussian; other options were left at their defaults. In all systems with Mn present the metal was defined as being in its high spin ground state; five unpaired electrons per Mn(II) and four unpaired electrons per Mn(I). In any model with more than one Mn centre the multiplicity was defined for the total, high spin, structure. All optimised geometries underwent harmonic vibrational frequency analysis.

Transition states were located using the QST3 optimisation option. This option applies the Synchronous Transit-Guided Quasi-Newton (STQN)[31] method to three specified geometries; the reactants, the products and an initial guess at the transition state. These input geometries are then manipulated to probe the potential energy surface to find an appropriate saddle point and hence converge on the transition state geometry. Subsequent calculations were performed on the transition states to find the intrinsic reaction coordinate (IRC) associated with the imaginary frequency located, and hence to verify that the transition state correctly connects reactants and products.

In some cases, no transition state could be found this way; usually this would occur when the two molecules undergoing the proposed reaction would not converge to either a reactant or product geometry. In these cases, a different method was employed to determine a plausible way for the reaction to occur. Specifically, bond forming/breaking reactions were explored manually along likely reaction coordinates (using the ModRedundant tool) to determine the presence or otherwise of an energy barrier and the associated transition state.

Solvent effects have been included for a selection of the reactions presented. These were chosen as two sets 1) representative reactions to determine the energetic effect of the inclusion of implicit solvent, e.g. the elimination of the precursor ligand *via* H_2 and 2) a series of reactions that include an explicit reactant solvent molecule, e.g. hexane replacing the precursor ligand before elimination. The polarizable continuum model (PCM)[32] was employed to include implicit solvation effects. Molecules were re optimised using the PCM starting at the gas phase geometries. Solvation was implemented using the Gaussian 09 default settings for each of the solvents considered; n-hexane, cyclohexane and toluene.

Self-consistent field (SCF) energies E are corrected using a statistical mechanical analysis of the harmonic vibrational frequencies to give Gibbs free energies G. The energies of the optimised reactants E_R, in the form of an association complex, are used to derive the other energies in a particular reaction profile, i.e. the energy of the associated products, E_P, the energy of the transition state, E_{TS}, and the energies of both the reactants and products when separated to an infinite distance, $E_{R@inf}$ and $E_{P@inf}$ respectively. This approach is also used to calculate the equivalent G analogs: G_R, G_P, G_{TS}, $G_{R@inf}$, and $G_{P@inf}$, using thermodynamic corrections from the harmonic vibrational frequency analyses.

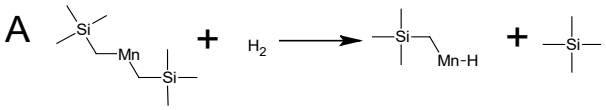
RESULTS AND DISCUSSION

There are two basic steps required to produce the extended manganese hydride structure from the bis(trimethylsilylmethyl) manganese (II) precursor ($MnTMSM_2$); elimination of the organic ligand to leave a hydride, and the growth of the material from its monomers to an integrated network. These steps could occur in either order. We also wish to understand how KMH-1 has a large percentage of Mn(I) centres.

ELIMINATION OF TETRAMETHYLSILANE VIA H_2

Dihydrogen attack on the manganese centre in $Mn(TMSM)_2$ could lead to an elimination reaction as seen in scheme 1. The elimination of tetramethylsilane (TMS) is very likely a key step in the production of KMH-1 as it leads to species containing hydrides; these could then further react by either losing the second organic ligand or combining to form the extended structure.

Scheme 1. Representation of the reaction between dihydrogen and $Mn(TMSM)_2$ to eliminate TMS.



The energies calculated for this reaction are given in table 1 and the energy surface is shown in figure 1. The reaction is exothermic from E_R to E_P by 26.4 kJ mol^{-1}; 11.8 kJ mol^{-1} at the Gibbs level. Bringing the reactants together from infinity to their optimised association complex geometry lowers the SCF energy of the system by 6.8 kJ mol^{-1}; at the Gibbs level this change is in the opposite direction, as would be expected when two species come together to reduce the entropy in the system. Similarly, when the products of the reaction are separated to an infinite distance there is an increase in SCF energy as the separate products are less stable than when interacting with each other; this is reversed at the Gibbs level again due to entropic effects. The barrier to the reaction, E_{TS}, is 65.4 kJ mol^{-1}

Table 1. Relative energies (kJ mol^{-1}) of the first reaction in scheme 1 (A), and second, reaction B, eliminations of tetramethylsilane from Mn(TMSM)$_2$ by H$_2$, Δ*E* (Δ*G*). Reaction coordinate given in figure 1.

Reaction	$E_{R@inf}$	E_P	$E_{P@inf}$	E_{TS}
A: Mn(TMSM)$_2$+H$_2$ → HMn(TMSM) + TMS	6.8 (-17.3)	-26.4 (-11.8)	2.5 (-27.8)	65.4 (78.4)
B: HMn(TMSM)+H$_2$ → MnH$_2$ + TMS	7.6 (-16.4)	-27.4 (-9.0)	0.5 (-17.9)	62.3 (79.5)

Table 2. PCM-corrected energies (kJ mol^{-1}) for reactions eliminating TMS from Mn(TMSM)$_2$ for the 3 solvents under consideration. Δ*E* (Δ*G*) *Tetramethylsilane with the implicit solvent was optimised with the standard Gaussian convergence criteria.

Reaction	Solvent	$E_{R@inf}$	E_P	$E_{P@inf}$ *	E_{TS}
A: Mn(TMSM)$_2$+H$_2$ → HMn(TMSM) + TMS	n-Hexane	6.1 (-21.0)	-29.1 (-9.3)	-8.9 (-43.1)	69.7 (83.8)
	Cyclohexane	6.0 (-21.6)	-29.8 (-13.1)	-9.8 (-44.8)	70.2 (84.2)
	Toluene	5.8 (-23.0)	-31.0 (-10.1)	-11.9 (-48.1)	71.4 (84.8)
B: HMn(TMSM)+H$_2$ → MnH$_2$ + TMS	n-Hexane	5.9 (-19.9)	-27.7 (-3.6)	-12.8 (-38.2)	68.9 (86.5)
	Cyclohexane	5.0 (-29.7)	-28.7 (-13.3)	-14.5 (-49.5)	69.2 (76.3)
	Toluene	4.2 (-29.0)	-29.8 (-13.0)	-17.3 (-51.7)	70.2 (79.0)

(Δ*G*: 78.4 kJ mol^{-1}). The transition state, figure 2, shows the H$_2$ molecule approaching the Mn-C bond; the blue arrow gives the displacement vector of the imaginary vibration, at 1044*i* cm^{-1}. The transition state geometry shows a lengthening of both the H-H distance to 1.05 Å, from 0.754 Å, atoms highlighted in orange, and the Mn-C distance to 2.25 Å, increased from 2.06 Å, as the bonds break and the products are formed. The associated IRC profile is given in figure 3, with 50 points in each direction away from the transition state geometry along the displacement vector of the imaginary vibration.

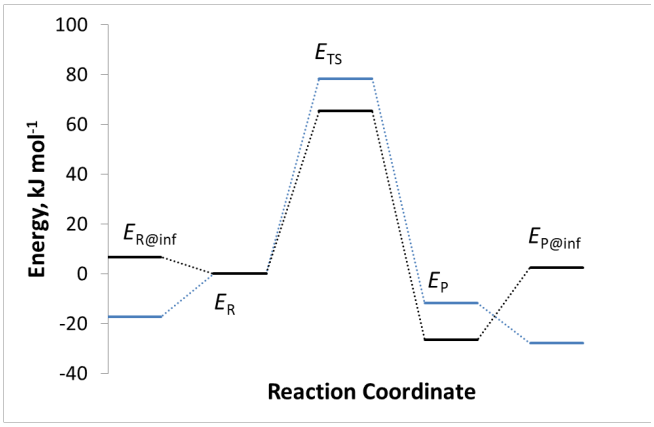


Figure 1. Energies of the elimination reaction (A) between H$_2$ and Mn(TMSM)$_2$ relative to E_R, the energy of the reactants' association complex. Black : Δ*E*, Blue : Δ*G*.

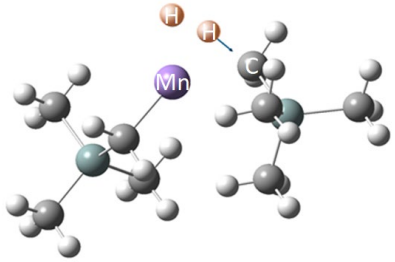


Figure 2. Transition state geometry for the elimination of TMS from the reaction between H$_2$ and Mn(TMSM)$_2$ (reaction A). Blue arrows show the direction of the displacement of the imaginary vibration. Atom colours: Mn = purple, C = gray, H = white and Si = teal. H$_2$ highlighted in orange.

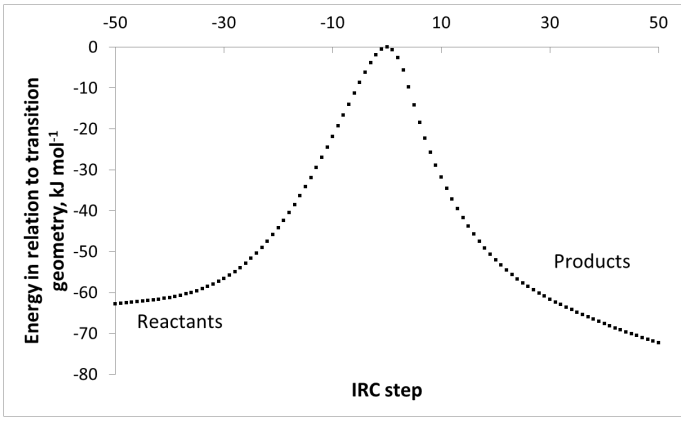


Figure 3. Intrinsic reaction coordinate for the reaction between H$_2$ and Mn(TMSM)$_2$ (reaction A) with 50 steps in each direction from the transition state geometry in figure 2.

The reaction profile for the second elimination of TMS from HMnTMSM by H$_2$ (reaction B) is given in figure 4. The calculated energies associated with this reaction are collated in table 1. A representation of the transition state geometry and the associated IRC can be found in the supplementary information, figures S1 and S2. The energy changes involved in this reaction are very similar to those for the first elimination. It is therefore reasonable to expect that if these reactions were to take place in excess H$_2$ the Mn(TMSM)$_2$ precursor would be converted to manganese hydride as the reactions are both exothermic; this is consistent with experiment[11, 19] as it is known that most of the organic parts of the precursor are eliminated.

Table 3. Energies (kJ mol^{-1}) for potential steps in the elimination of TMS from Mn(TMSM)$_2$ involving intermediates generated through intramolecular reactions; reaction labelling (D-F) refers to schemes 2 and 3. ΔE (ΔG)

Reaction	$E_{R@inf}$	E_P	$E_{P@inf}$	E_{TS}
C	0.0	78.5 (73.3)	105.6 (63.3)	155.8 (153.4)
D	0.0	164.2 (159.4)	200.9 (152.2)	232.4 (215.4)
E	16.0 (-17.8)	-93.9 (-91.6)	-93.9 (-91.6)	43.4 (44.7)
F	33.3 (-7.4)	-171.8 (-170.0)	-171.8 (-170.0)	66.3 (54.6)

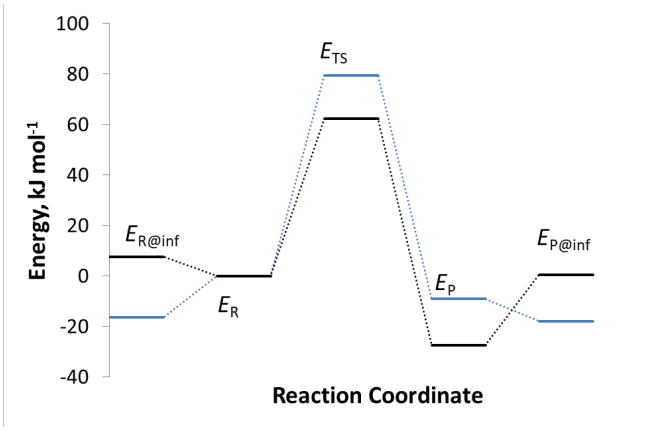


Figure 4. Energies of the elimination reaction B between H_2 and HMn(TMSM) relative to E_R, the energy of the reactants' association complex. Black : ΔE, Blue : ΔG.

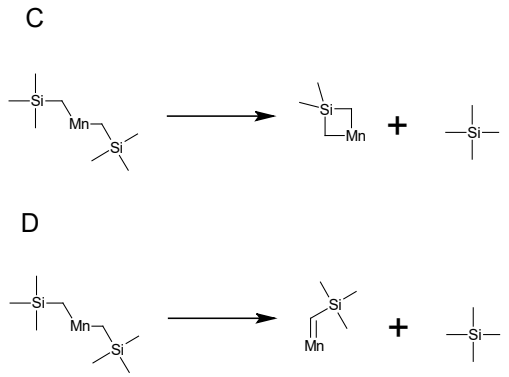
The effects of the implicit solvents n-hexane, cyclohexane and toluene on the E_P and E_{TS} are given in table 2. In general, these effects are minor. The first elimination of TMS shows, for all the solvents tested, that it is slightly more favourable to form the products in solvent compared with the gas phase. The smallest change is seen for hexane, with a 2.7 kJ mol^{-1} increase in energy released on product formation compared to the gas phase calculation. The reaction is more stable in cyclohexane by 3.4 kJ mol^{-1} and more stabilised in toluene compared to the gas phase by 4.6 kJ mol^{-1}. However the Gibbs energy trends for these reactions are different, with cyclohexane stabilising vs the gas phase reaction by 1.3 kJ mol^{-1}, and n-hexane and toluene making the reaction less favourable by 2.5 and 1.7 kJ mol^{-1} respectively. The differences in solvent-corrected E_{TS} are a little more pronounced; 4.3 (5.4), 4.8 (5.8) and 6.0 (6.4) kJ mol^{-1} for hexane, cyclohexane and toluene respectively; the order of the solvent effect on these energies is the same at both the ΔE and ΔG levels.

The PCM implicit solvent model also has a minor effect on the second elimination reaction (B). As with the first elimination, the reaction is more likely to occur in solvent, with the same order of stabilising effect; at the Gibbs level n-hexane causes an unfavourable effect on the reaction reducing the energy released by 5.4 kJ mol^{-1}, toluene and cyclohexane have a very minor stabilising effect. All of the solvents have a destabilising effect on the transition state energies, in the same order as for the first elimination. At the Gibbs level there is a small stabilising effect for cyclohexane and toluene, with n-hexane showing the largest destabilising effect (7.0 kJ mol^{-1}).

ABSTRACTION INTERMEDIATES

Other reactions may eliminate TMS via an intermediate; potential intermediates could be produced either through an intramolecular reaction or by interaction with the solvent. Presented here are two potential intramolecular elimination reactions to remove the organic part of the precursor leaving a hydride. The first of these reactions is the abstraction of tetramethylsilane via interaction with the γ-hydrogen on the ligand, shown in scheme 2C. Alternatively, the α-hydrogens could be involved in this reaction, scheme 2D.

Scheme 2. Abstraction of tetramethylsilane from bis(trimethylsilylmethyl) manganese (II) employing (C) a γ-hydrogen and (D) an α-hydrogen.



Energies relative to that of the reactant are given in table 3, and suggest that if the mechanism for the loss of tetramethylsilane followed an intramolecular path the most likely route would be through γ-abstraction to produce the cyclic product. The Gibbs energies are similar to the energies calculated at the SCF level; major variation is seen only when the products are taken to infinite separation, in both cases C and D the energy change is reduced, a most likely entropically driven effect.

Optimised transition state geometries, figure 5, enable the calculation of the IRCs, figure S3. The transition state imaginary frequencies are 1255i cm^{-1} for reaction C and 433i cm^{-1} for reaction D. Both IRC plots show a smooth curve up to and down from their respective transition states; fewer steps could be located for the α-abstraction reaction.

Table 4. Reaction energies (kJ mol^{-1}) for the exchange of a trimethylsilylmethyl ligand on the precursor with an explicit solvent molecule in the gas phase, and including PCM solvent model. Δ*E* (Δ*G*) *Tetramethylsilane and cyclohexane with the implicit solvent were optimised with the standard Gaussian convergence criteria.

	Solvent	$E_{R@inf}$	E_P	$E_{P@inf}$*	E_{TS}
G1	Hexane	36.6 (-12.8)	39.9 (25.5)	68.2 (13.1)	143.2 (131.9)
G2	w/ PCM	27.9 (-27.1)	36.5 (26.7)	57.5 (-7.3)	142.3 (126.7)
G3	Cyclohexane	32.8 (-9.7)	35.8 (41.2)	63.9 (21.4)	137.7 (143.6)
G4	w/ PCM	22.9 (-24.2)*	29.0 (30.5)	53.8 (5.6)	138.3 (139.3)
G5	Toluene (Methyl)	55.1 (-1.2)	16.6 (10.3)	43.0 (-7.9)	115.1 (115.3)
G6	w/ PCM	41.6 (-7.6)	9.9 (16.3)	32.4 (-12.5)	118.3 (116.2)
G7	Toluene (Ortho)	55.1 (-1.2)	35.1 (25.5)	68.2 (11.7)	131.0 (120.4)
G8	w/ PCM	41.1 (-7.7)	28.3 (38.1)	51.8 (5.8)	129.8 (127.2)
G9	Toluene (Meta)	48.8 (-7.3)	29.2 (18.7)	63.3 (5.5)	129.0 (116.5)
G10	w/ PCM	42.5 (-12.3)	23.8 (19.8)	52.9 (-6.9)	133.9 (116.8)
G11	Toluene (Para)	54.1 (-1.0)	34.3 (26.0)	68.3 (11.2)	134.1 (120.8)
G12	w/ PCM	42.0 (-9.5)	28.8 (32.7)	52.2 (-4.9)	133.0 (127.9)

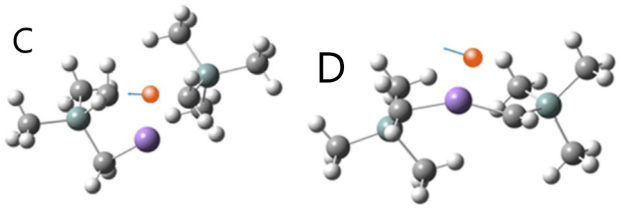
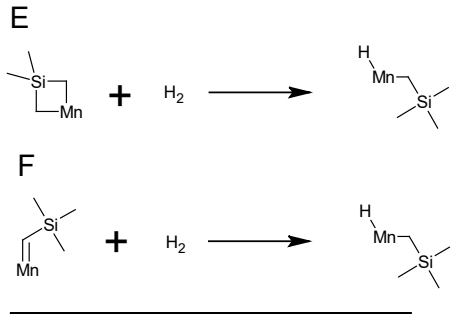


Figure 5. Transition states for the (C) γ and (D) α tetramethylsilane abstraction reactions. Blue arrows show the displacement of the imaginary vibration. Atom colours: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

Both transition states show the migration of a hydrogen atom from one of the TMSM ligands across the Mn and onto the other ligand, which is eliminated as tetramethylsilane. The major difference between the two transition states is the origin of the hydrogen atom; either from a methyl group for C or a methylene for D.

Following the intramolecular elimination of the ligand, the next step in the production of manganese hydride would be the addition of H_2 to the Mn, either opening the cyclic structure, reaction E, or hydrogenating the carbene, reaction F. In both cases the same product is formed, HMnTMSM. These reactions are shown scheme 3, and the energetic data associated with them are collected in table 3. The transition states associated with these reactions, figure 6, have imaginary frequencies of 754*i* and 438*i* cm^{-1} for E and F respectively. Reaction E's transition state geometry is similar to those found for reactions C and D, early transition states, as there is a lengthening of the H-H bond in H_2 present at the transition state to 0.96 Å. At the transition state for reaction F, however, the H_2 bond has already broken with the distance between the atoms lengthened to 2.74 Å. The IRC plots associated with these transition states, figure S4, again show smooth progression through the transition state.

Scheme 3. Dihydrogen addition reactions from the (E) cyclic and (F) carbene products of the abstraction of tetramethylsilane from the precursor.



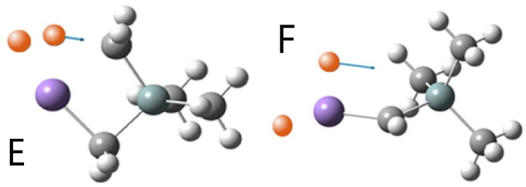


Figure 6. Transition states for reactions (E) and (F). Blue arrows show the displacement of the imaginary vibration. Atom colours: Mn = purple, C = gray, H = white and Si = teal. H_2 highlighted in orange.

Reaction C followed by reaction E can be thought of as one path, CE, for the overall reaction to replace one of the organic ligands with a hydride; in this case via a cyclic intermediate. This overall reaction also takes place when taking a route through D and F; this proceeds via the carbene intermediate, DF. CE is the more likely route as the overall energy released is greater and that required to overcome the first transition state is 76.6 (62.0) kJ mol^{-1} lower than the corresponding barrier in DF. However, these two routes are overall equivalent to reaction A shown in scheme 1 and in comparison to that reaction these routes have much greater energy barriers; E_{TS} is 155.8 (153.4) kJ mol^{-1} for the initial step in CE whereas the reaction A has a barrier of only 65.4 (78.4) kJ mol^{-1}. We therefore conclude that the single step reaction is much more likely to occur.

Table 5. Energies (kJ mol^{-1}) for the β–hydride elimination and solvent elimination by H_2 reactions upon the solvent substituted complexes (Scheme 5). ΔE(*ΔG*) *Cyclohexane with the implicit solvent was optimised with the standard Gaussian convergence criteria

	Solvent	$E_{R@inf}$	E_P	$E_{P@inf}$	E_{TS}
H1	Hexane – β-hydride	0.0	57.0 (49.9)	123.3 (59.5)	78.2 (70.9)
H2	w/ PCM	0.0	62.6 (52.8)	113.5 (48.0)	79.0 (67.1)
I1	Cyclohexane – β-hydride	0.0	48.8 (31.1)	135.7 (59.7)	50.2 (37.3)
I2	w/ PCM	0.0	51.5 (34.8)	123.3 (47.0)	107.6 (88.8)
J1	Hexane – with H_2	7.7 (-17.9)	-59.6 (-41.7)	-28.1 (-54.2)	60.3 (73.8)
J2	w/ PCM	6.0 (-32.6)	-61.3 (-44.8)	-38.6 (-74.5)	63.9 (67.5)
J3	Cyclohexane – with H_2	8.8 (-16.4)	-55.2 (-45.0)	-26.6 (-58.0)	63.8 (75.0)
J4	w/ PCM	6.3 (-23.3)	-61.0 (-44.6)	-40.4 (-76.3)*	66.6 (73.6)
J5	Toluene (Methyl) – with H_2	8.7 (-17.9)	-38.7 (-22.7)	16.5 (-21.6)	57.0 (69.4)
J6	w/ PCM	6.4 (-26.8)	-39.0 (-33.2)	-2.2 (-47.0)	64.1 (66.7)
J7	Toluene (Ortho) – with H_2	8.5 (-16.0)	-64.1 (-40.3)	-8.9 (-39.3)	51.2 (66.5)
J8	w/ PCM	7.3 (-20.9)	-58.1 (-45.8)	-21.2 (-59.5)	58.6 (66.7)
J9	Toluene (Meta) – with H_2	9.7 (-17.3)	-64.3 (-41.6)	-9.1 (-40.6)	54.7 (64.7)
J10	w/ PCM	7.6 (-21.3)	-57.5 (-38.0)	-20.5 (-51.7)	61.4 (70.5)
J11	Toluene (Para) – with H_2	8.2 (-13.4)	-65.5 (-37.1)	-10.3 (-36.1)	53.4 (69.7)
J12	w/ PCM	5.4 (-28.0)	-59.5 (-44.0)	-22.6 (-57.7)	59.5 (66.1)

SUBSTITUTION WITH SOLVENT

Another route to the elimination of the organic ligand from the precursor to leave a hydride is via an intermediate in which a solvent molecule replaces a TMSM ligand before itself being eliminated. Experimentally, n-hexane, cyclohexane and toluene have all been employed as solvents in the production of KMH-1[19]. We have therefore investigated reactions involving cyclohexane, n-hexane binding via its α carbon, and toluene coordinating at the ortho, meta and para ring positions, as well as the methyl position; scheme 4 presents these reactions.

Scheme 4. The reaction between solvent and the precursor. Sol can be n-hexane, cyclohexane, or toluene.

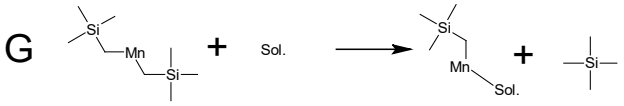


Table 4 gives key energies for each of these reactions, both in the gas phase and with implicit solvation. Representations of the transition states are given in the supplementary information, figures S5-S10, as well as the corresponding IRC plots, figures S11-S16. The data in table 4 show that all of these reactions are endothermic; the most facile reaction (G5) involves toluene reacting via its methyl carbon, which has both the lowest E_p, 16.6 (10.3) kJ mol^{-1}, and the smallest activation barrier, 115.1 (115.3) kJ mol^{-1} in the gas phase. The least likely reaction to occur at the SCF level is that involving hexane (G1), as both the E_P, 39.9 (25.5) kJ mol^{-1}, and E_{TS}, 143.2 (131.9) kJ mol^{-1}, are larger than the rest. The differences between the toluene ring sites are small, the largest difference in E_P is only 5.9 (7.3) kJ mol^{-1} between the meta (G9) and ortho (G7) positions, however the methyl site (G5) gives a much lower E_P, around half that of the other toluene sites.

The reaction profile for substitution with hexane is provided in figure 7; the other reactions follow a similar profile. Comparison with the initial steps for the abstraction reactions, table 3, shows that involving the solvent significantly lowers the E_P however the energetic barriers to the transition state are similar; the γ-abstraction step, C, has an E_{TS} of 155.8 (153.4) kJ mol^{-1} in the gas phase, which is only 12.6 (9.8) kJ mol^{-1} larger than the largest barrier for solvent involvement (1).

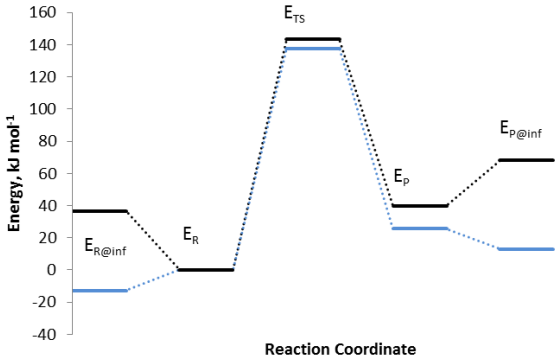


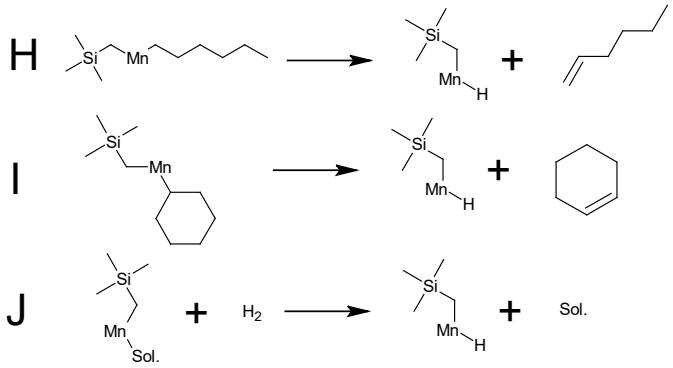
Figure 7. Energies of ligand substitution with hexane reaction relative to E_R, the energy of the reactants' association complex. Black: Δ*E*, Blue: Δ*G*.

As with the elimination reactions (scheme 1, table 2), Table 4 shows that the inclusion of implicit solvation has only a minor influence on the solvent substitution reactions, with the trends being similar to those in the gas phase. In general, the presence of the continuum solvent makes the reaction less unfavourable; the largest difference seen is for cyclohexane (G3 and G4) and toluene at the ortho position (G7 and G8), each at 6.8 kJ mol^{-1}. At the Gibbs level the behaviour is quite different with the majority of the products being destabilised compared with their reactants; only the cyclohexane reaction (G4) is favoured in calculations with implicit solvent present compared with the gas phase calculations. E_{TS} are not affected in a consistent manner on going from gas phase to implicit solvent. The transition states for toluene reacting at the ortho

(G8) and para (G12) positions yield lower E_{TS}, by 1.2 and 1.1 kJ mol^{-1} respectively, with the inclusion of implicit solvent effects, whereas the other reactions have lower barriers in the gas phase. The Gibbs energies of the barriers are lowered for the reactions in hexane (G2) and cyclohexane (G4) and increased for the toluene reactions, but again the effects are not large, between 0.3 and 7.1 kJ mol^{-1}.

The solvent ligated complex might undergo a further reaction to eliminate the solvent and leave HMnTMSM. There are two potential mechanisms for eliminating the ligating solvent depending on its hydrogens; if there are β-hydrogens present, such as for n-hexane and cyclohexane, then the solvent ligand could be removed *via* β-hydride elimination, however if no β-hydrogen is present (toluene) then the elimination will likely occur via reaction with H_2. Both of these types of reaction lead to the same Mn-containing product, HMnTMSM as shown in scheme 5. The computed energy data are collated in table 5. Representations of the transition states and the corresponding IRC plots can be found in the supplementary information, figures S17-S32.

Scheme 5. Reactions of the solvent substituted complexes to produce HMnTMSM either via β–hydride elimination or reaction with H_2. Toluene can bond to the complex via any of its carbons, which have all been considered. Sol can be n-hexane , cyclohexane , or toluene.



E_P for the β-hydride eliminations of hexane (H1) and cyclohexane (I1) are both positive. By contrast, the addition of H_2 to eliminate the solvent-ligand is exothermic, with modest activation barriers (51.2 – 63.8 (64.7-75.0) kJ mol^{-1}). Hence reaction with H_2 is much the more likely route. As with the reactions in scheme 4, the differences between the toluene ring sites are small. The toluene methyl site (J5) gives a lower E_P than the ring sites which is likely due to the methyl intermediate being energetically disfavoured. These elimination reactions give less negative E_Ps than reactions E and F; this is due to the solvent-based intermediates being less energetically disfavoured than the abstraction intermediates.

When implicit solvent effects are included in the reactions in scheme 5 (table 5) the β-hydride elimination reactions are less favourable at both the SCF and Gibbs levels. The barrier for the β-hydride elimination of hexene (H2) increases only marginally (a small decrease is seen for the Gibbs energy) however the barrier for the elimination of cyclohexene (I2) is more than doubled. The cause of the large change in barrier is a change in the transition state geometry when the PCM is used; the geometries with and without the PCM are shown in figure 8. The bonds that are breaking and forming involve the highlighted H atom. Without the PCM the Mn-H distance is 1.66 Å, extending to 1.75 Å with the PCM. The distance between the H and cyclohexene carbon, C1, changes much more significantly, from 3.12 Å without the PCM to 1.64 Å with. The Mn to C2 on cyclohexene distance shortens in the presence of the PCM, from 2.43 Å to 2.23 Å. Overall these geometry changes show that the transition state without the PCM is much more like the products than with the PCM which leads to the large change in energy barrier.

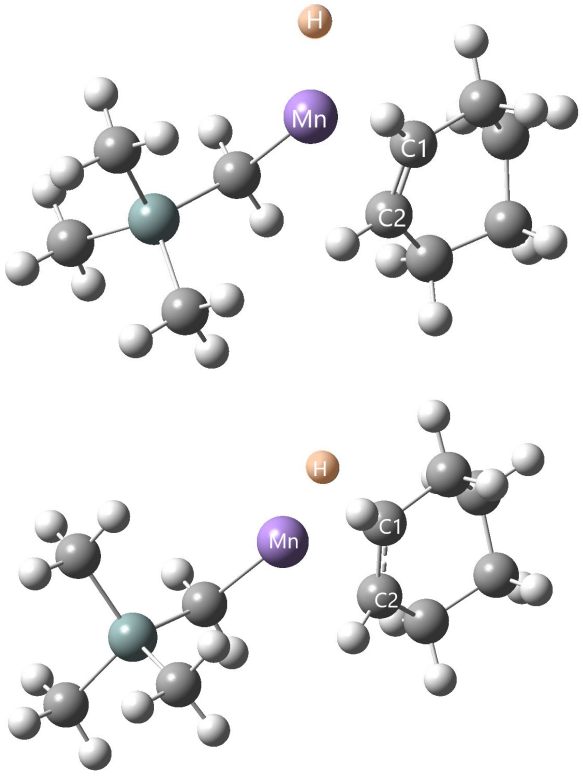


Figure 8. Ball and stick representations of the transition state of the β-hydride elimination of cyclohexene on the cyclohexene substituted precursor with and without the PCM, reactions (I1) and (I2). Mn = purple, C = gray, H = white and Si = teal. Hydrogen involved in the reaction highlighted in orange.

The toluene/H_2 elimination reactions at the toluene ring positions occur less readily with the inclusion of implicit solvation due to larger transition state barriers and lower reaction energies. E_Ps for the elimination via H_2 for hexane, cyclohexane, and toluene at the methyl position are stabilised in the solvent. The toluene methyl position (J6) is still the least favourable E_P of this reaction set. The order of preference for reaction on the ring positions changes from para (J11) > meta (J9) > ortho (J7) to para (J12) > ortho (J8) > meta (J10). At the Gibbs level, the inclusion of implicit solvent disfavours the reactions eliminating cyclohexane (J2) and toluene at the meta position (J10) while the other reactions are more favourable in solvent. Overall, the effect of implicit solvent on the elimination reaction E_Ps is only a few kJ mol^{-1}, as noted for the other reactions studied to this point.

E_{TS} are all increased in solvent vs the gas phase calculations at the SCF level. At the Gibbs level the barrier is lowered in the majority of cases with the only exceptions being toluene

Table 6. Energies (kJ mol^{-1}) of the condensation of two units of Mn(TMSM)$_2$ and/or MnTMSM. L, M and N refer to labels in scheme 7. $\Delta E(\Delta G)$.

Reaction	Reactants	$E_{R@inf}$	E_P	$E_{P@inf}$	E_{TS}
L	2 x Mn(TMSM)$_2$	74.6 (6.8)	-12.0 (-14.3)	22.7 (-29.3)	99.3 (91.5)
M	Mn(TMSM)$_2$ + MnTMSM	188.8 (131.5)	70.5 (57.7)	As E_P	125.7 (113.0)
N	2 x MnTMSM	67.1 (21.9)	-35.3 (-50.5)	-4.3 (-52.4)	74.4 (51.6)

at the ortho and meta positions (J8 and J10); for ortho the difference is very small at 0.2 kJ mol^{-1} whereas for the meta position the difference is 5.8 kJ mol^{-1}.

HOMOLYTIC CLEAVAGE OF MN(TMSM)$_2$

Another possible way to eliminate TMS from the precursor is via homolytic cleavage at one of the Mn-C bonds; scheme 6 reaction K. This reaction is different from those previously discussed as it proved impossible to produce an optimised structure for the associated products, unsurprising given that they are both radicals. To explore the energy profile for the Mn-C breaking process, we turned to the ModRedundant method described in the methodology. Lengthening the chosen Mn-C bond produced the SCF energies plotted in figure 9. Starting from the optimised structure, the separation continues smoothly until 3.80 Å – the energy profile is typical of barrierless radical reactions.[32] Comparing the energies of the reactant with the products at infinite separation gives an $E_{p@inf}$ of 279.3 (220.5) kJ mol^{-1} and so this cleavage reaction is unlikely to occur.

Scheme 6. Homolytic cleavage of an Mn(TMSM)$_2$ Mn-C bond, K.

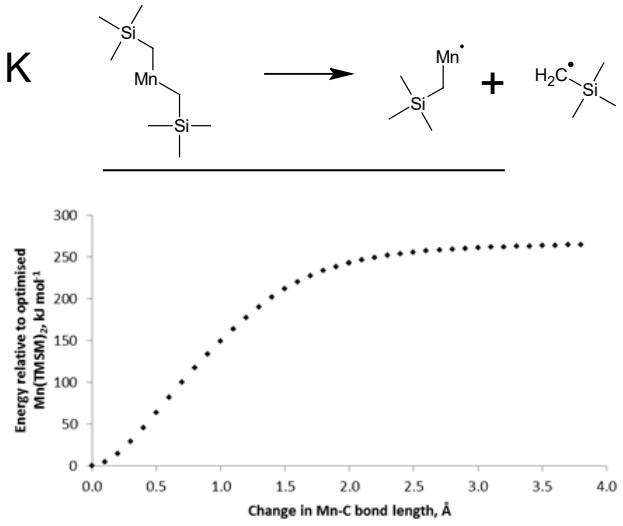


Figure 9. Energy profile for increasing the Mn-C distance in Mn(TMSM)$_2$, reaction K in scheme 6.

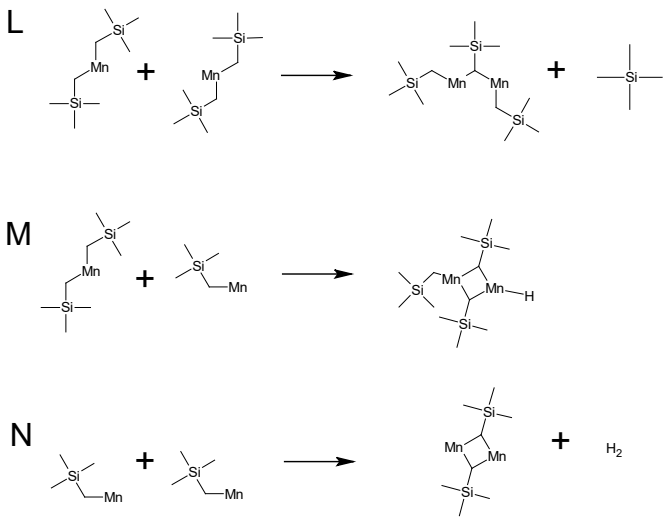
We have also tested the effect of the PCM of the different solvents on the radicals; the effect on the energy is very minor. In the hexane PCM there is a slight decrease in the energy required to form the products of 1.9 (6.1) kJ mol^{-1} vs the gas phase value. The other two solvents behave similarly, with cyclohexane giving 277.4 (214.2) kJ mol^{-1} and toluene giving 277.6 (213.8) kJ mol^{-1}.

STRUCTURE EXTENSION VIA CONDENSATION OF MN(TMSM)$_2$ AND MNTMSM

Another likely process in the production of KMH-1 is building up the extended structure from small components; we here limit our scope to examining the interaction of two species each with a single Mn centre. This task has been split into two sections; first we probe the reactions that can occur when the TMSM ligands are still present and then we examine systems where these have been eliminated and replaced with hydrides. This should provide insight into whether or not the elimination occurs prior to condensation. Also studied are complexes containing either Mn(II) or Mn(I) as we do not know whether the metal centres are reduced before or after the extended structures are formed.

The first set of reactions, with TMSM still present, is given in scheme 7. The first reaction in this set, L, shows two Mn(TMSM)$_2$ complexes coming together to produce a structure with two metal centres whilst releasing TMS. The product of this reaction has a TMSM group bridging between the two metal centres.

Scheme 7. Condensation of Mn(TMSM)$_2$, reaction L, and/or MnTMSM, reactions M and N, to form species with two metal centres.



Reactions M and N are somewhat different as Mn(I) centres are present. The reaction between MnTMSM and Mn(TMSM)$_2$, M, is a single species whereas the combination of two MnTMSM, N, releases H_2. The Mn-containing products are also distinct from reaction L as the products have two bridging TMSM ligands.

Table 6 collects the calculated energies for the steps along these condensation reactions. Representations of the transition

states and the corresponding IRC plots can be found in the supplementary information, figures S33-S36. The reaction of two $Mn(TMSM)_2$ units, L, is slightly exothermic, by 12.0 (14.3) kJ mol^{-1}, and has a barrier of 99.3 (91.5) kJ mol^{-1}. For reaction N, formation of the products is more favourable, along with a smaller transition state barrier, than the completely Mn(II) system, L. The reaction involving both Mn(I) and Mn(II), M, is very endothermic, 70.5 (57.7) kJ mol^{-1}, thus unlikely to be a major factor in the formation of KMH-1.

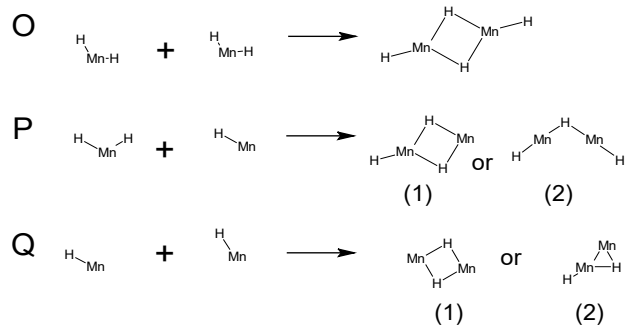
Hence the reactions involving either only Mn(I), N, or Mn(II), L, are both favourable. KMH-1 could, therefore, be produced from an initial condensation as described here followed by elimination of the organic ligands via a route similar to those discussed above for monometallic species.

STRUCTURE EXTENSION VIA CONDENSATION OF MnH_2 AND MNH

The second set of possible condensation reactions, scheme 8, involves the hydrides of Mn(I) and Mn(II). Calculation of these reactions encountered similar difficulties to those seen for homolytic cleavage, reaction K, and so we have followed the same method as used there. For these reactions we chose the Mn-Mn coordinate for extension as this is applicable to all of the structures, and produces the desired reactants and products.

The first reaction, O, is the condensation of two MnH_2 complexes; the energy difference, E_P is -166.1 (-118.0) kJ mol^{-1}. We also calculate the energy at a Mn separation of 5.00 Å, -149.4 kJ mol^{-1}. The E_p of these systems is impractical to calculate as the associated reactants are difficult to calculate at an energy minimum due to the very facile nature of the reaction. The change in energy with variation in the Mn-Mn distance is plotted in figure 10; these data were obtained in two ways (i) starting from the product geometry and pulling the MnH_2 units apart until an increase in separation of 3.60 Å was reached, black crosses and (ii) pushing the MnH_2 fragments together from this distance along the reaction trajectory, red diamonds. While both approaches yield the same result, these curves are not as smooth as in figure 9; there is an abrupt change in the gradient at an Mn-Mn coordinate of +1.00 Å; the geometries before and after this point are very different, suggesting a jump from one potential energy surface to another occurs at this point when approached from either direction; figure 11 shows these two geometries.

Scheme 8. Condensation of MnH_2, reaction K, and/or MnH, reactions L and M.



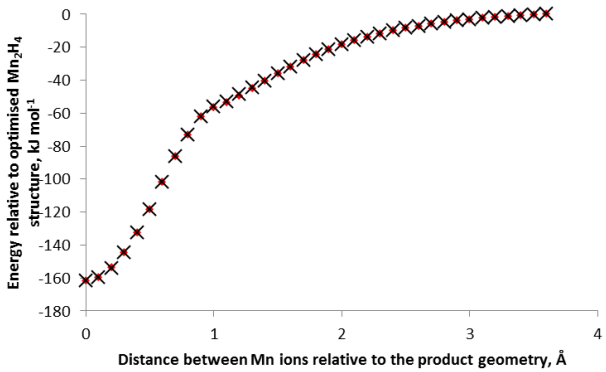


Figure 10. Energy profile for varying the Mn-Mn distance between two MnH_2 species, reaction O scheme 8. From Mn_2H_4 to 2 x MnH_2: black crosses. From 2 x MnH_2 to Mn_2H_4: red diamonds.

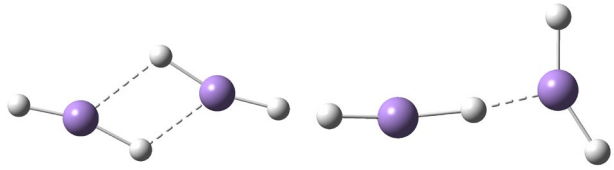


Figure 11. Ball and stick representations of key geometries along the reaction coordinate for reaction O in scheme 8. Left: Extension of Mn-Mn by 1.0 Å from equilibrium, Right: Extension of Mn-Mn by 1.1 Å from equilibrium. Mn: Purple, H: white.

The second reaction of this set, P, is between MnH and MnH_2. The product P2 is more favourable than the cyclic product P1 by 22.5 (26.6) kJ mol^{-1} and so is the focus of this investigation. The energy gained when the molecules approach each other from an infinite separation is -599.2 (-542.2) kJ mol^{-1}, much greater than any other reaction energies we have thus far determined. An energy profile of this process along the Mn-Mn coordinate can be found in figure S39 along with a detailed discussion; although the energy surface is not entirely smooth, there is no barrier to the reaction, as with reaction O.

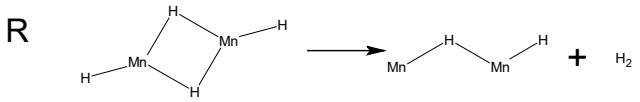
Of the two possibilities for Mn_2H_2, reaction Q, the most stable product is Q1, by 13.4 (13.6) kJ mol^{-1}. The energy difference vs infinite separation is extremely large: -983.2 (-910.7) kJ mol^{-1}. The energy profile of this system following the Mn-Mn coordinate, together with a discussion, can be found in figures S40 and S41.

In summary, the reactions between the Mn(I) and Mn(II) hydride monomers are barrierless and strongly exothermic, with energy releases ranging from -166.1 to -983.2 kJ mol^{-1}. Should such species be formed in the production of KMH-1, there are very strong thermodynamic drivers to their forming multimetallic species.

REDUCTION OF MN(II) TO MN(I)

As discussed earlier, we believe there to be a significant amount of Mn(I) in KMH-1[11]. In addition to the cleavage reaction discussed earlier, reaction K, we now consider two other reactions that could account for the reduction from the bis(trimethylsilylmethyl) manganese (II) precursor. The first reaction, scheme 9, shows the release of H_2 from Mn_2H_4, leaving M_2H_2, a small model structure for the extended system.

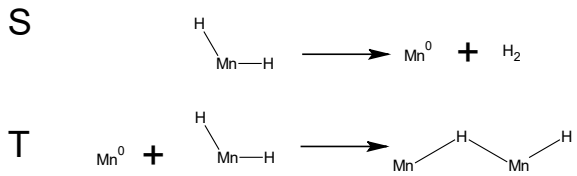
Scheme 9. Reactions showing the release of H_2 from Mn_2H_4, leaving M_2H_2.



The reaction is endothermic, with an energy barrier of 69.0 (65.0) kJ mol^{-1} to products that lie 53.3 (60.8 kJ mol^{-1} higher in energy than the reactant. It is also of note that there is a large energy requirement to separate the product molecules to infinite distance, 120.3 (103.9) kJ mol^{-1}, as the H_2 produced has a strong affinity for the Mn(I) centres and prefers to bind with the new system; this reflects well what we have seen for H_2 interacting with KMH-1 as the strength of binding in that system increases with the amount of Mn(I) present. The transition state and intrinsic reaction coordinate plot for this reaction are shown in figures S42 and S43 respectively

The other route we have considered for the production of Mn(I) ions is presented as reactions S and T in scheme 10. This is a two step process; the first step generates Mn metal via the release of H_2 from MnH_2 and the second sees the Mn metal atom reacting with a further unit of MnH_2 to generate Mn_2H_2.

Scheme 10. The reduction of Mn(II) to Mn(I) *via* the generation of Mn^0 in one step (S) and then the reaction of this atom with MnH_2 (T).



These reactions are barrierless and so the method used for the combination of the hydrides, reactions O, P and Q, was also used in these cases. The energy changes of reaction S in scheme 10 was tracked by following the H-Mn-H angle as the reaction coordinate. The energy profile can be found in figure S44. The energy required to generate the products, H_2 forming a complex with the Mn atom, from MnH_2 was found to be 125.3 (124.8) kJ mol^{-1}. When the H_2 is pulled to infinite distance this increases to 201.0 (187.4) kJ mol^{-1}. These high energies suggest that this process is very unlikely to occur.

The energy profile for reaction T in scheme 10 was generated by plotting the energy along the Mn-Mn coordinate, this can be found in figure S45. When the reactants are started at an Mn-Mn distance 7.8 Å greater than the product geometry we find an energy gain of 211.5 kJ mol^{-1} when bringing the fragments together, which offsets the energy requirement of the first step in the mechanism.

CONCLUSIONS

We have explored several series of reactions that could occur in the production of KMH-1 from the Mn(II) precursor material $Mn(TMSM)_2$, including the formation of hydrides, ways to generate the extended structure and reactions to produce species with Mn(I) centres.

Single-step elimination of TMS from the precursor via reaction with H_2, reactions A and B, is more likely than the two step elimination reactions C through F and G though J, as the latter processes have higher barriers. Of those two-step processes, substituting one of the TMS ligands with a molecule of solvent, reactions G1 through G12, is the most likely initial step. The other processes - abstraction of tetramethylsilane via interaction with γ- or α-hydrogens on the ligand (reactions C and D) have higher barriers.

Condensation of $Mn(TMSM)_2$ or dimerization of MnTMSM, reactions L and N, are viable reactions to grow the network from its molecular components as both of these reactions are exothermic. Condensation reactions of species post TMS elimination, reactions O, P and Q, are all barrierless and very exothermic and are therefore also likely to contribute to the growth of the system.

Of the reactions R and ST, and the cleavage reaction K - possible routes to Mn(I) ions in KMH-1 - the most likely is the release of H_2 from the extended structure, reaction R, as the other two have at least one step with a large reaction energy.

Implicit solvation effects have a minor impact on reaction energies, in most cases less than 10 kJ mol^{-1}.

In summary, we propose that the most likely route to the formation of Mn hydrides is via elimination of TMS by reaction with H_2, reactions A and B. These hydrides could then react to grow the extended KMH-1 structure via reactions O-Q. Alternatively, multimetallic TMS-containing products could be formed via reactions L-N, after which the TMS ligand would be eliminated via reactions analogous to A and B. The formation of Mn(I) centres from Mn(II) hydrides is most likely via reaction R.

ASSOCIATED CONTENT

Supporting Information

(Word Style "TE_Supporting_Information**").** A listing of the contents of each file supplied as Supporting Information should be included. For instructions on what should be included in the Supporting Information as well as how to prepare this material for publication, refer to the journal's Instructions for Authors.

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Notes:
The authors declare no financial conflicts of interest.

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Formation of Mn hydrides from bis(trimethylsilylmethyl) Mn(II): a DFT study

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Reference for Gaussian 09 Revision D.01 :

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Supplementary Figures

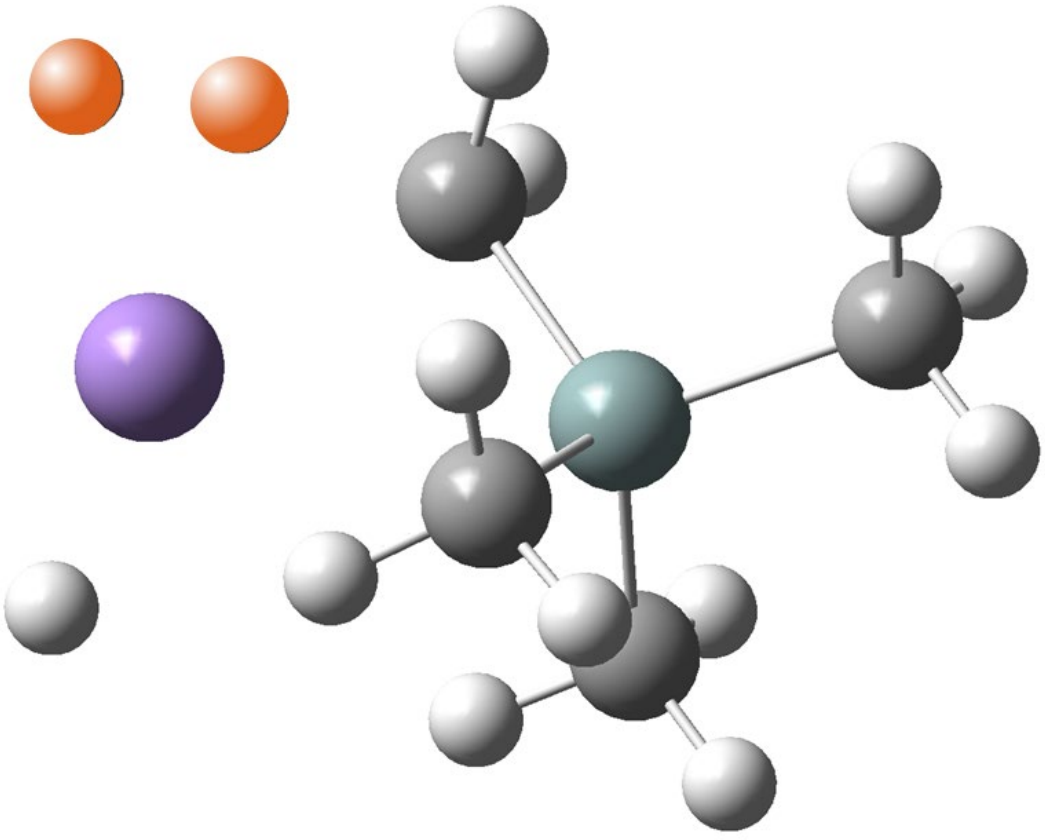


Figure S1. Transition state geometry for the reaction B between H_2 and HMnTMSM eliminating TMS. Imaginary mode: 1036 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H_2 highlighted in orange.

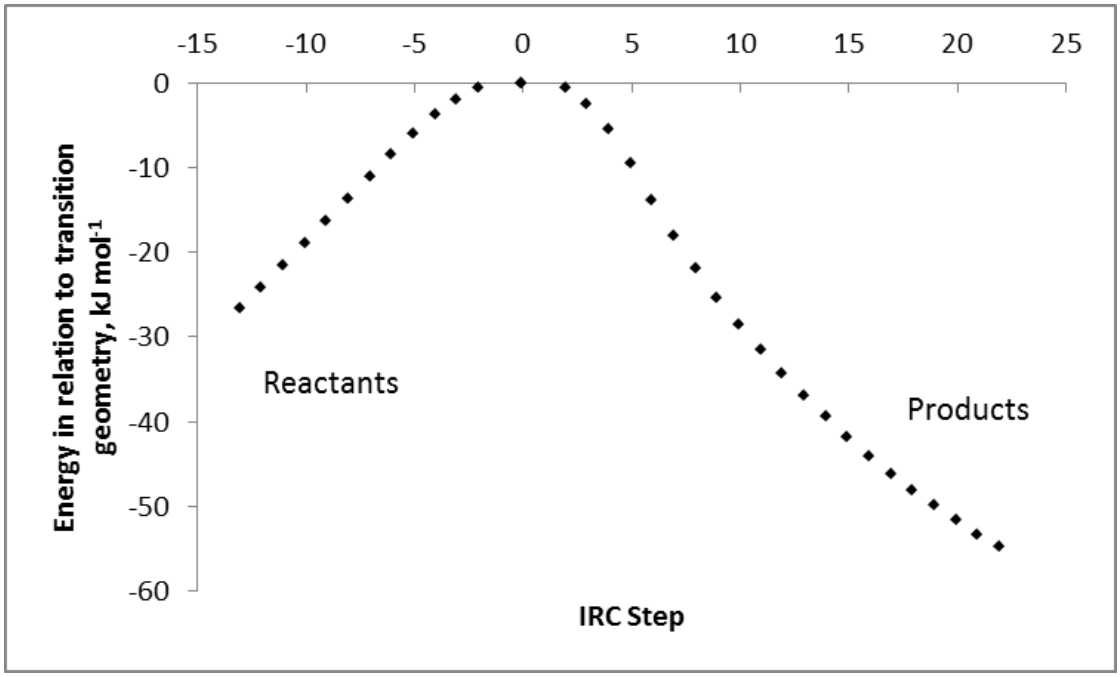
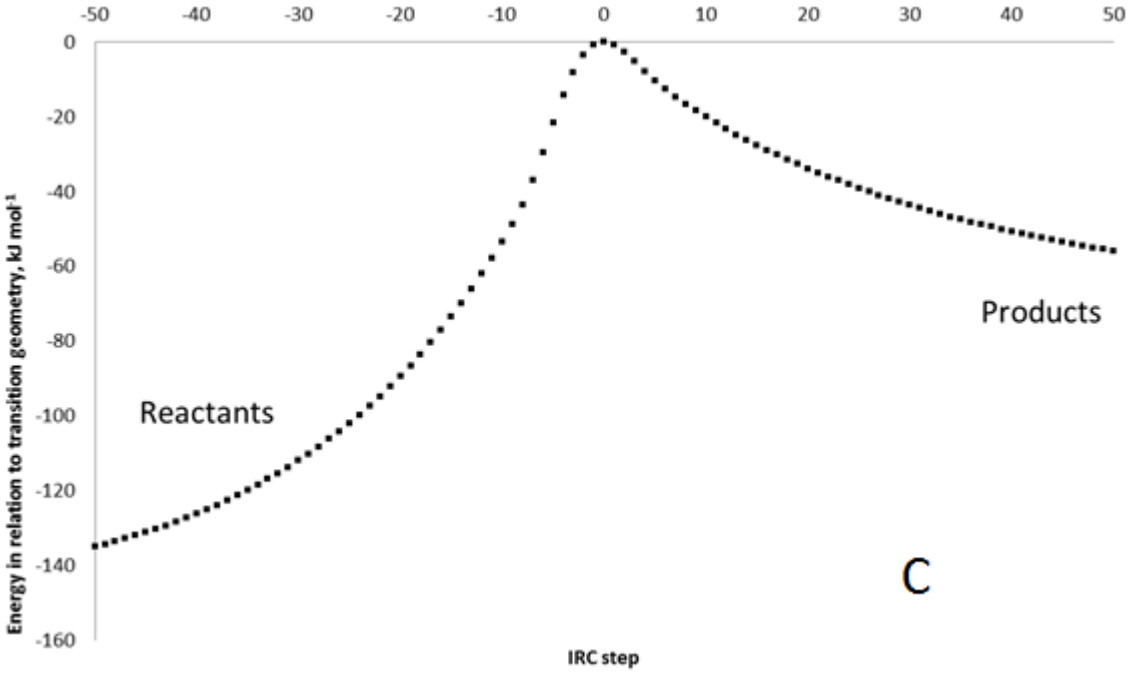
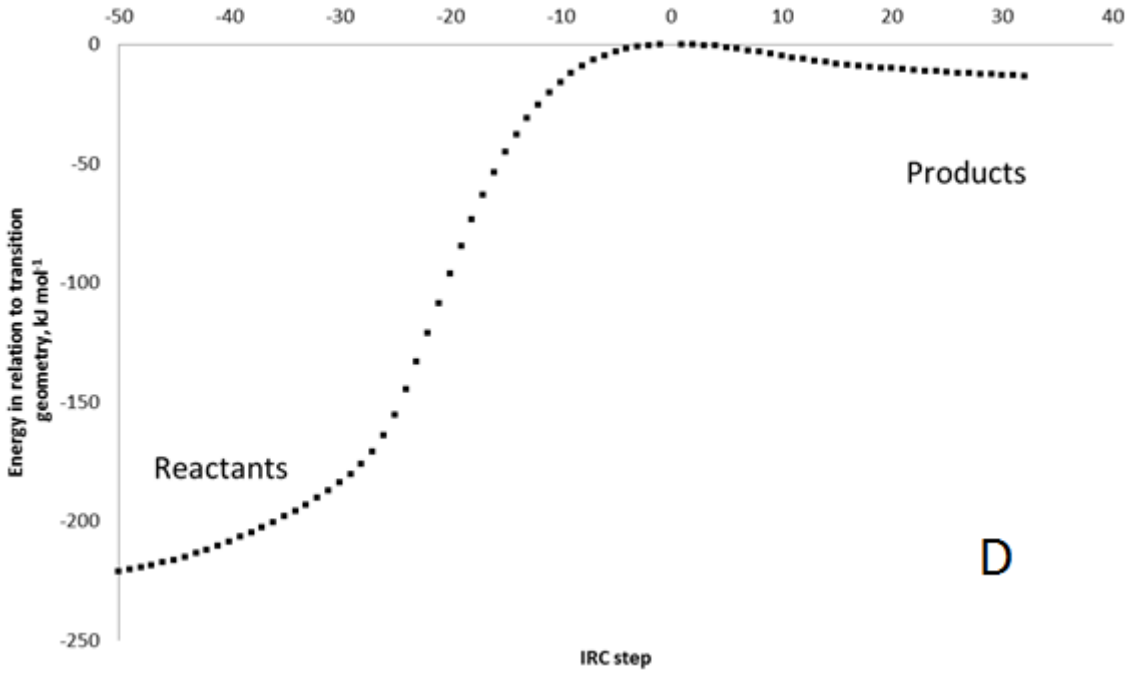


Figure S2. IRC from the transition state geometry in figure S1.





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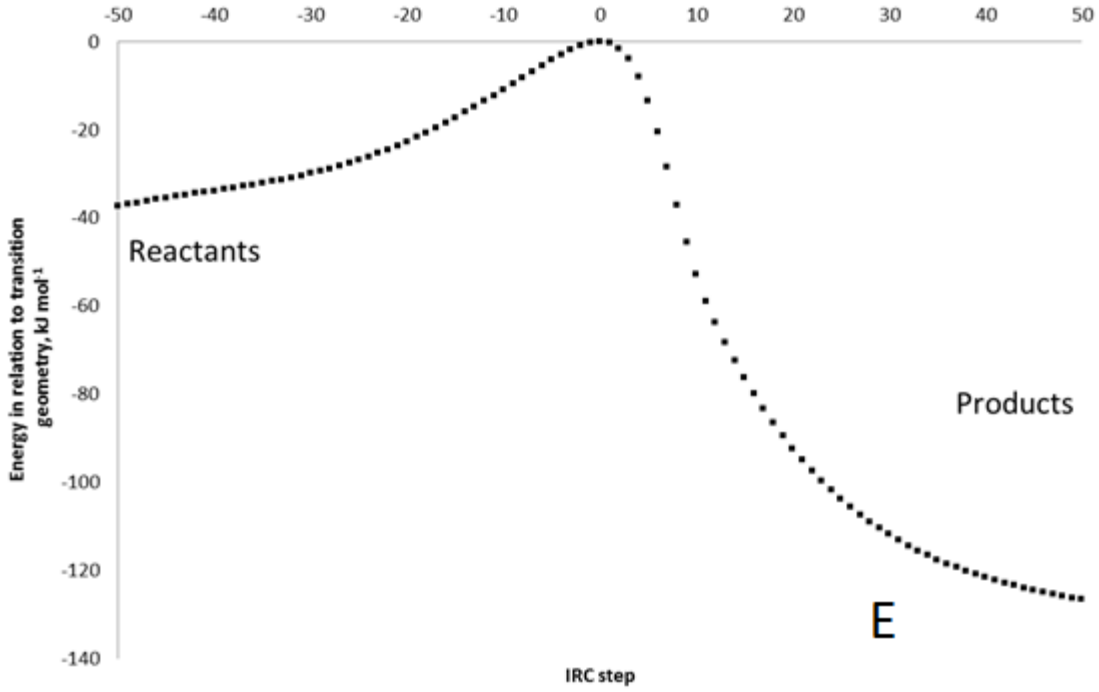

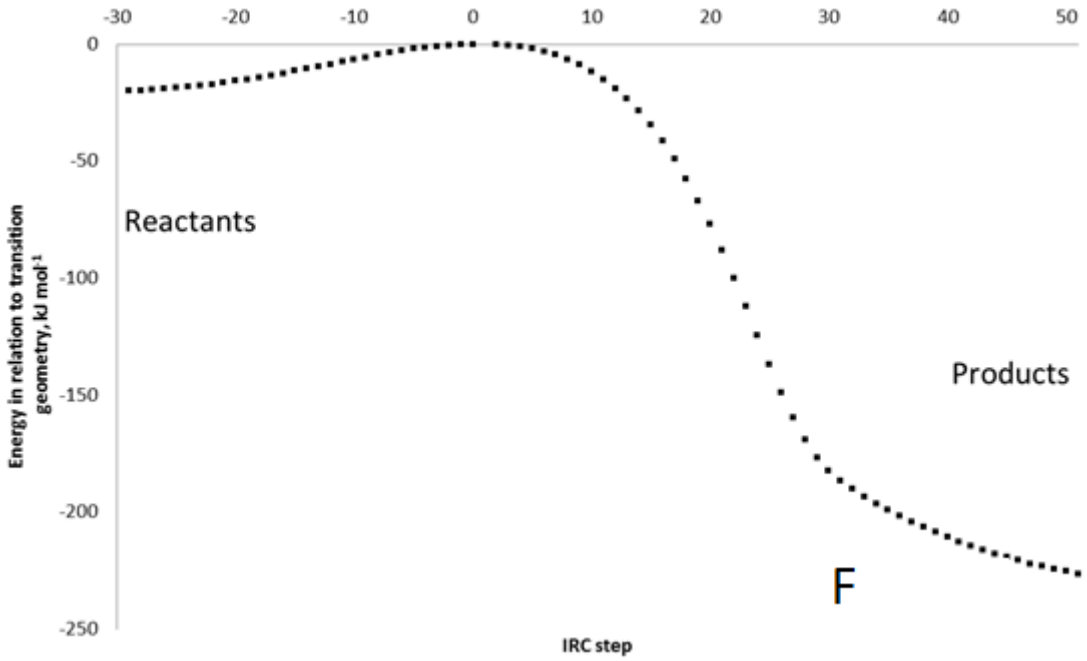

Figure S4. IRC from the transition state geometries in figure 6.

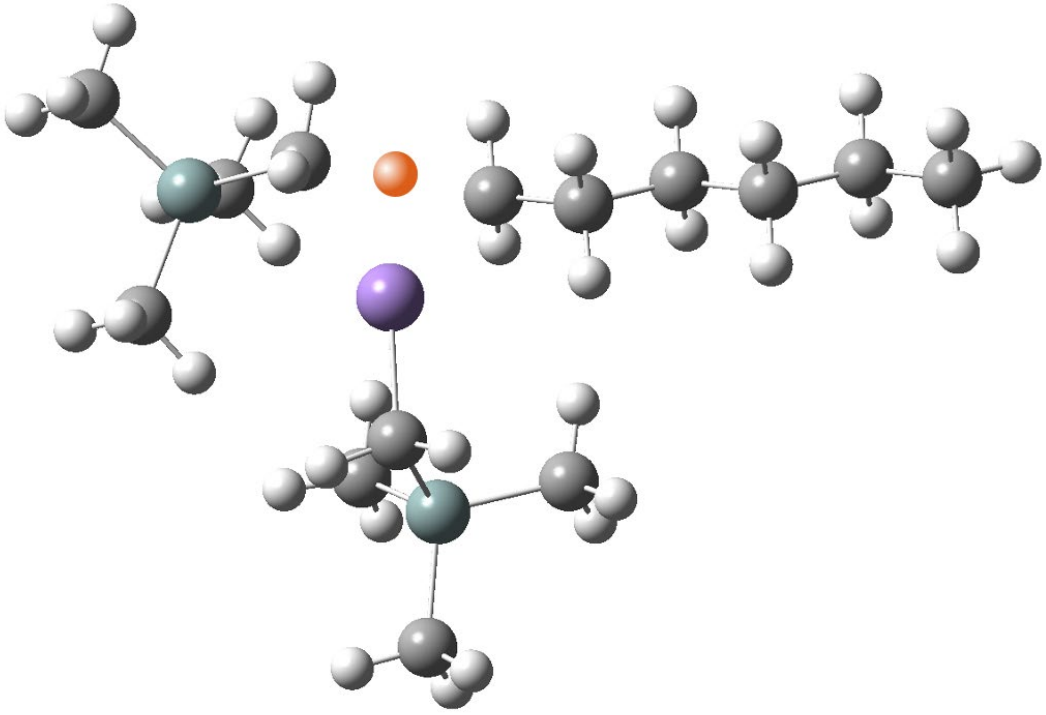

Figure S5. Transition state geometry for the reaction G1 between hexane and $Mn(TMSM)_2$ substituting TMSM for hexane. Imaginary mode: 1266 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

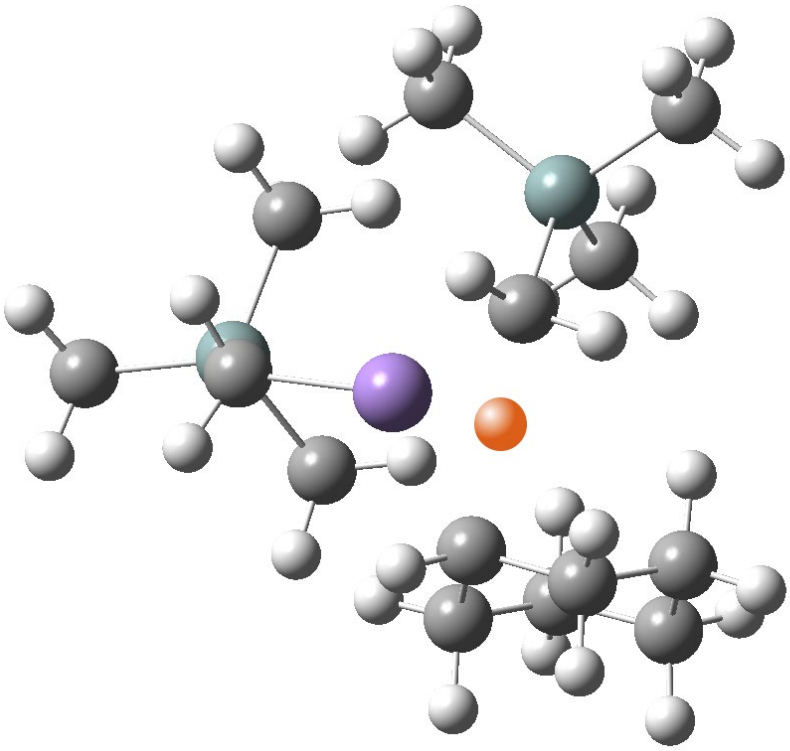

Figure S6. Transition state geometry for the reaction G3 between cyclohexane and $Mn(TMSM)_2$ substituting TMSM for cyclohexane. Imaginary mode: 1214 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

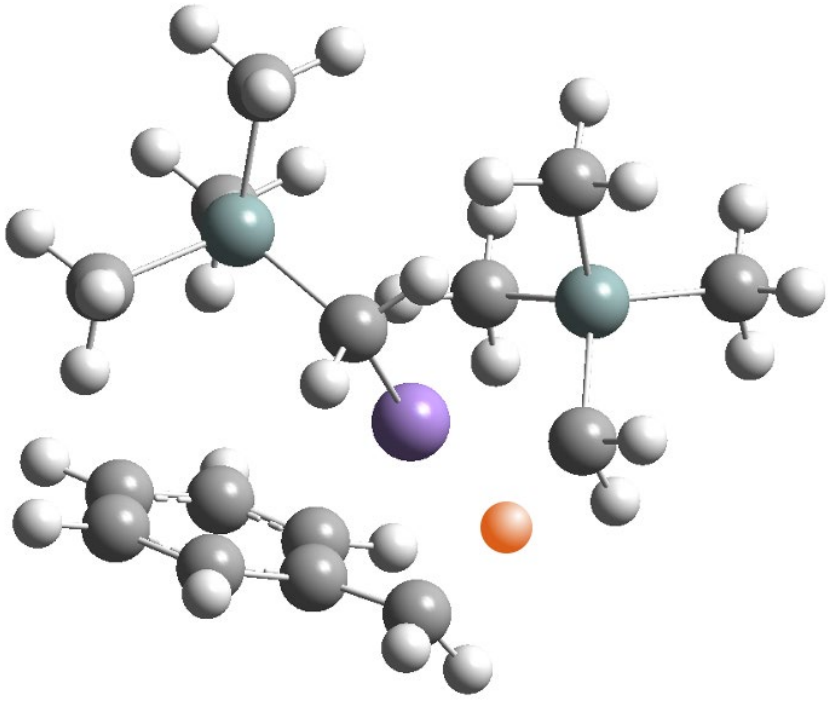

Figure S7. Transition state geometry for the reaction G5 between toluene and $Mn(TMSM)_2$ substituting TMSM for toluene at the methyl position. Imaginary mode: 1236 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

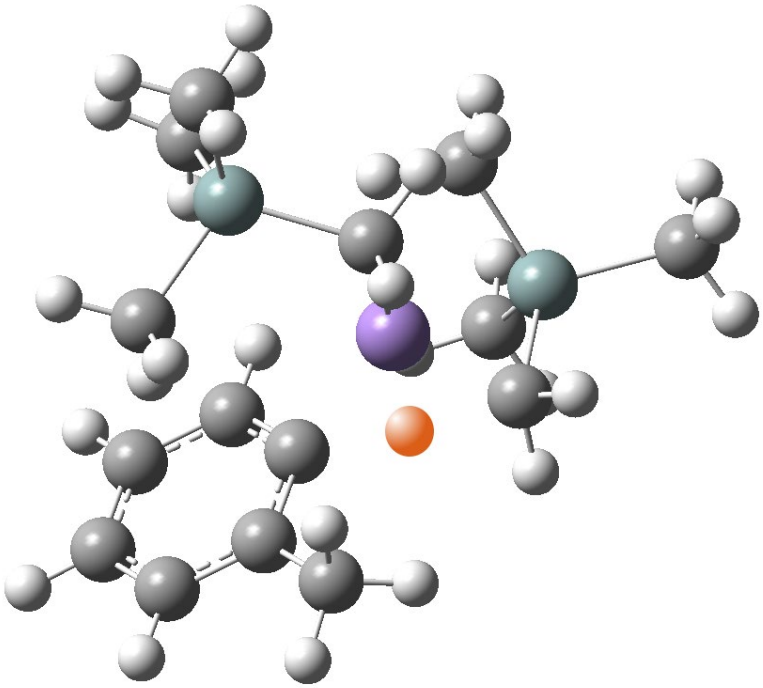

Figure S8. Transition state geometry for the reaction G7 between toluene and $Mn(TMSM)_2$ substituting TMSM for toluene at the ortho position. Imaginary mode: 1256 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

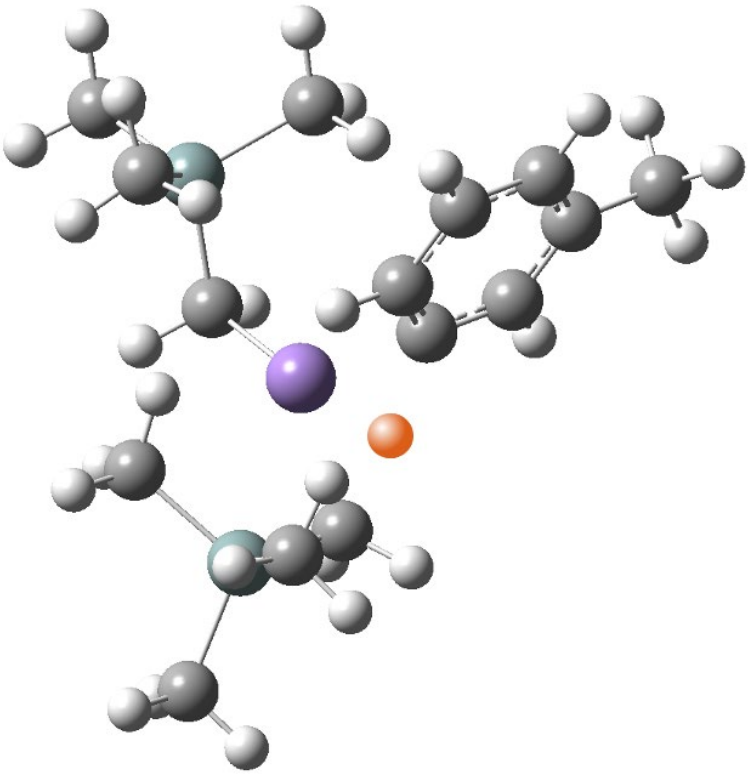

Figure S9. Transition state geometry for the reaction G9 between toluene and $Mn(TMSM)_2$ substituting TMSM for toluene at the meta position. Imaginary mode: 1272 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

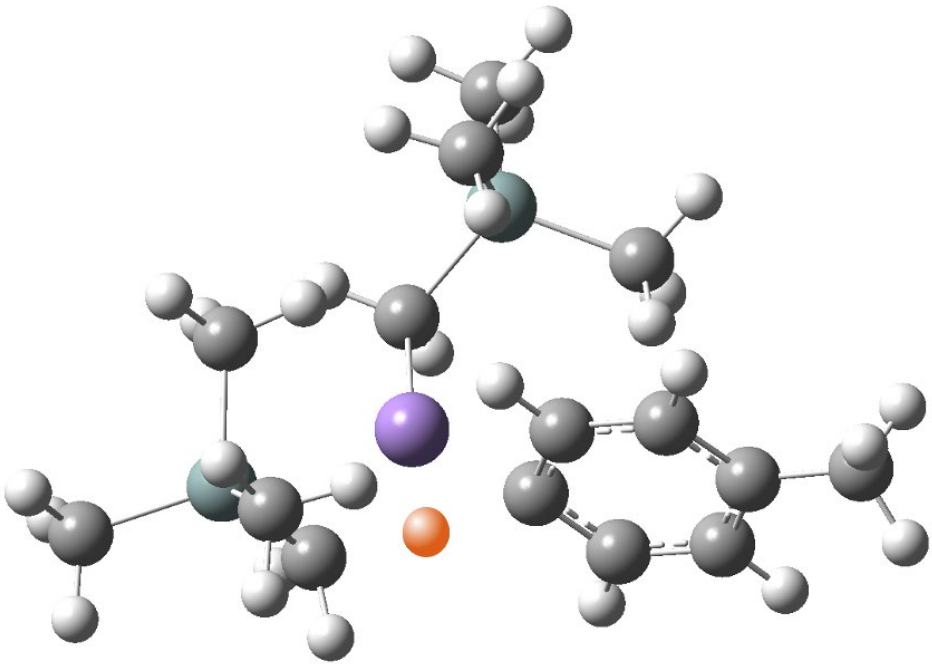

Figure S10. Transition state geometry for the reaction G11 between toluene and $Mn(TMSM)_2$ substituting TMSM for toluene at the para position. Imaginary mode: 1272 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

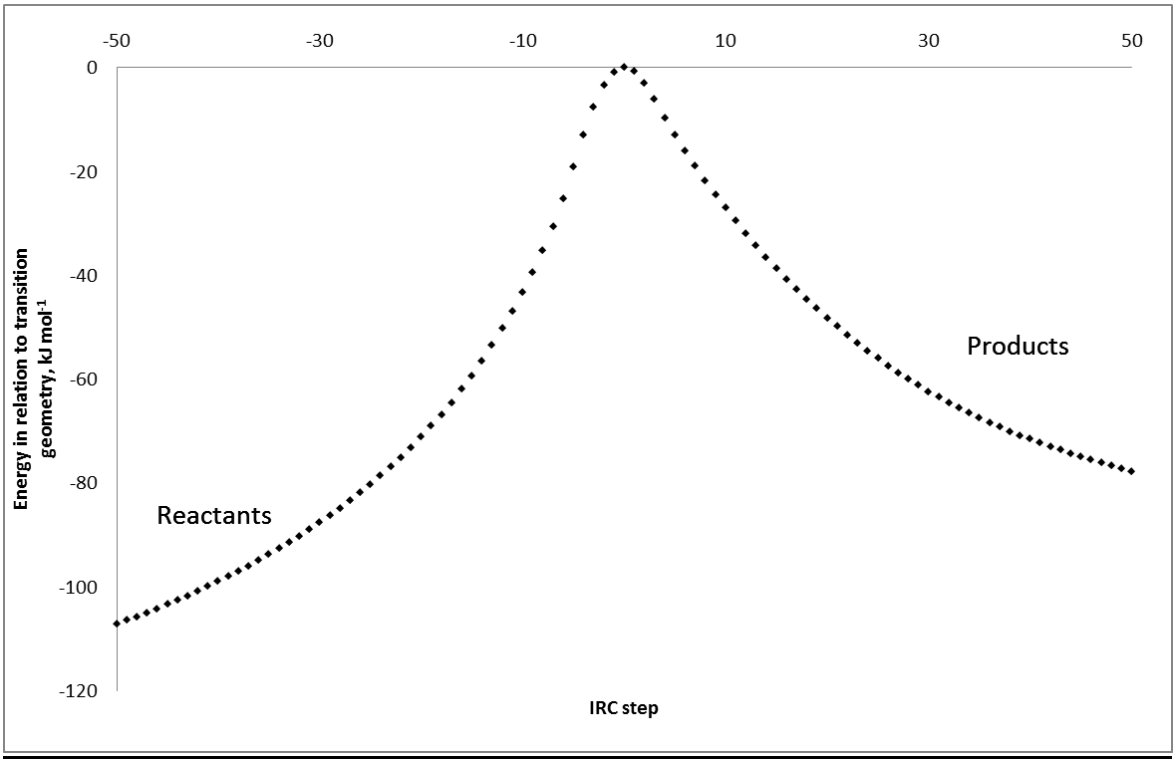

Figure S11. IRC from the transition state geometry in figure S5.

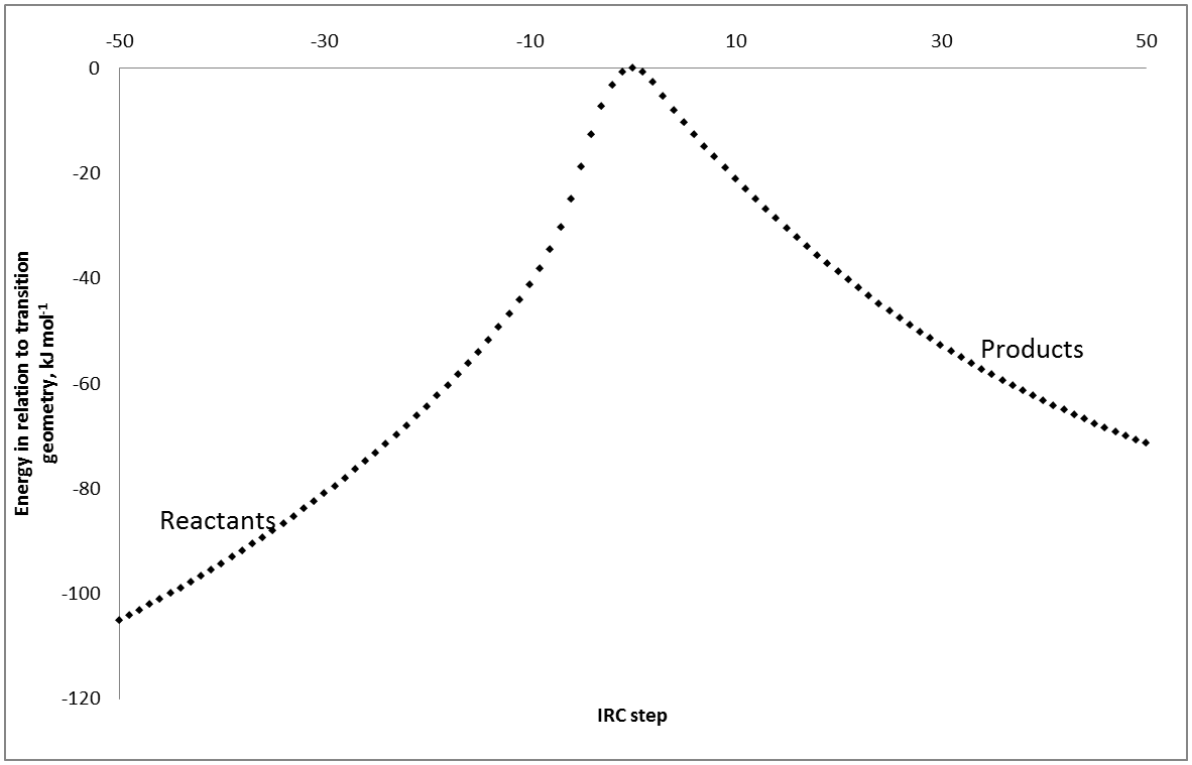

Figure S12. IRC from the transition state geometry in figure S6.

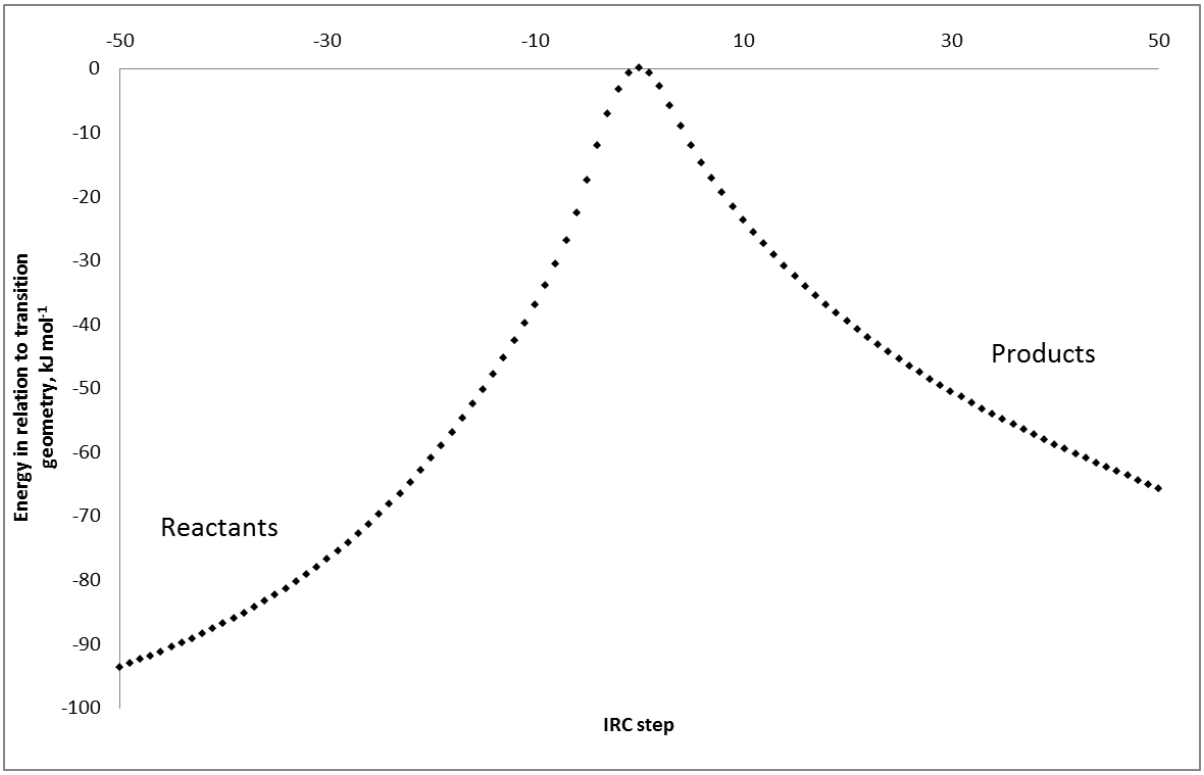

Figure S13. IRC from the transition state geometry in figure S7.

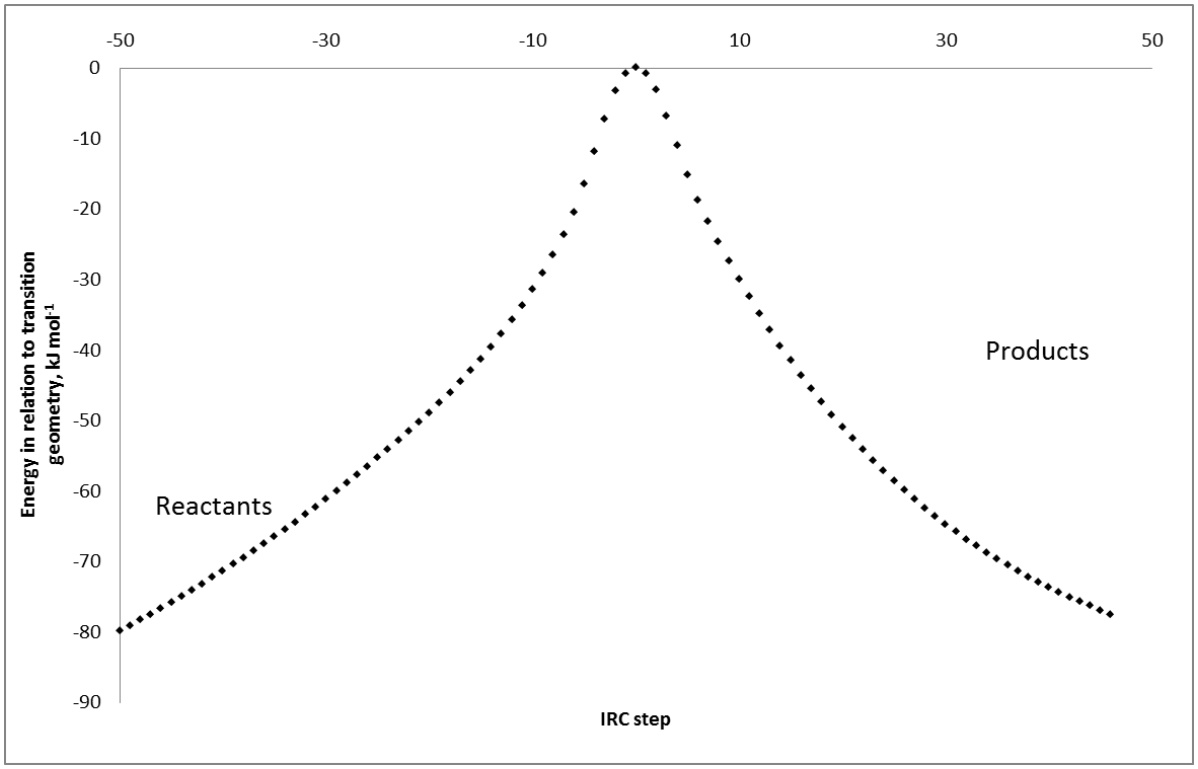

Figure S14. IRC from the transition state geometry in figure S8.

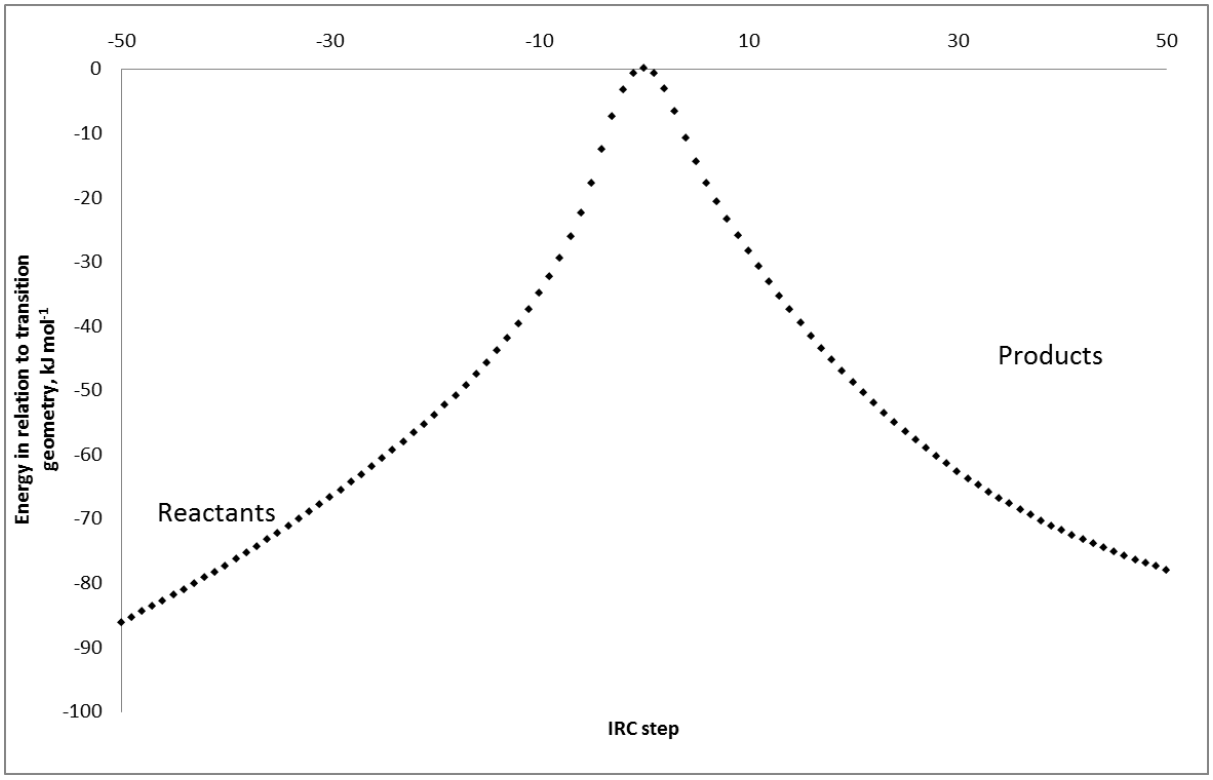

Figure S15. IRC from the transition state geometry in figure S9.

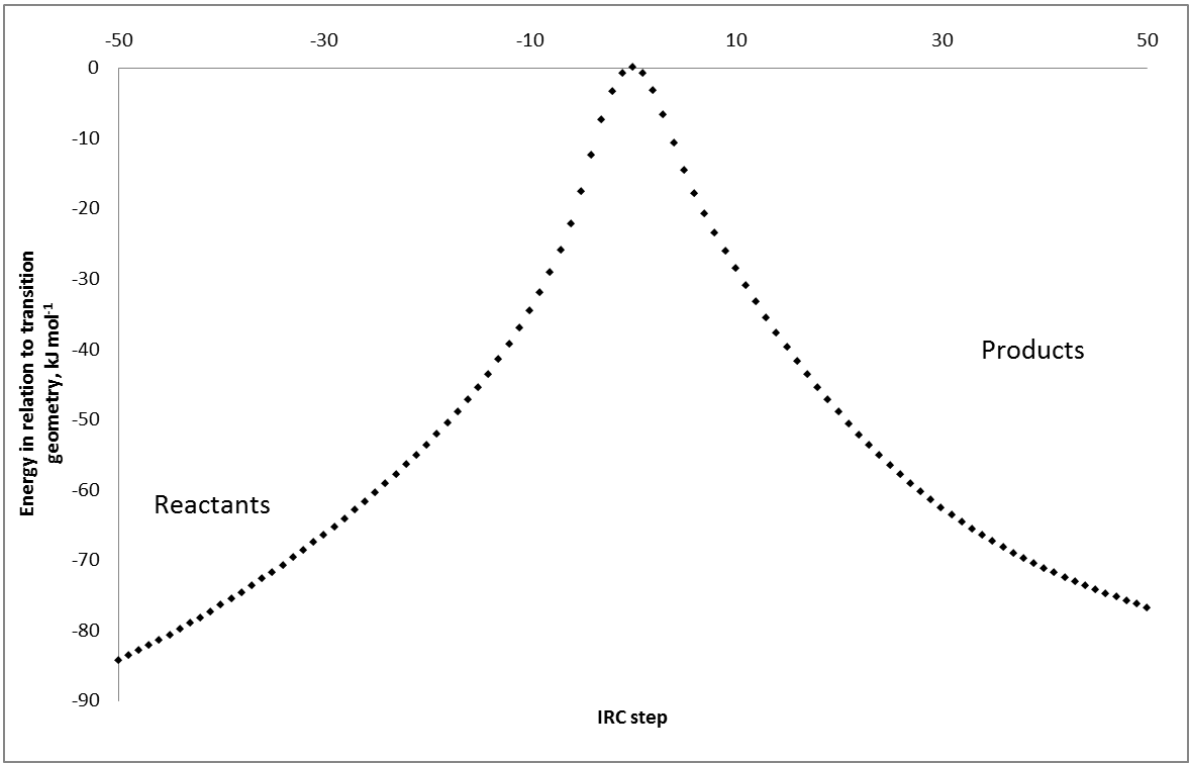

Figure S16. IRC from the transition state geometry in figure S10.

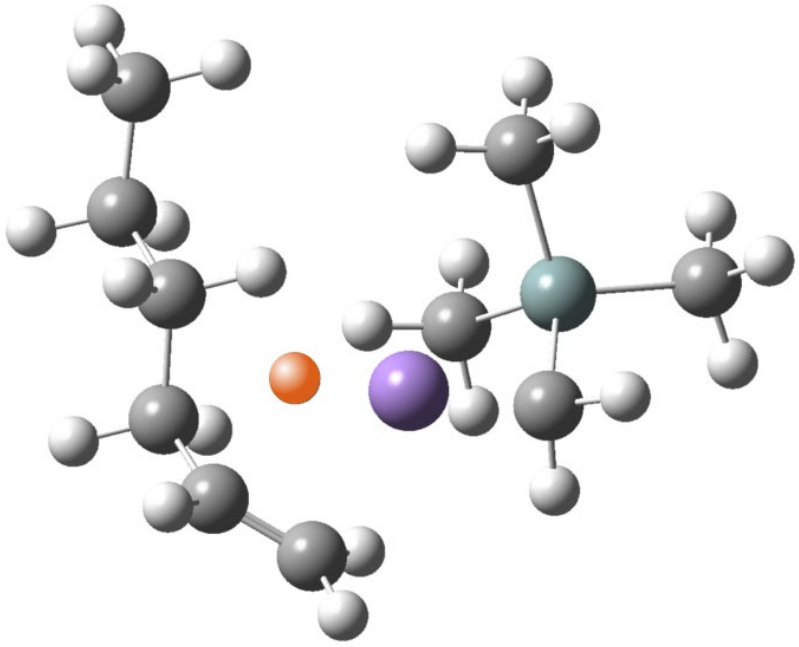

Figure S17. Transition state geometry for the β-hydride elimination reaction H1 of $Mn(TMSM)C_6H_{13}$. Imaginary mode: 98 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

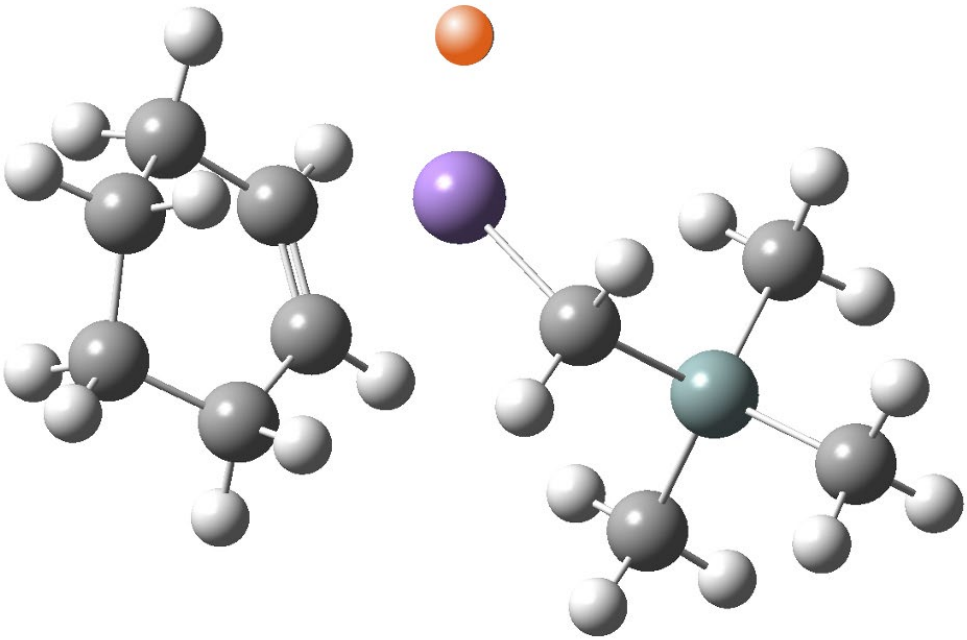

Figure S18. Transition state geometry for the β-hydride elimination reaction I1 of Mn(TMSM)C_6H_{11}. Imaginary mode: 23 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

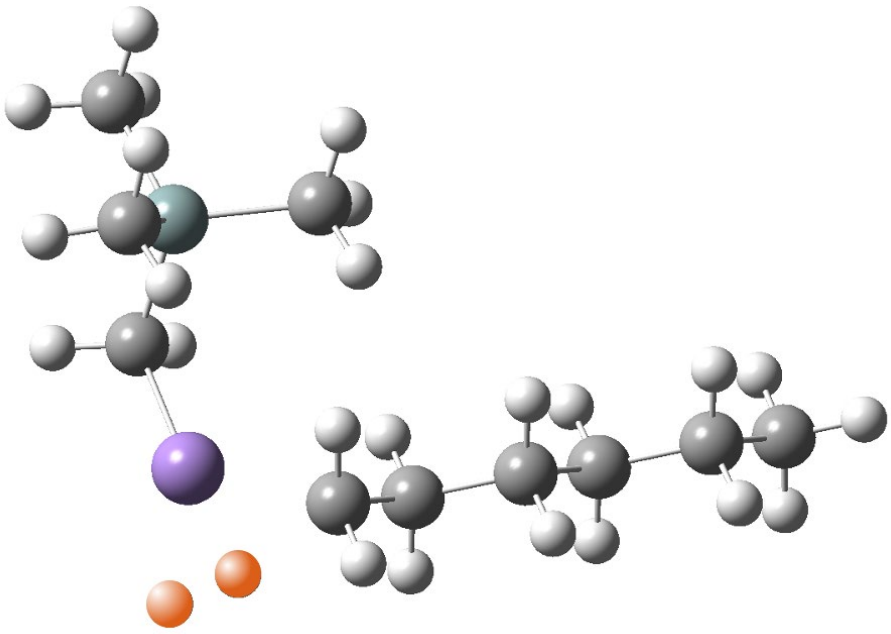

Figure S19. Transition state geometry for the reaction J1 between Mn(TMSM)C_6H_{13} and H_2 eliminating C_6H_{14}. Imaginary mode: 945 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H2 highlighted in orange.

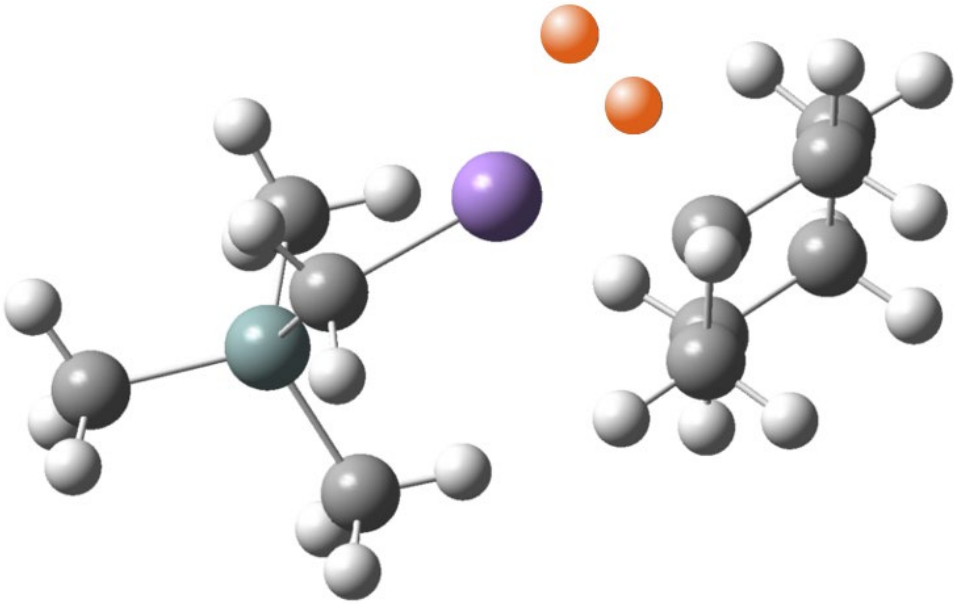

Figure S20. Transition state geometry for the reaction J3 between Mn(TMSM)C_6H_{11} and H_2 eliminating C_6H_{12}. Imaginary mode: 901 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H2 highlighted in orange.

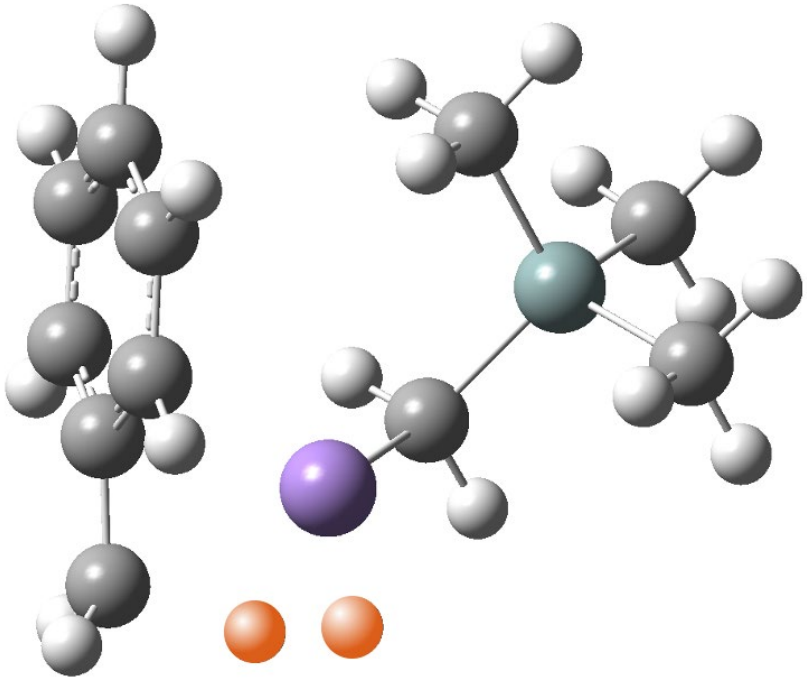

Figure S21. Transition state geometry for the reaction J5 between Mn(TMSM)C_6H_7 (methyl sub.) and H_2 eliminating C_6H_8. Imaginary mode: 937 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H2 highlighted in orange.

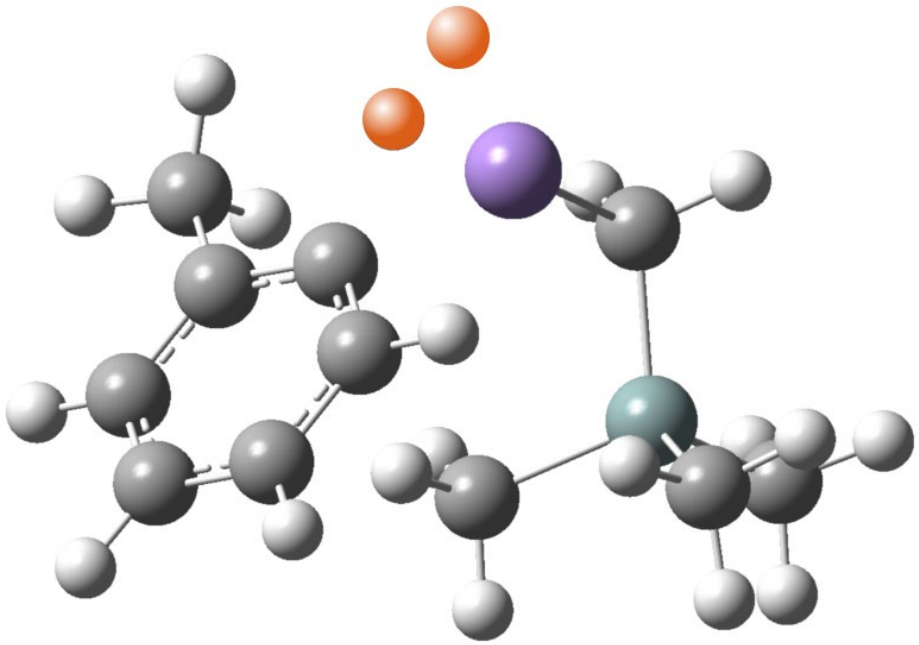

Figure S22. Transition state geometry for the reaction J7 between Mn(TMSM)C_6H_7 (ortho sub.) and H_2 eliminating C_6H_8. Imaginary mode: 983 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H2 highlighted in orange.

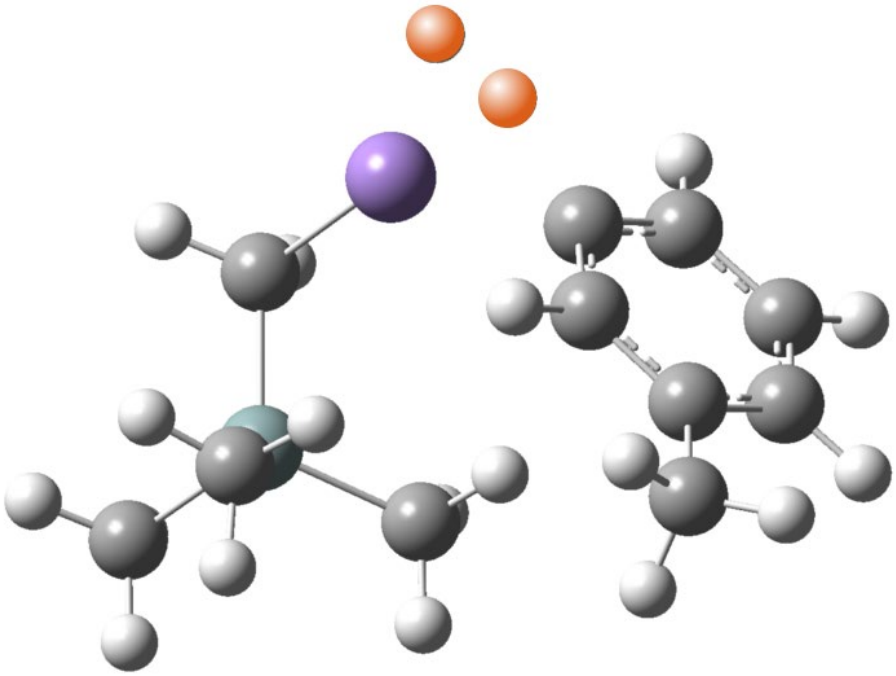

Figure S23. Transition state geometry for the reaction J9 between Mn(TMSM)C_6H_7 (meta sub.) and H_2 eliminating C_6H_8. Imaginary mode: 965 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H2 highlighted in orange.

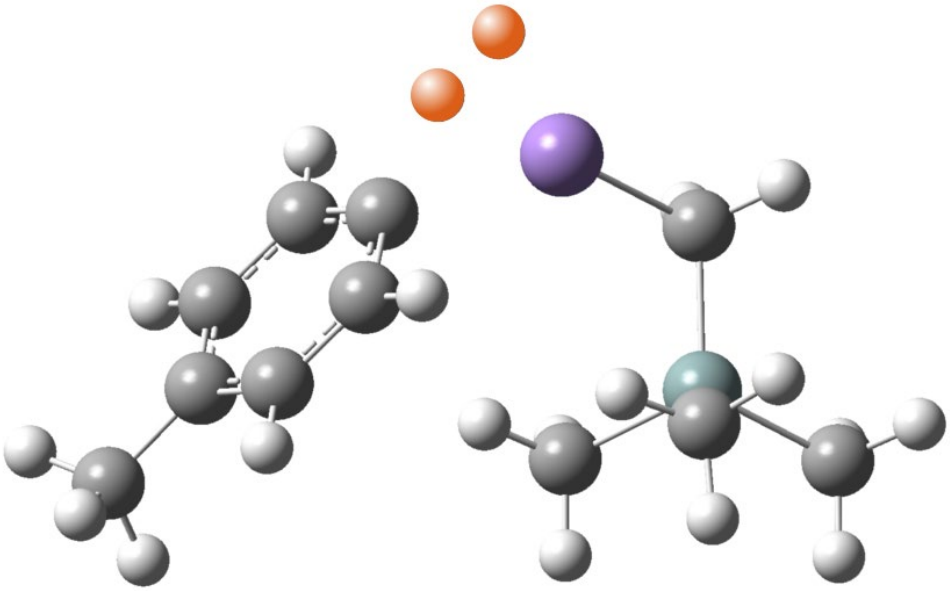

Figure S24. Transition state geometry for the reaction J11 between Mn(TMSM)C6H7 (para sub.) and H_2 eliminating C_6H_8. Imaginary mode: 974 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. H2 highlighted in orange.

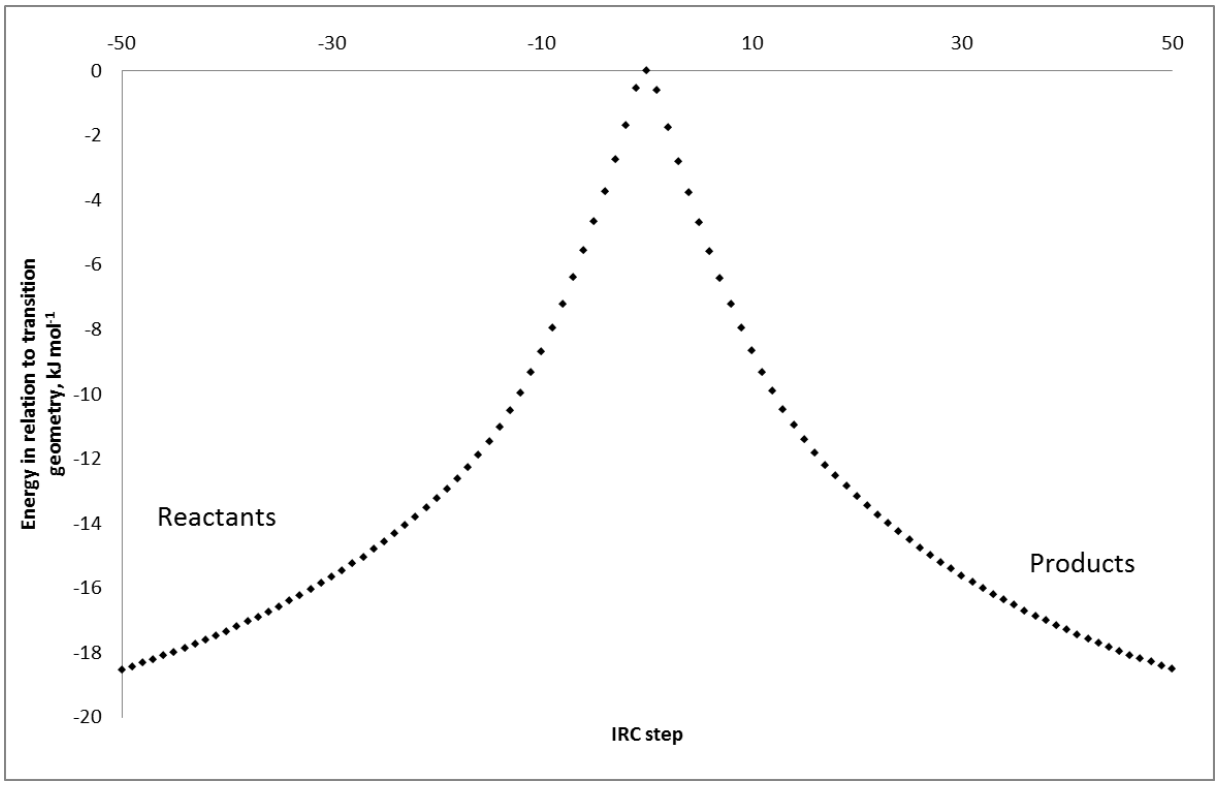

Figure S25. IRC from the transition state geometry in figure S17.

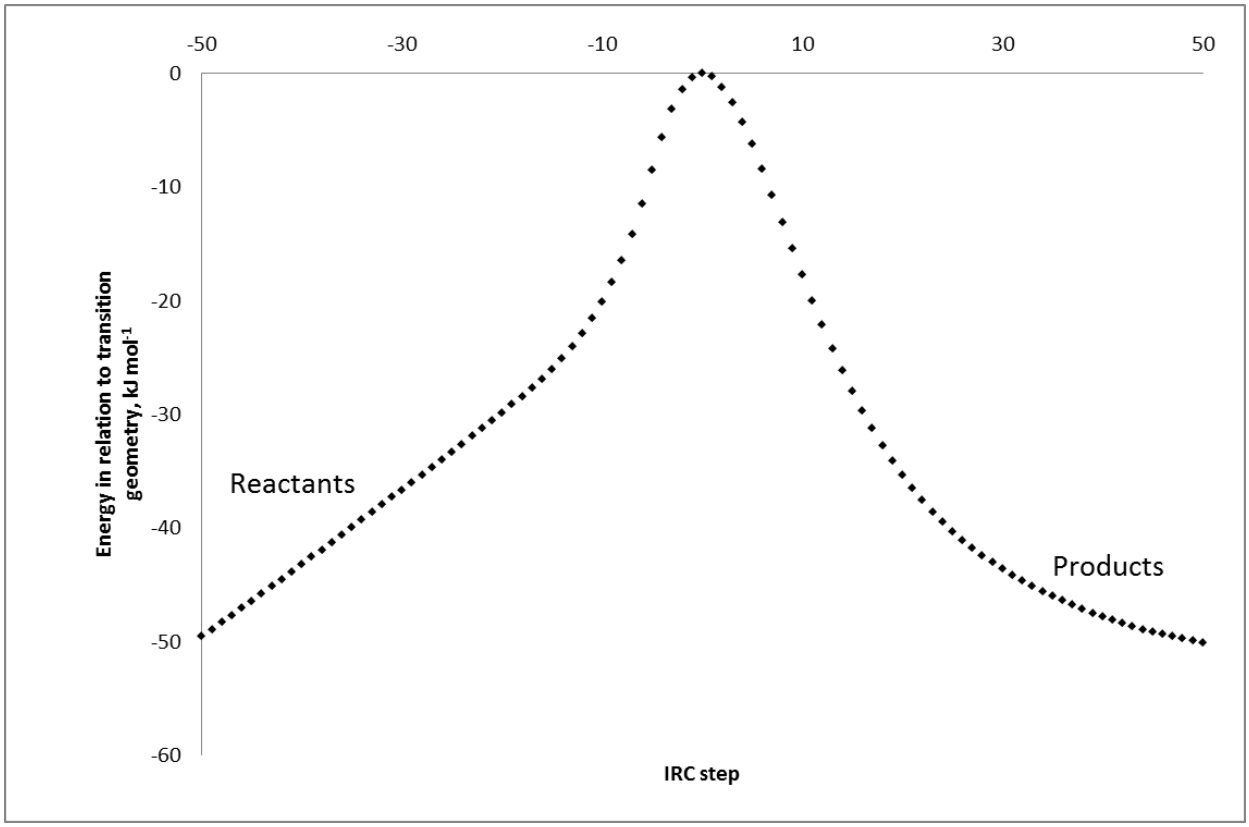

Figure S26. IRC from the transition state geometry in figure S18.

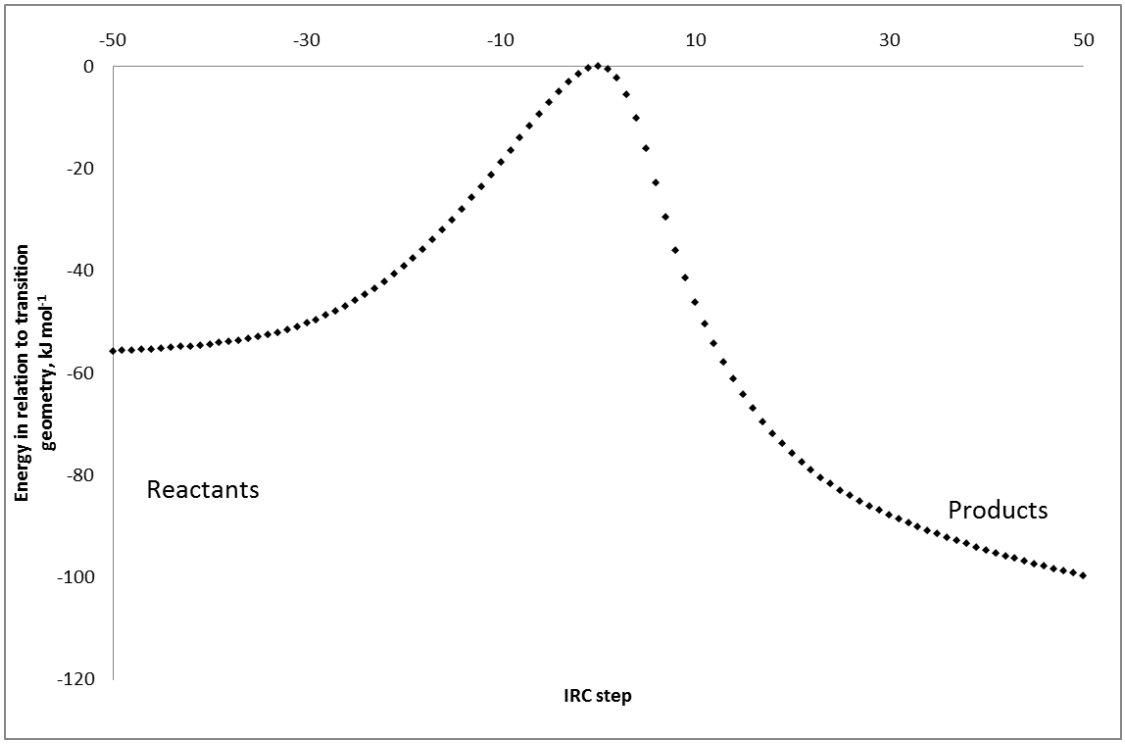

Figure S27. IRC from the transition state geometry in figure S19.

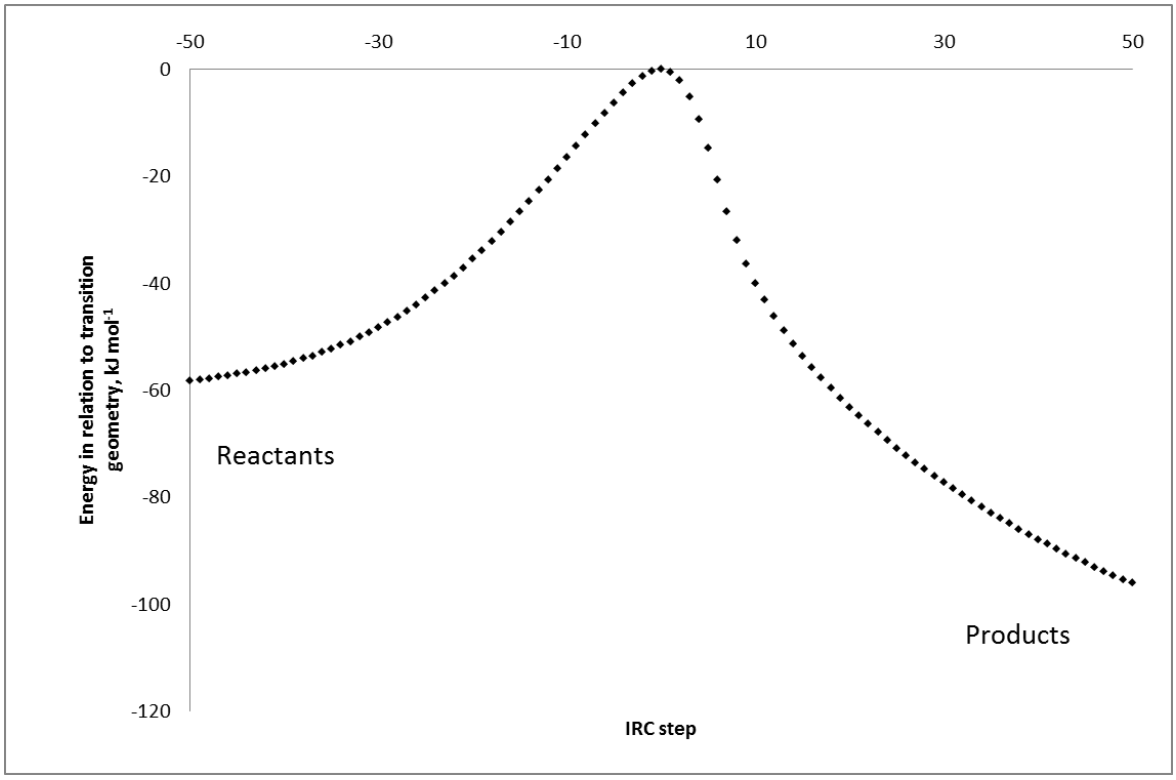

Figure S28. IRC from the transition state geometry in figure S20.

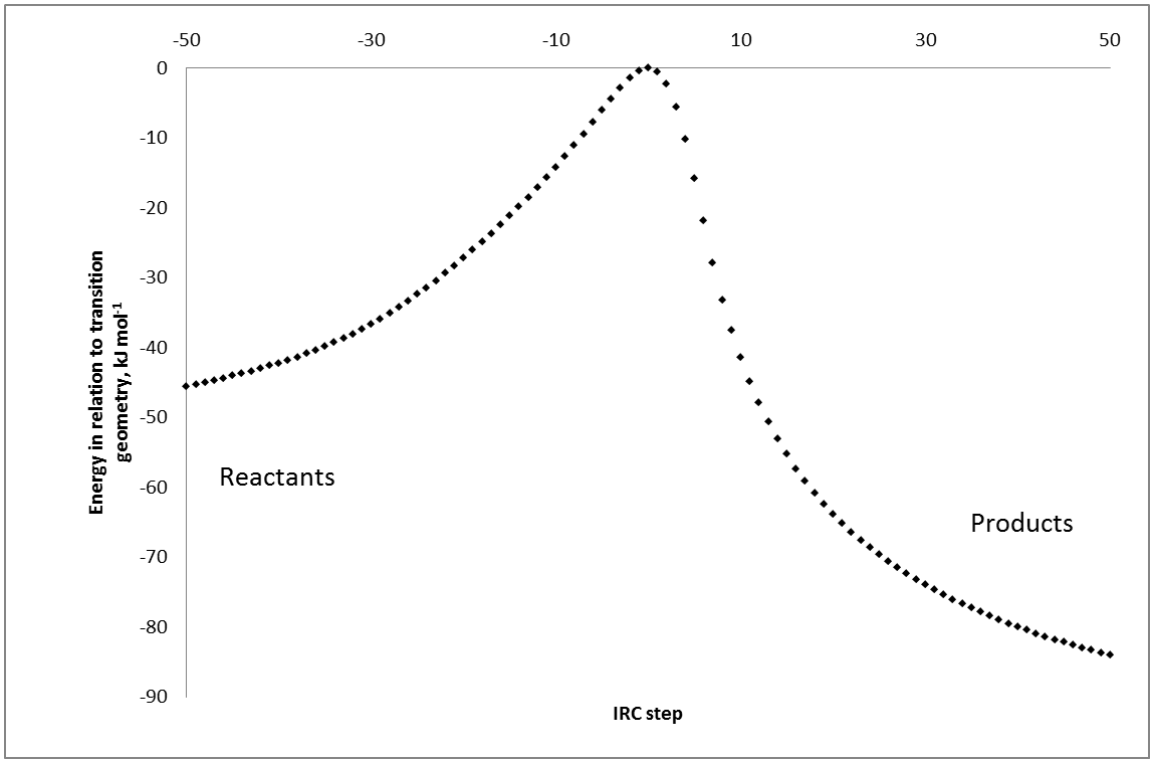

Figure S29. IRC from the transition state geometry in figure S21.

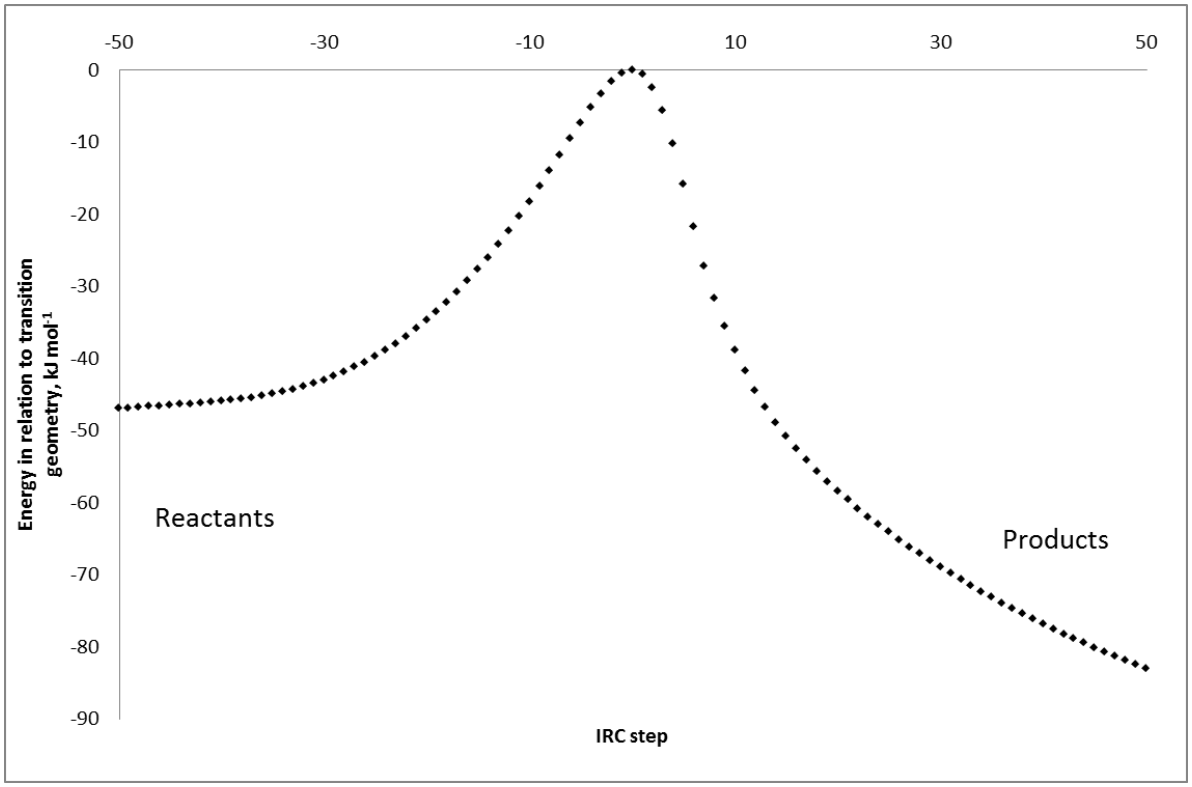

Figure S30. IRC from the transition state geometry in figure S22.

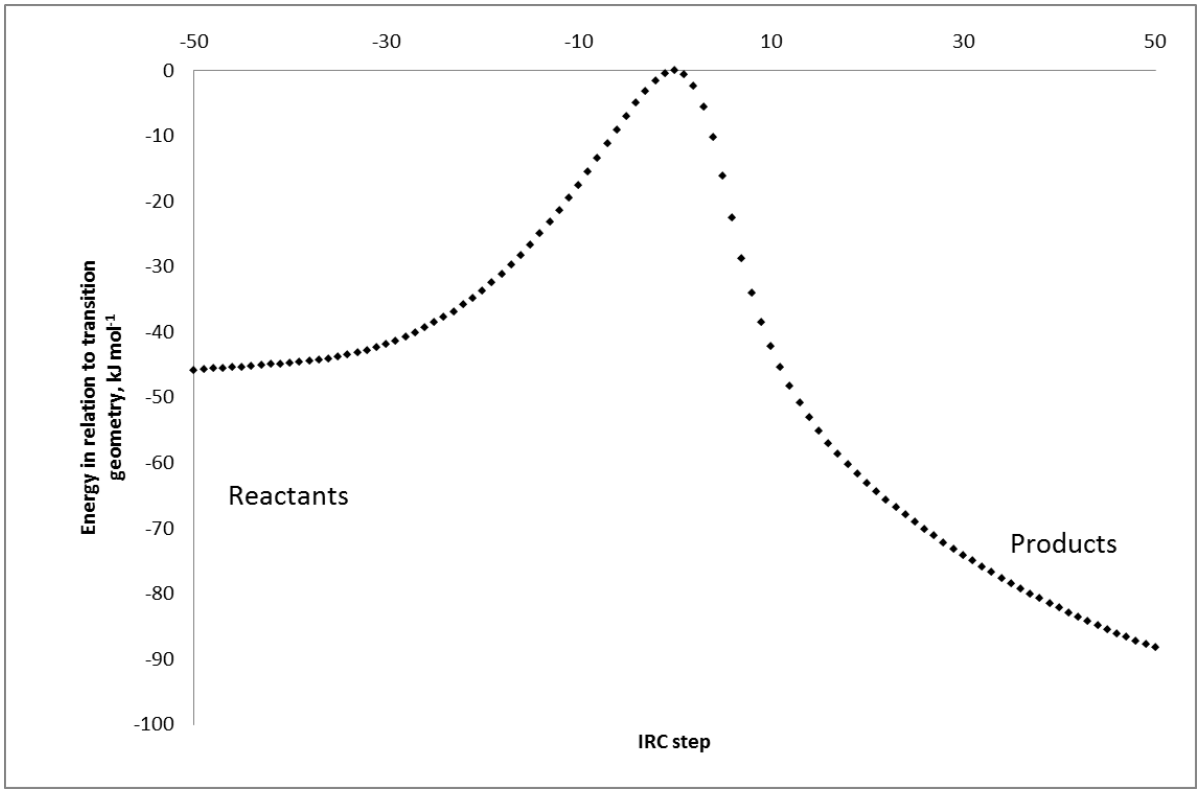

Figure S31. IRC from the transition state geometry in figure S23.

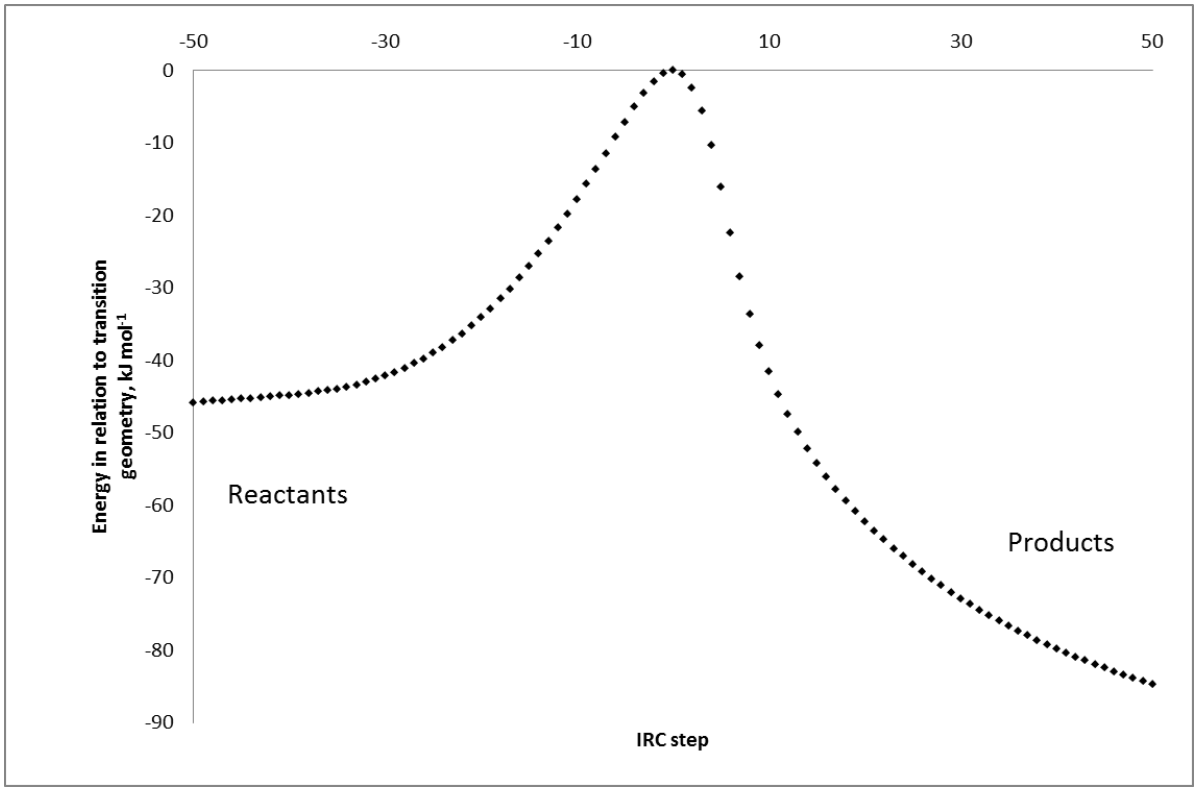

Figure S32. IRC from the transition state geometry in figure S24.

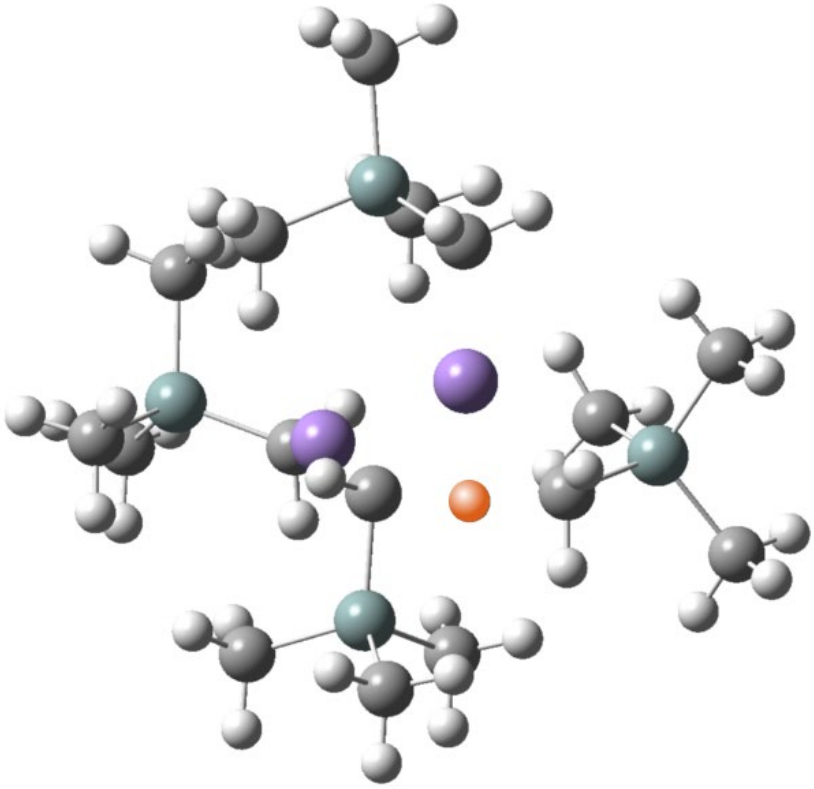

Figure S33. Transition state geometry for the condensation reaction L between two units of $Mn(TMSM)_2$. Imaginary mode: 1301 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

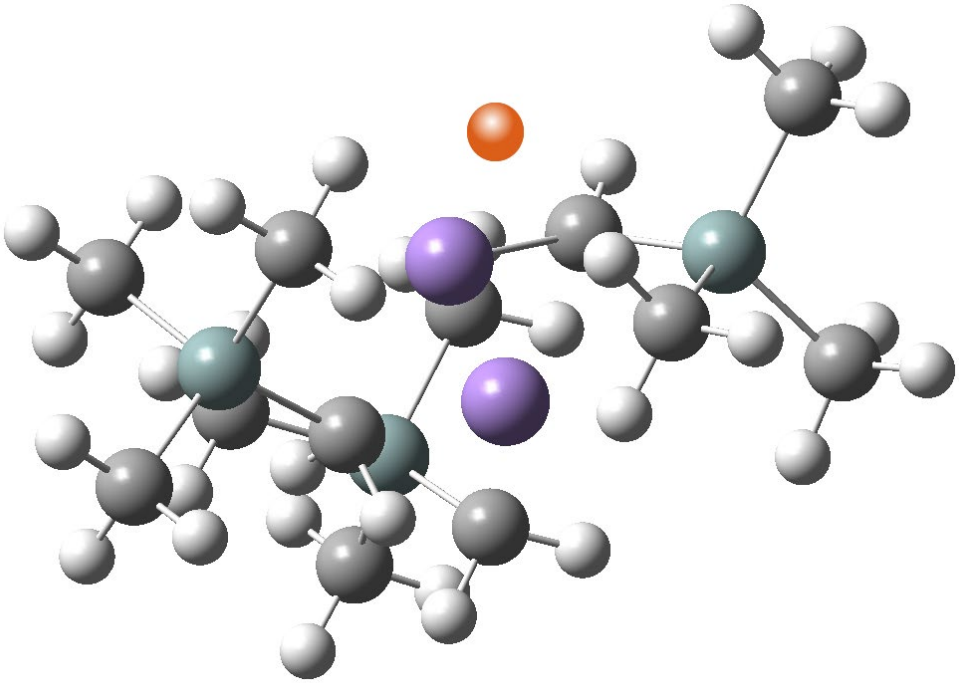

Figure S34. Transition state geometry for the condensation reaction M between $Mn(TMSM)_2$ and Mn(TMSM). Imaginary mode: 776 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

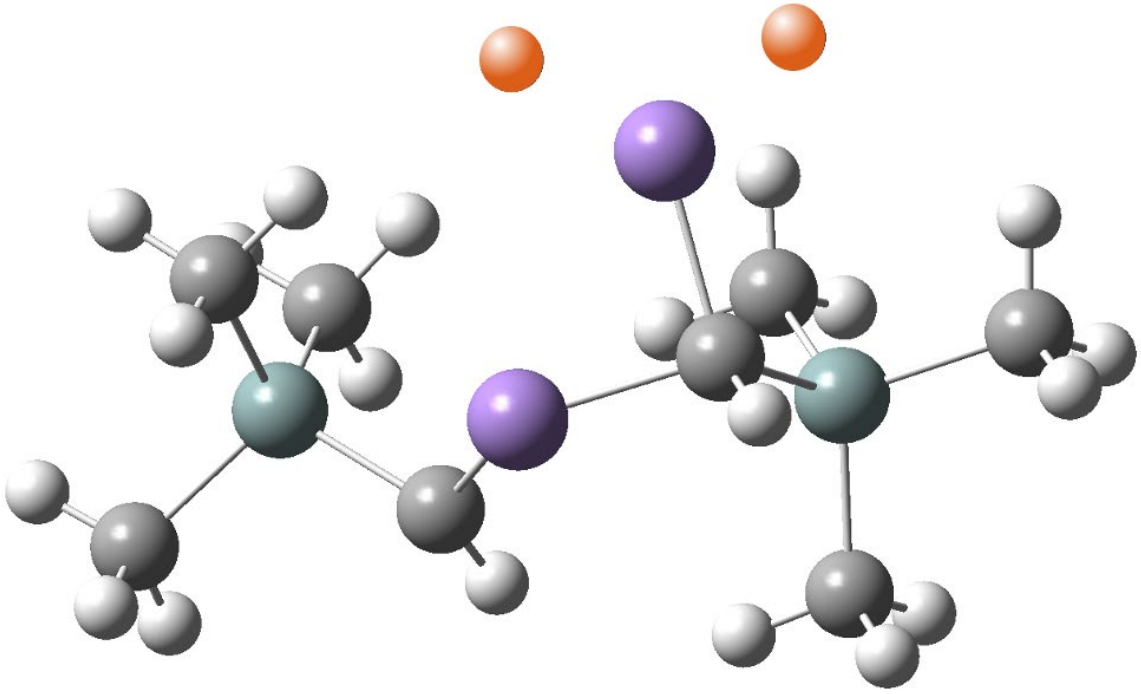

Figure S35. Transition state geometry for the condensation reaction N between two units of MnTMSM: 57 i cm^{-1}. Atom colours correspond to: Mn = purple, C = gray, H = white and Si = teal. Migrating H highlighted in orange.

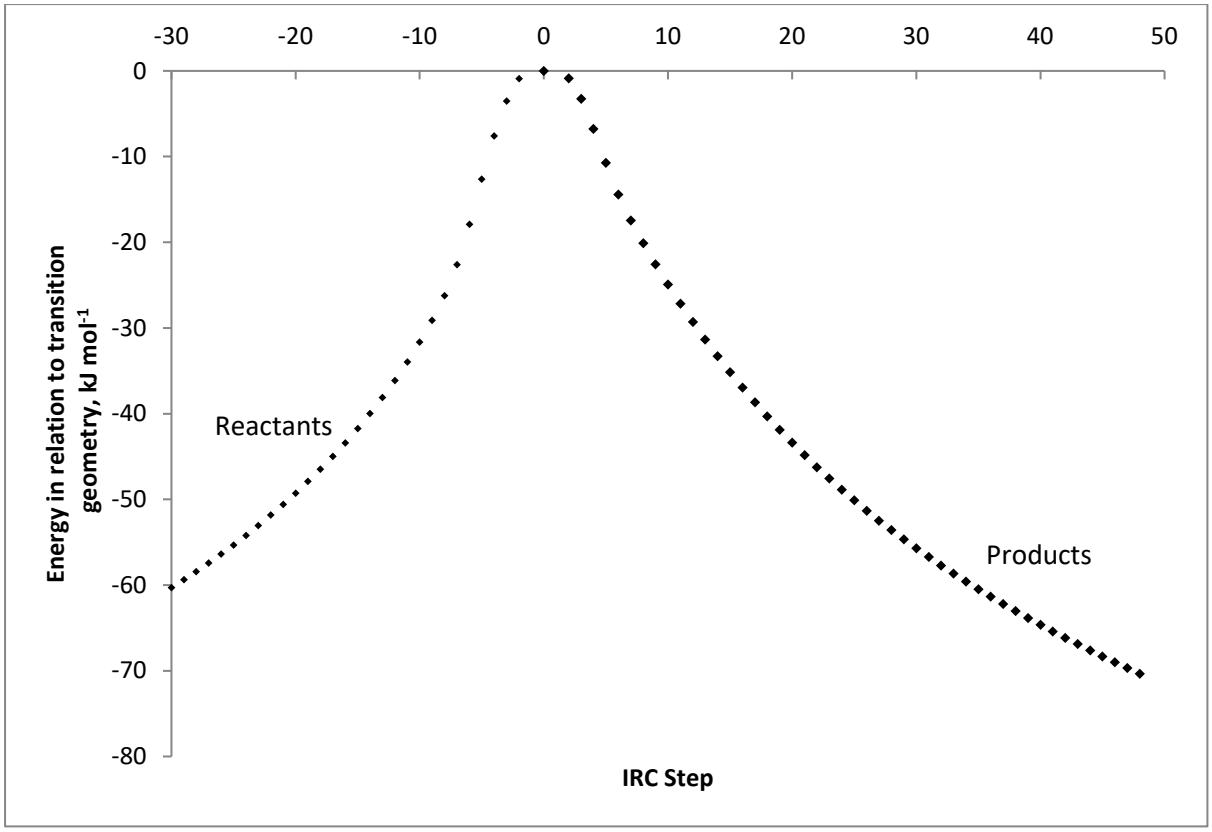

Figure S36. IRC from the transition state geometry in figure S33.

Figure S37. IRC from the transition state geometry in figure S34.

Figure S38. IRC from the transition state geometry in figure S35.

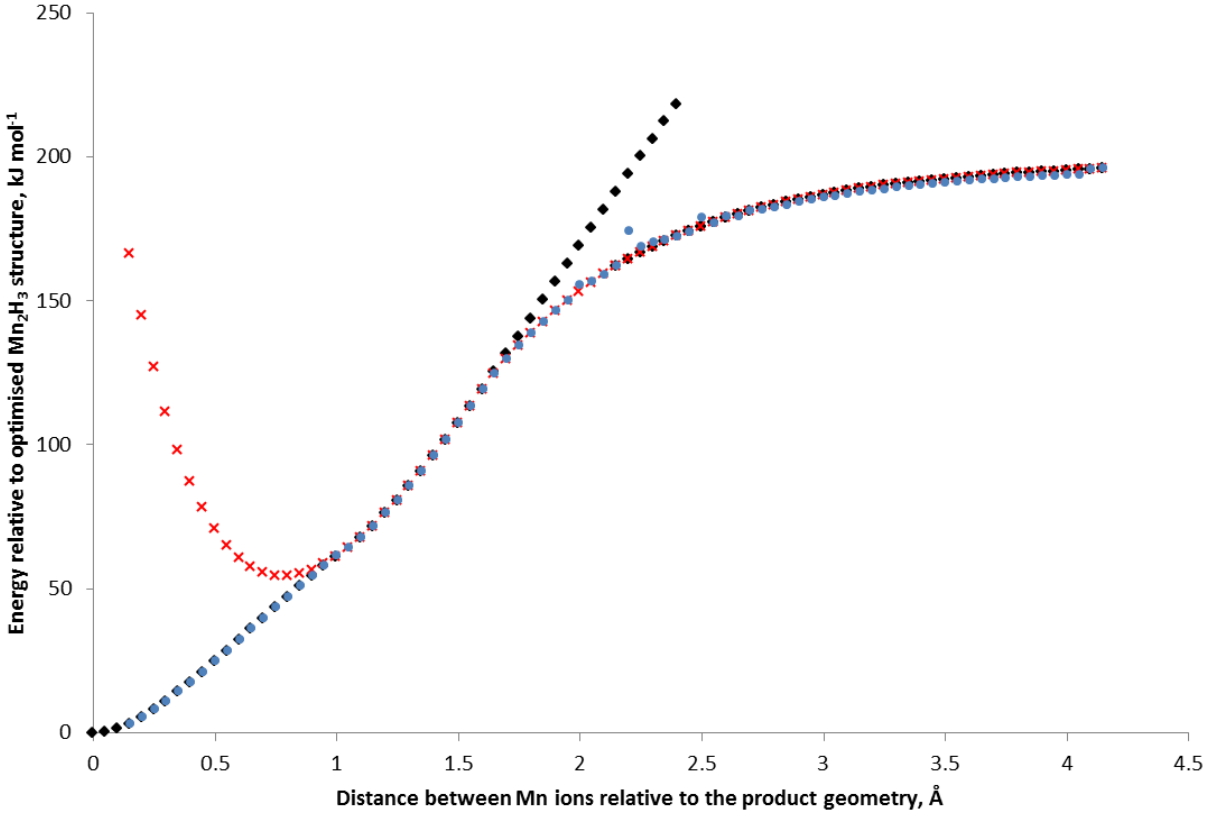

Figure S39. Energy profile of varying the Mn-Mn distance between a MnH and a MnH_2 complex, reaction P. From Mn_2H_3 to MnH + MnH_2: black diamonds. From MnH +MnH_2 to Mn_2H_3: red crosses. From MnH +MnH_2 to Mn_2H_3 no imposed symmetry: blue dots.

The black path in shows the energy profile following the extension of the Mn-Mn coordinate from the optimised product to an increase of 4.15 Å. there are two potential energy surfaces: one where the bridging hydrogen is closer to one of the Mn, and the other, higher in energy, with a hydrogen held equidistant between the Mn. The red crosses show the data calculated by bringing the two Mn together from the maximum extension; initially this follows the lower energy path as a unit of MnH and MnH_2 come together. Then, the calculation follows the same path as the extension calculation until reaching an extension of +0.95 Å, at which point the energy of this path starts increasing rapidly. This rapid increase is due to the system being constrained to adopt a linear geometry rather than the "v"-like shape in scheme 8. The calculation was then ran again without imposing any symmetry on the system, the blue dots, this is a smooth and continuous pathway from the separated molecules to the optimised product geometry; there is no barrier to this reaction.

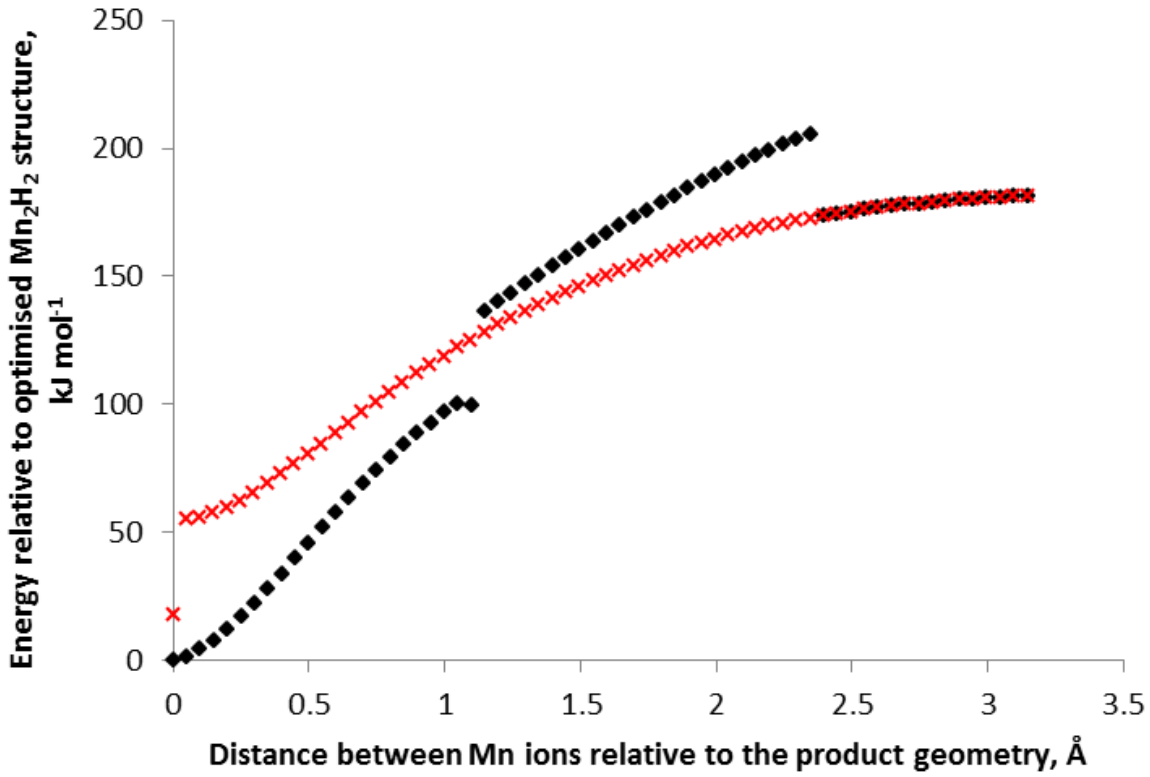

Figure S40. Energy profile of varying the Mn-Mn distance between two MnH complexes, reaction Q. From Mn_2H_2 to 2 x MnH: black diamonds. From 2 x MnH to Mn_2H_2: red crosses.

When the Mn-Mn distance is extended beyond 0.60 Å from the M1 product the molecule adopts the configuration of the other product M2 and so the rest of the analysis is on that product. The energy profile generated by increasing the Mn-Mn distance in Mn_2H_2 M1 is shown in figure S38 in black, the reverse in red. There are two discontinuities in the extension. The first discontinuity at +1.05-1.10 Å arises from one of the hydrogens moving from a bridging to a terminal position as the system changes from M1 to M2; the system looks like two Mn-H separated by an Mn-Mn distance of 1.1 Å. The second discontinuity comes from a small reorientation of the Mn-H relative to each other, the geometry of this is given in figure S41, this occurs at +2.35-2.40 Å. When the Mn-Mn bond shortened from its greatest extension these discontinuities are not present; however, the system follows a different potential energy surface for most of its path, this is the same surface as the final few steps in

the extension profile. Between an extension of 0.05 and 0.00 Å on the reverse pathway the structure quickly changes from a system with no bridging hydrogen to one with a hydrogen bridging the Mn ions.

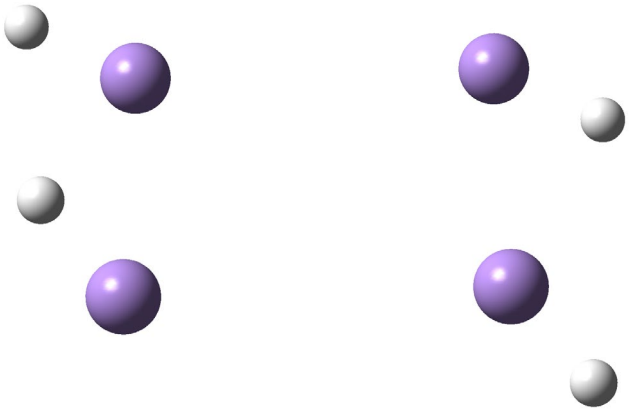

Figure S41. The geometry change occurring during the second discontinuity from the extension of the Mn-Mn bond from +2.35 to +2.40 Å in Mn_2H_2.

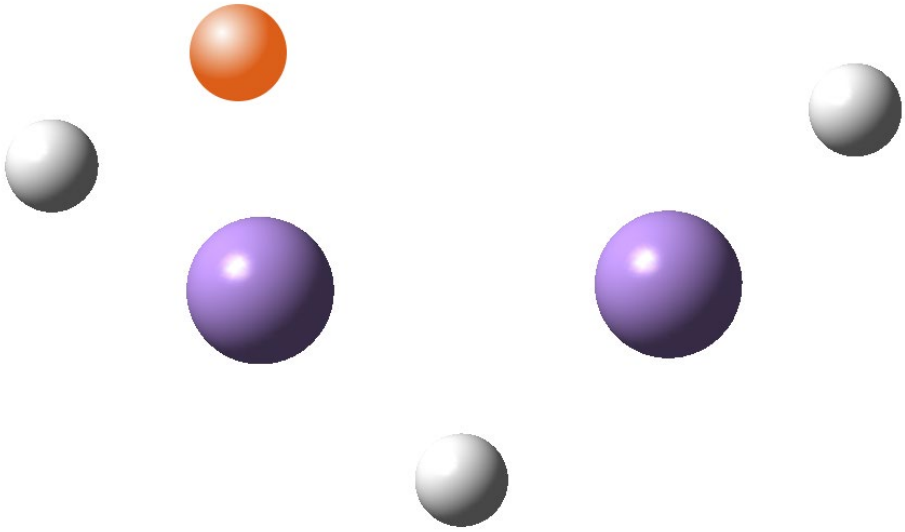

Figure S42. Transition state geometry for the reaction releasing H_2 from Mn_2H_4 to generate Mn(I) ions: 233i cm^{-1}. Atom colours correspond to: Mn = purple, and H = white. Migrating H highlighted in orange.

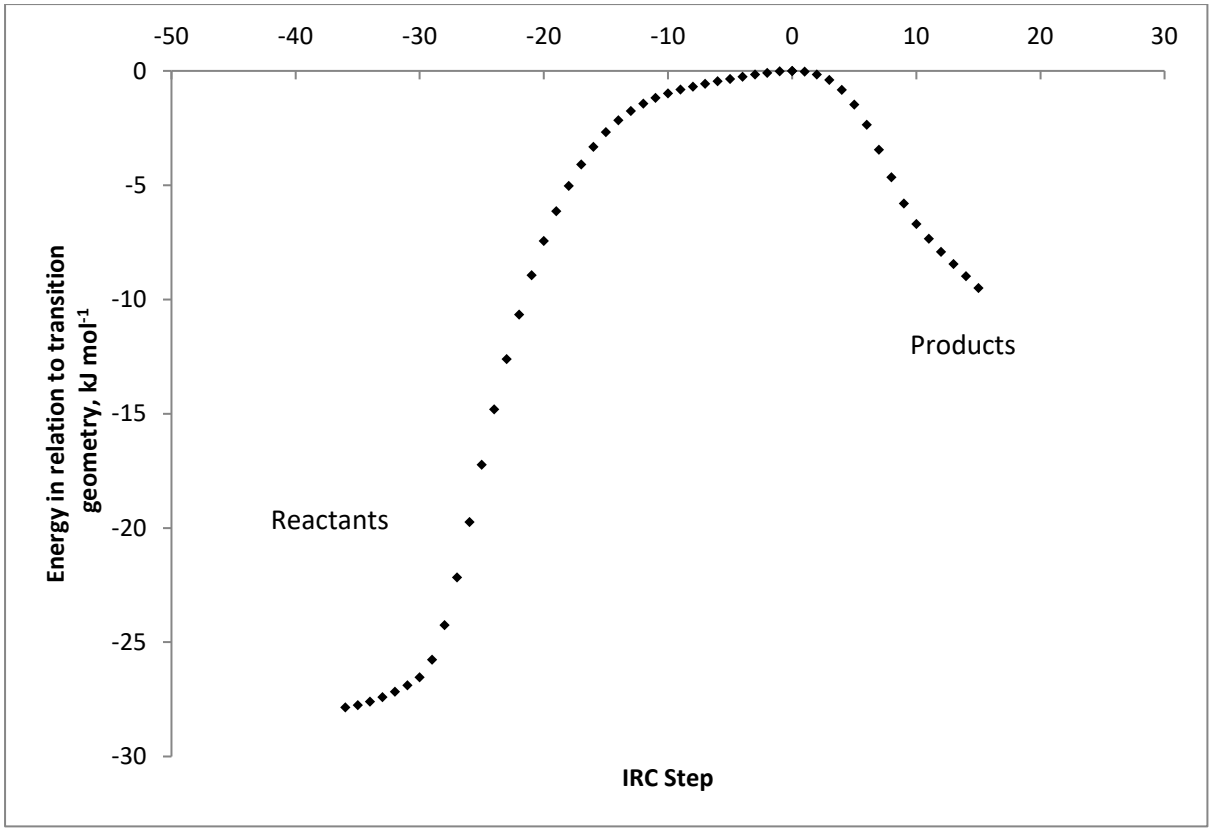

Figure S43. IRC from the transition state geometry in figure S42.

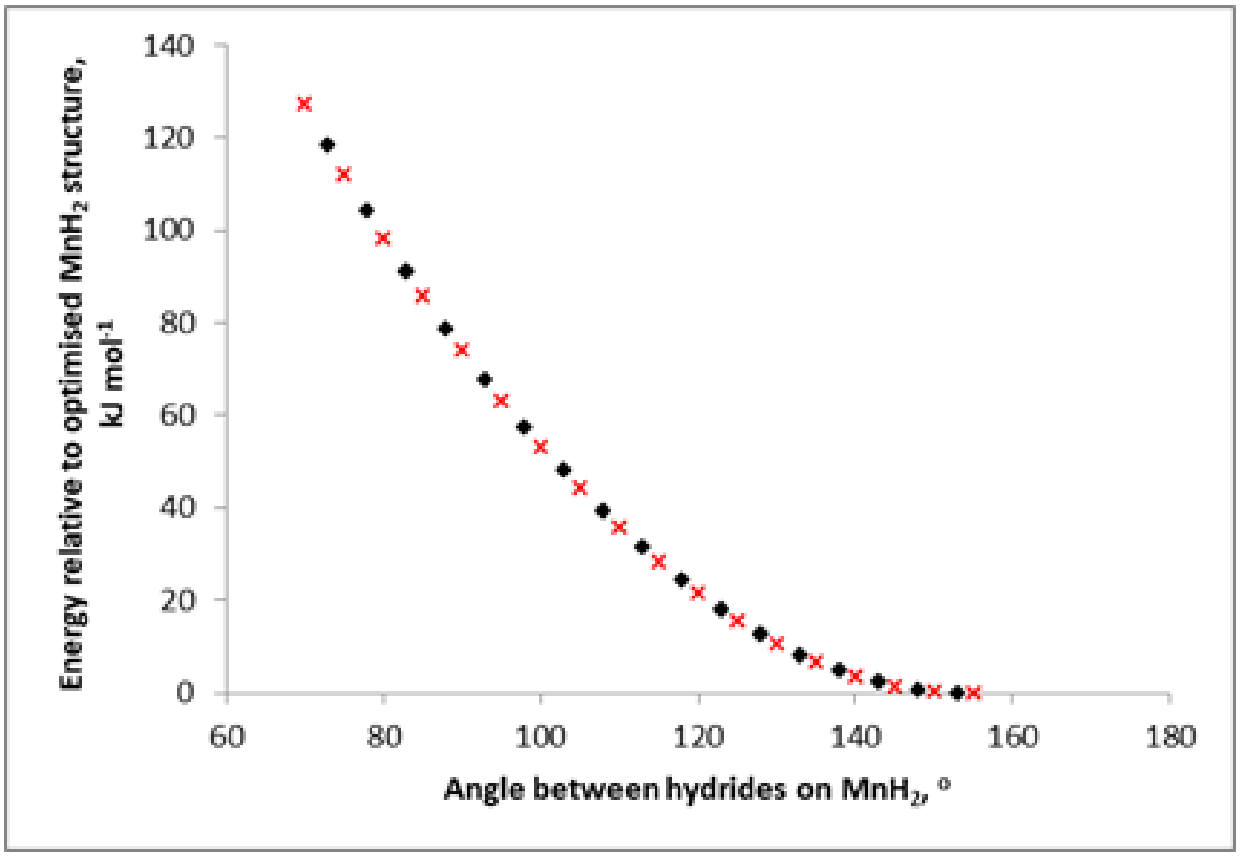

Figure S44. Energy profile of varying the H-Mn-H angle of MnH_2, reaction S. From Mn + H_2 to MnH_0: black diamonds. From MnH_2 to Mn + H_2: red crosses.

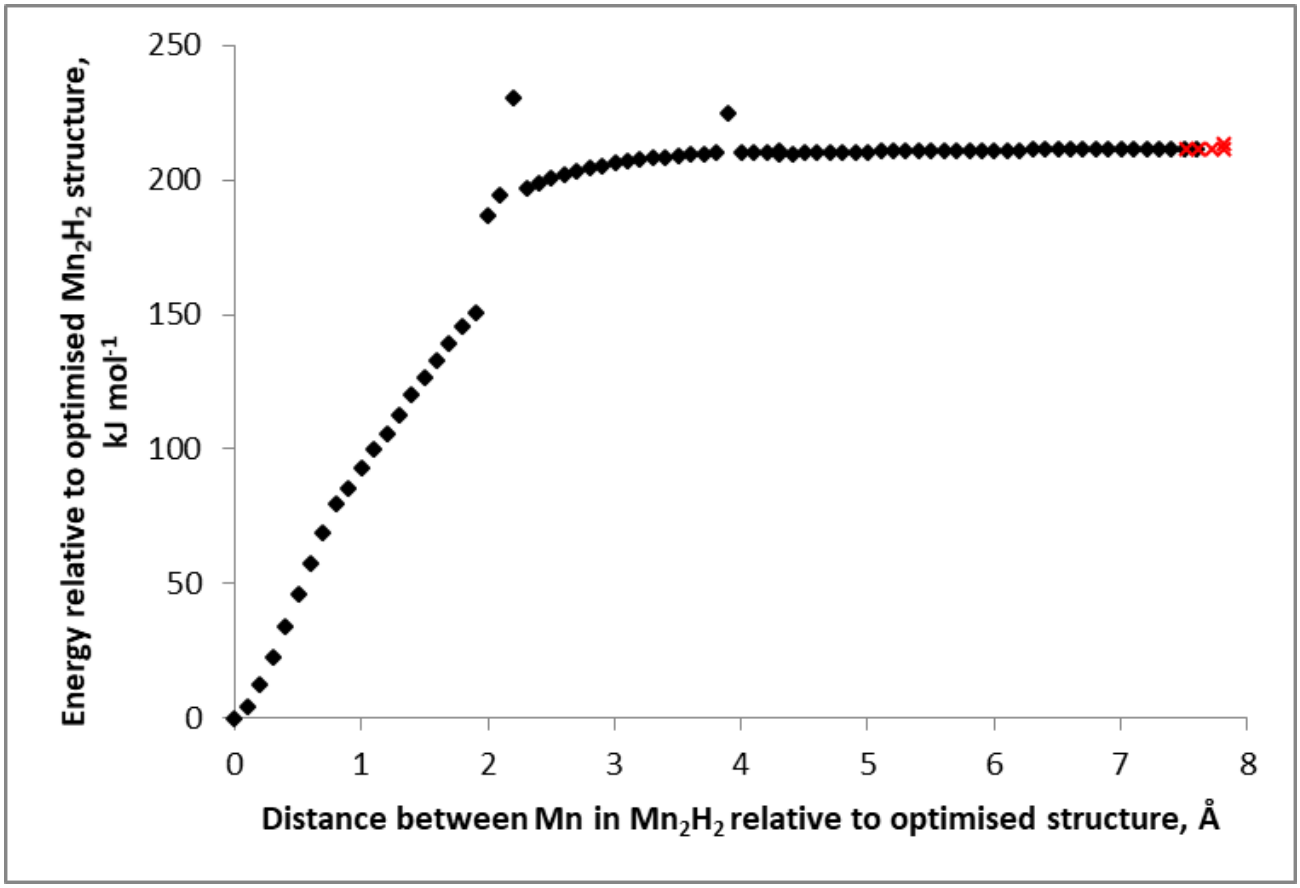

Figure S45. Energy profile of varying the Mn-Mn distance in Mn_2H_2, reaction T. From Mn_2H_2 to Mn + MnH_2: black diamonds. From Mn + MnH_2 to Mn_2H_2: red crosses.

Cartesian Coordinates of Optimised Geometries

Data is collated as shown in the example below:

Example Molecule, SCF energy (Atomic Units), *Thermally corrected Gibbs Free Energy* (Atomic Units)

```
Atom  X      Y      Z
```

H2, -1.1658575, *-1.167534*

```
H    0.000000  0.000000  0.375989
H    0.000000  0.000000 -0.375989
```

Tetramethyl silane, -448.853087, *-448.742531*

```
C  -0.338303  1.840020 -0.296576
H  -0.478795  2.051869 -1.368785
H   0.498424  2.461621  0.060864
C  -1.464464 -1.021279 -0.632776
H  -1.297105 -2.098775 -0.473719
H  -2.396191 -0.746829 -0.112448
H  -1.624197 -0.862942 -1.711534
C   1.572349 -0.510066 -0.924984
H   2.443735  0.068464 -0.578200
H   1.796687 -1.577851 -0.770915
H   1.469380 -0.342542 -2.009202
C   0.230469 -0.308638  1.854455
H   0.428964 -1.372928  2.059766
H   1.077369  0.272931  2.253107
H  -0.669603 -0.020709  2.421260
Si -0.000054 -0.000034 -0.000168
H  -1.248222  2.167946  0.231444
```

Bis(tetramethylsilylmethyl) manganese (II), -2047.240318, *-2047.029719*

```
Mn  0.020313 -1.452708 -0.016014
C   2.075880 -1.458913  0.012092
H   2.458000 -1.986241  0.908839
H   2.470195 -1.998784 -0.871378
C   1.962017  1.249058  1.475225
H   2.326015  2.288381  1.520098
H   0.860421  1.293689  1.417294
H   2.223433  0.761882  2.428978
C   4.606990  0.422287  0.131893
H   5.089298 -0.103047 -0.707961
H   4.950305  1.470027  0.118783
H   4.965726 -0.040191  1.065430
C   2.168173  1.156211 -1.608521
H   2.499422  2.206656 -1.644868
H   2.592073  0.640566 -2.485667
H   1.070821  1.152885 -1.720966
Si  2.716861  0.310599  0.001790
C  -1.867180 -1.181742 -0.784569
H  -2.482035 -2.083399 -0.587653
H  -1.823274 -1.060432 -1.884744
C  -4.556377  0.426250 -0.473292
```

```
H  -5.031761  1.308999 -0.014450
H  -4.687470  0.499288 -1.564828
H  -5.101372 -0.468165 -0.130935
C  -1.854869  1.905174 -0.600232
H  -2.355620  2.798073 -0.192079
H  -0.800789  1.944009 -0.280011
H  -1.870623  1.986094 -1.699330
C  -2.574341  0.211046  1.874584
H  -3.007250 -0.729021  2.254589
H  -1.522850  0.254109  2.210175
H  -3.103923  1.043947  2.365225
Si -2.716027  0.315269 -0.020880
```

HMnTMSM, -1599.554717, *-1599.458704*

```
Mn -2.139840 -0.048240 -0.039432
C  -0.405528 -0.317564 -1.096875
H  -0.351917 -1.343885 -1.511674
H  -0.399717  0.378690 -1.959318
C   1.089393 -1.206850  1.446250
H   1.980263 -1.079031  2.082323
H   0.205526 -1.055267  2.089919
H   1.073677 -2.253242  1.100199
C   2.739122 -0.222802 -0.966397
H   2.794604  0.468022 -1.822835
H   3.609082 -0.028872 -0.317374
H   2.830281 -1.248587 -1.357971
C   1.031431  1.775133  0.650926
H   1.908827  2.004640  1.277050
H   1.005568  2.509575 -0.170408
H   0.133739  1.941256  1.271139
Si  1.109109  0.000413 -0.021791
H  -3.547966  0.739422  0.406395
```

MnH2, -1151.8702058, *-1151.884273*

```
Mn  0.000000  0.000000  0.015197
H   0.000000  1.668534 -0.189960
H   0.000000 -1.668534 -0.189960
```

Mn(TMSM)2 + H2 elimination (Reactants), -2048.4087692, *-2048.190645*

```
Mn  0.004472 -1.182811  0.186239
C  -1.661423 -0.521813  1.197790
H  -2.202463 -1.351060  1.694640
H  -1.349909  0.181462  1.995893
C   1.690580 -0.867043 -0.950546
H   2.220552 -1.811410 -1.183843
H   1.391974 -0.418835 -1.919768
C  -3.390705 -0.852149 -1.332206
H  -4.110468 -0.380946 -2.021047
H  -2.543081 -1.211828 -1.940365
H  -3.882048 -1.733802 -0.888605
C  -4.359931  1.077204  0.868453
H  -4.075300  1.802063  1.647961
H  -5.018616  1.593098  0.150209
```

```
H  -4.945269  0.279066  1.352662
C  -1.885914  1.789866 -0.831114
H  -2.537118  2.337666 -1.531416
H  -1.506109  2.511621 -0.090025
H  -1.017874  1.421278 -1.403924
Si  2.860128  0.306655 -0.058343
C   4.406591  0.731023 -1.074263
H   4.130513  1.213135 -2.025835
H   5.072207  1.418776 -0.526743
H   4.981717 -0.177527 -1.314861
C   1.940756  1.920098  0.346335
H   1.569726  2.408532 -0.569237
H   1.068740  1.737820  0.997306
H   2.598865  2.635325  0.865940
C   3.411292 -0.495669  1.574747
H   2.553714 -0.682004  2.244133
H   3.909009 -1.462459  1.394135
H   4.119332  0.148610  2.120822
Si -2.821790  0.367192  0.012298
H  -0.656377 -3.559415 -1.093339
H  -1.327735 -3.451835 -0.761205
```

Mn(TMSM)2 + H2 elimination (Products), -2048.418808, *-2048.195126*

```
Mn  0.279339 -1.511934 -0.051000
H  -0.102387 -3.006551  0.610183
C   1.487564 -0.202295 -1.084056
H   1.909544 -0.722724 -1.967237
H   0.905221  0.658658 -1.469907
C   2.204323  1.376756  1.473688
H   1.601645  0.722975  2.126667
H   3.013969  1.799497  2.090574
H   1.561131  2.212756  1.152465
C   3.917312 -1.042054  0.615857
H   4.334315 -1.625949 -0.220793
H   4.759075 -0.709964  1.244957
H   3.300490 -1.727865  1.221304
C   4.065908  1.601667 -0.966634
H   3.520587  2.484880 -1.336611
H   4.890155  1.956303 -0.325716
H   4.509341  1.094075 -1.838316
Si  2.905368  0.433159 -0.021518
Si -3.046905  0.367302 -0.000375
C  -1.706685  0.400358  1.346191
H  -2.003808  1.053083  2.183778
H  -1.537058 -0.602888  1.779570
H  -0.751817  0.806002  0.965848
C  -2.513370 -0.822359 -1.380510
H  -2.360237 -1.848161 -0.999013
H  -3.288544 -0.889231 -2.161767
H  -1.589865 -0.481737 -1.882246
C  -4.670625 -0.235852  0.753544
H  -5.004490  0.430511  1.564884
H  -5.471045 -0.270332 -0.002720
H  -4.560976 -1.248541  1.173234
C  -3.246553  2.105822 -0.713891
H  -2.302043  2.464519 -1.153688
H  -4.013876  2.126312 -1.504189
```

```
H  -3.548523  2.824005  0.065100
```

Mn(TMSM)2 + H2 elimination (TS), -2048.3838644, *-2048.160768*

```
Mn  0.023817 -1.267085 -0.103008
C  -1.379370 -0.266999 -1.180423
H  -0.949506  0.600298 -1.717848
H  -1.835866 -0.929326 -1.942059
C  -1.980698  1.420925  1.346100
H  -2.753691  1.763352  2.053265
H  -1.216547  0.878939  1.929816
H  -1.495394  2.314140  0.920943
C  -4.075584  1.334663 -0.910144
H  -4.558608  0.733410 -1.696963
H  -4.859124  1.671735 -0.211484
H  -3.642385  2.227096 -1.389696
C  -3.552216 -1.175888  0.807682
H  -4.358819 -0.870051  1.493626
H  -3.989590 -1.849703  0.053152
H  -2.824955 -1.765245  1.391931
Si -2.736986  0.329295 -0.015965
H   0.331474 -2.894729  0.682243
C   1.698770  1.962837  0.025630
H   1.601733  2.366336  1.046157
H   2.187206  2.730141 -0.596441
H   0.683526  1.805219 -0.370408
C   1.879119 -0.940251  1.135640
H   1.052300 -2.187085  0.967920
H   2.679498 -1.653807  1.407876
H   1.542954 -0.476446  2.081965
C   2.815307 -0.307421 -1.757878
H   3.385973  0.384163 -2.399166
H   3.321791 -1.285798 -1.787803
H   1.820197 -0.426540 -2.222378
C   4.464790  0.722221  0.628429
H   4.956680  1.476573 -0.007697
H   4.452831  1.104887  1.661261
H   5.084971 -0.188323  0.613716
Si  2.706073  0.359803  0.019040
```

HMnTMSM + H2 elimination (Reactants), -1600.72347, *-1600.619993*

```
Mn -2.036297 -0.150762  0.045104
H  -3.221665 -1.220251 -0.465904
C  -0.386809  1.058238 -0.137841
H  -0.420473  1.569331 -1.121001
H  -0.382272  1.851588  0.636041
C   1.248642 -0.820231  1.675277
H   0.412845 -1.532130  1.789311
H   2.182364 -1.390977  1.805671
H   1.183229 -0.093725  2.501690
C   1.213433 -1.262401 -1.380062
H   1.163282 -0.797187 -2.377962
H   2.129977 -1.873104 -1.341338
H   0.354930 -1.950184 -1.292336
C   2.761625  1.123225 -0.179543
H   2.800720  1.890324  0.610428
```

```
H    3.677014   0.513101 -0.105100
H    2.779052   1.642738 -1.151000
Si   1.202594   0.054451 -0.011790
H   -3.529477   2.158238 -0.112932
H   -4.079758   1.645972 -0.205087
```

HMnTMSM + H2 elimination (Products), -1600.733918, *-1600.623413*

```
Mn -2.409698   0.000000   0.000000
H  -2.803619  -1.629844   0.000003
H  -2.803619   1.629844   0.000002
Si  1.328818   0.000000   0.000000
C   0.222687  -0.000001  -1.546202
H   0.833163  -0.000001  -2.464488
H  -0.411442  -0.904743  -1.599506
H  -0.411443   0.904740  -1.599506
C   2.399974  -1.555133   0.000001
H   3.048938  -1.590484  -0.889562
H   3.048940  -1.590481   0.889563
H   1.779009  -2.465086   0.000003
C   0.222688   0.000001   1.546202
H   0.833164   0.000002   2.464488
H  -0.411442   0.904743   1.599505
H  -0.411442  -0.904741   1.599507
C   2.399972   1.555134  -0.000001
H   1.779005   2.465086  -0.000003
H   3.048936   1.590486   0.889562
H   3.048938   1.590484  -0.889563
```

HMnTMSM + H2 elimination (TS), -1600.6997417, *-1600.589709*

```
Mn   2.007357   0.040026 -0.006445
H    2.440362   1.621215   0.081585
C    0.243043  -1.255226  -0.503307
H    0.207347  -1.422049  -1.596113
H   -0.048932  -2.211163  -0.029648
C   -0.832437   0.543766   1.791071
H    0.093481   1.133039   1.912863
H   -1.663542   1.182614   2.131964
H   -0.777536  -0.323204   2.469243
C   -1.040403   1.506644  -1.148681
H   -1.186302   1.214267  -2.201040
H   -1.833769   2.225173  -0.886471
H   -0.074892   2.032864  -1.070474
C   -2.812260  -0.819063  -0.138388
H   -2.887212  -1.691503   0.530131
H   -3.610462  -0.110777   0.138801
H   -3.006897  -1.163717  -1.166270
Si  -1.106769  -0.001356  -0.007227
H    1.648525  -1.662849  -0.159159
H    2.663016  -1.662295   0.102706
```

Reaction A ring product, -1598.347007, *-1598.263065*

```
Mn   1.747978   0.000000   0.000000
C    0.329154  -0.000003  -1.487101
H    0.264301   0.896771  -2.125679
H    0.264301  -0.896779  -2.125675
```

```
C  -1.943681  1.573562 -0.000003
H  -2.585780  1.618794  0.893543
H  -1.301443  2.468829 -0.000004
H  -2.585780  1.618791 -0.893548
C   0.329155  0.000002  1.487101
H   0.264301  0.896778  2.125676
H   0.264301 -0.896771  2.125678
C  -1.943682 -1.573562  0.000003
H  -2.585781 -1.618790  0.893548
H  -2.585781 -1.618793 -0.893543
H  -1.301444 -2.468829  0.000004
Si -0.888308  0.000000  0.000000
```

Reaction B carbene product, -1598.310726, *-1598.229218*

```
Mn -2.086592  0.003874 -0.040144
C  -0.574895 -0.057630 -1.048619
H  -0.640533  0.126044 -2.132040
C   1.956175  1.618708 -0.261802
H   1.350975  2.484117  0.050380
H   2.883830  1.609799  0.335110
H   2.234522  1.769061 -1.317146
C   0.521845 -0.165427  1.798518
H  -0.023121 -1.102902  2.003312
H   1.436353 -0.184165  2.414960
H  -0.086320  0.683078  2.157636
C   2.130326 -1.443538 -0.494462
H   2.412320 -1.402335 -1.558495
H   3.056105 -1.413562  0.104319
H   1.629937 -2.407941 -0.317485
Si  0.979287  0.002091 -0.049912
```

Reaction A associated products, -2047.210423, *-2047.001793*

```
Mn -0.631124 -1.219655  0.000001
C  -1.796411 -0.381597 -1.481052
H  -1.323865  0.344030 -2.164064
H  -2.414698 -1.073720 -2.077789
C  -2.545577  2.283127  0.000012
H  -3.011899  2.727954  0.893352
H  -1.479879  2.563341  0.000020
H  -3.011888  2.727964 -0.893329
C  -1.796425 -0.381614  1.481052
H  -1.323887  0.344005  2.164077
H  -2.414718 -1.073745  2.077775
C  -4.554940 -0.130238 -0.000012
H  -5.076130  0.247397  0.893866
H  -5.076120  0.247405 -0.893893
H  -4.637494 -1.229075 -0.000017
Si -2.732892  0.395841  0.000000
C   2.307762 -1.556618 -0.000009
H   3.119083 -2.302789 -0.000022
H   1.703878 -1.755349  0.908389
H   1.703863 -1.755334 -0.908400
C   4.011752  0.495525  1.553496
H   4.869987 -0.194616  1.583770
H   4.406817  1.523318  1.592019
```

```
H   3.414792  0.331952  2.464936
C   4.011714  0.495554 -1.553516
H   3.414732  0.332000 -2.464945
H   4.406781  1.523347 -1.592028
H   4.869948 -0.194587 -1.583825
C   1.492252  1.412336  0.000028
H   1.825693  2.462848  0.000037
H   0.859758  1.269190 -0.892481
H   0.859773  1.269169  0.892545
Si  2.969521  0.228287  0.000000
```

Reaction B associated products, -2047.177793, *-2046.968988*

```
Mn  0.640258 -1.492586  0.008494
C   2.462180 -1.411525  0.039187
H   3.173179 -2.248412 -0.015862
C   3.996712  0.798891 -1.578640
H   3.376628  0.637136 -2.474370
H   4.323143  1.852766 -1.565939
H   4.894253  0.167296 -1.677728
C   1.504072  1.505774  0.063876
H   0.936249  1.393227  1.003959
H   1.835620  2.557117  0.016145
H   0.815568  1.354327 -0.786583
C   4.126607  0.799626  1.487457
H   5.033638  0.174230  1.505926
H   4.443334  1.855693  1.448420
H   3.587369  0.631322  2.432739
Si  3.032409  0.342435 -0.001571
Si -3.292325  0.293840 -0.007312
C  -4.550194 -0.658248 -1.044729
H  -4.105517 -1.014138 -1.987762
H  -4.938412 -1.534482 -0.501594
H  -5.408883 -0.017699 -1.302191
C  -1.825342 -0.871043  0.389073
H  -1.391458 -1.167937 -0.598523
H  -1.104421 -0.302680  1.009996
H  -2.136252 -1.772250  0.938257
C  -2.601427  1.764140 -0.967658
H  -3.397070  2.486587 -1.209833
H  -1.829766  2.294470 -0.387187
H  -2.142969  1.442193 -1.916549
C  -4.057454  0.854453  1.624927
H  -4.429488 -0.001597  2.209866
H  -3.325338  1.395831  2.244906
H  -4.907971  1.531392  1.444964
```

Reaction A TS, -2047.180979, *-2046.971304*

```
Mn  0.391909 -1.424248  0.037371
C  -1.523306 -0.956756 -1.022699
H  -1.781206 -0.885688 -2.093933
H  -1.767142 -2.007425 -0.745264
C  -2.151086  2.019957 -0.645738
H  -2.713402  2.783288 -0.084451
H  -1.077957  2.243142 -0.536852
H  -2.409534  2.128922 -1.711356
```

```
C  -4.406655 -0.057749 -0.204397
H  -4.666680 -1.063550  0.162268
H  -5.001290  0.673778  0.367340
H  -4.717287  0.006179 -1.259434
C  -2.077132  0.141079  1.812137
H  -2.675196  0.836567  2.423849
H  -2.251915 -0.876271  2.198983
H  -1.015176  0.384746  1.988044
Si -2.552413  0.279837 -0.020242
C   2.067009 -1.075141  1.141046
H   2.799919 -1.896790  1.049114
H   1.946773 -0.830522  2.208020
C   4.249566  0.551275 -0.519032
H   4.390278  1.384400 -1.226759
H   4.894626  0.726252  0.357657
H   4.591209 -0.373023 -1.011477
C   1.864630  2.004453  0.842135
H   1.933716  2.861332  0.152614
H   0.818517  1.931765  1.181704
H   2.485638  2.226206  1.724783
C   1.263288  0.035292 -1.458356
H   1.737833 -0.608566 -2.223393
H  -0.232703 -0.478318 -1.308632
H   0.884890  0.939662 -1.963644
Si  2.431733  0.400567  0.002096
```

Reaction B TS, - 2047.1518062, -*2046.947665*

```
Mn  0.107508  1.467677 -0.092553
C  -1.715032  1.006099 -0.773919
H  -2.293645  1.767731 -1.331783
C  -3.348988 -1.478675 -1.410671
H  -2.485335 -1.924660 -1.927018
H  -3.965416 -2.296300 -1.001616
H  -3.950523 -0.935344 -2.155465
C  -1.772250 -1.324211  1.247430
H  -1.406087 -0.678808  2.062884
H  -2.378502 -2.122728  1.704833
H  -0.900605 -1.802612  0.772119
C  -4.310546  0.399316  0.864236
H  -4.939195  0.961594  0.156176
H  -4.926361 -0.400329  1.308170
H  -4.009600  1.086047  1.670502
Si -2.788982 -0.327440 -0.004667
Si  2.731925 -0.343966  0.009318
C   4.593423 -0.519062 -0.314842
H   4.852668 -0.165615 -1.325490
H   5.175159  0.074504  0.408126
H   4.914471 -1.570515 -0.229170
C   2.139905  1.439197 -0.138026
H   2.450486  1.870603 -1.112219
H  -0.636871  2.306728  1.054947
H   2.580256  2.065346  0.659829
C   1.800565 -1.410449 -1.263204
H   2.098139 -2.469039 -1.187815
H   0.705838 -1.367237 -1.126422
H   2.013728 -1.074909 -2.291293
C   2.347417 -0.987338  1.752021
```

```
H   2.855615 -0.377423  2.516251
H   1.267061 -0.958795  1.969172
H   2.682882 -2.029748  1.875858
```

Reaction C associated reactants, -1599.518965, *-1599.423806*

```
Mn -1.677930  0.000000  0.000000
C  -0.227530 -0.000003  1.451634
H  -0.196851  0.896658  2.093595
H  -0.196850 -0.896668  2.093591
C   2.074380  1.567113  0.000003
H   2.717511  1.608349 -0.893461
H   1.439680  2.468017  0.000004
H   2.717512  1.608346  0.893466
C  -0.227531  0.000002 -1.451634
H  -0.196851  0.896666 -2.093592
H  -0.196851 -0.896660 -2.093595
C   2.074382 -1.567112 -0.000002
H   2.717513 -1.608345 -0.893466
H   2.717513 -1.608347  0.893461
H   1.439683 -2.468016 -0.000004
Si  1.007618  0.000000  0.000000
H  -3.641311  0.000001  0.398347
H  -3.641310  0.000002 -0.398348
```

Reaction D associated reactants, -1599.489272, *-1599.393944*

```
Mn -2.005303 -0.145301  0.000001
C  -0.442011 -1.089660  0.000010
H  -0.322983 -2.184773  0.000021
C   2.161420 -0.328880 -1.539769
H   1.594389 -0.119473 -2.460115
H   3.056800  0.315134 -1.530302
H   2.497516 -1.377061 -1.584407
C   0.562809  1.805420 -0.000012
H  -0.027208  2.066173  0.895936
H   1.449587  2.461276 -0.000020
H  -0.027214  2.066160 -0.895960
C   2.161425 -0.328857  1.539770
H   2.497522 -1.377037  1.584423
H   3.056805  0.315158  1.530291
H   1.594398 -0.119437  2.460115
Si  1.086346 -0.033383  0.000000
H  -3.553873  0.852816  0.406509
H  -3.553874  0.852808 -0.406524
```

Reaction C TS, -1599.502451, *-1599.406776*

```
Mn -1.742049 -0.099332 -0.099602
C  -0.210048  0.332650  1.460351
H   0.014176  1.257734  2.014405
H  -0.261036 -0.502145  2.184393
C   1.665813  1.645814 -0.613736
H   2.276656  2.134874  0.161842
H   2.296566  1.499019 -1.504964
```

```
H   0.853086  2.337724 -0.888177
C  -0.227429 -0.721212 -1.291889
H  -0.146476 -0.291762 -2.302376
H  -0.195265 -1.822557 -1.372255
H  -1.834320  0.869102  1.357621
C   2.377403 -1.192017  0.465826
H   3.015746 -1.399121 -0.408683
H   3.006513 -0.766184  1.264060
H   1.975015 -2.152034  0.826164
Si  0.973704 -0.005739  0.002166
H  -2.715731  1.007585  1.004385
```

Reaction D TS, -1599.464017, *-1599.373147*

```
Mn  2.224229 -0.014864 -0.075359
C   0.432314  0.015423 -0.964377
H   0.332578  0.425997 -1.987762
C  -2.321637 -1.289830 -0.821016
H  -1.864424 -2.290734 -0.817200
H  -3.274537 -1.345851 -0.269182
H  -2.545141 -1.017811 -1.863951
C  -0.840452 -0.506101  1.789732
H  -0.177525  0.222185  2.285565
H  -1.772128 -0.555409  2.376041
H  -0.361443 -1.497251  1.845726
C  -2.017127  1.698130 -0.040486
H  -2.249041  2.004664 -1.072199
H  -2.959479  1.677967  0.531557
H  -1.363117  2.463805  0.404193
Si -1.183974 -0.005366 -0.004492
H   2.053807  1.541360  0.273372
H   3.631768 -0.687931  0.457584
```

Hexane, - -236.7979279, *-236.647261*

```
C  -1.892786 -0.550668  0.000000
H  -1.844717 -1.214775  0.882172
H  -1.844717 -1.214775 -0.882172
C  -0.669090  0.373868  0.000000
H  -0.716044  1.039336  0.882776
H  -0.716044  1.039337 -0.882776
C   0.669090 -0.373868  0.000000
H   0.716044 -1.039337  0.882776
H   0.716044 -1.039336 -0.882777
C   1.892786  0.550668  0.000000
H   1.844717  1.214775  0.882172
H   1.844717  1.214774 -0.882172
C   3.223529 -0.208595  0.000000
H   3.312388 -0.855235 -0.888572
H   4.084137  0.478420  0.000000
H   3.312388 -0.855235  0.888573
C  -3.223529  0.208596  0.000000
H  -4.084137 -0.478420  0.000001
H  -3.312388  0.855235  0.888573
H  -3.312388  0.855235 -0.888573
```

Cyclohexane, -235.6049218, *-235.468576* *Not fully optimised, see table 4

```
C   1.133095  0.930740  0.230854
C   1.372703 -0.515931 -0.230446
C   0.239450 -1.446618  0.230760
C  -1.133092 -0.930740 -0.230863
C  -1.372709  0.515930  0.230447
C  -0.239454  1.446622 -0.230752
H   0.409161 -2.471310 -0.140859
H   1.431390 -0.537946 -1.335323
H   2.344844 -0.881340  0.141454
H   1.181190  0.970367  1.335743
H   1.935677  1.590051 -0.140728
H  -1.181170 -0.970366 -1.335746
H  -1.935670 -1.590065  0.140710
H  -2.344849  0.881344 -0.141451
H  -1.431399  0.537927  1.335322
H  -0.249455  1.508181 -1.335632
H  -0.409155  2.471313  0.140870
H   0.249476 -1.508171  1.335637
```

Toluene -271.2700917, *-271.177152*

```
C   0.918323  0.000000 -0.011922
C   0.195976 -1.205961 -0.009396
C   0.195976  1.205961 -0.009396
C  -1.203587 -1.208905  0.002197
H   0.739363 -2.155683 -0.018775
C  -1.203587  1.208906  0.002197
H   0.739363  2.155683 -0.018775
C  -1.909682  0.000000  0.008858
H  -1.744212 -2.158857  0.001487
H  -1.744212  2.158858  0.001487
H  -3.002226  0.000000  0.014629
C   2.427905  0.000000  0.009469
H   2.807084  0.000003  1.045829
H   2.838450 -0.891014 -0.488958
H   2.838450  0.891011 -0.488963
```

Mn(TMSM)C6H13 (Hexane derivative), -1835.1731462, *-1834.924595*

```
Mn -1.070043 -1.653514 -0.264444
C  -2.481760 -0.463685 -1.176626
H  -2.014073  0.028059 -2.053316
H  -3.341804 -1.049667 -1.555255
C  -1.594870  1.800233  0.718246
H  -1.912426  2.611300  1.393505
H  -0.924269  1.137948  1.292808
H  -0.998070  2.251767 -0.091094
C  -4.270052  2.103939 -0.783992
H  -5.160876  1.598328 -1.189939
H  -4.610505  2.861752 -0.058962
H  -3.776252  2.629805 -1.616883
C  -3.993660  0.013551  1.466659
H  -4.381326  0.755311  2.183646
H  -4.847663 -0.583630  1.107642
```

```
H  -3.324858 -0.664330  2.024480
Si -3.089940  0.853506  0.020751
C   0.871758 -1.861699  0.388421
H   1.315064 -2.820716  0.054386
H   0.900131 -1.885460  1.496851
C   1.711664 -0.679877 -0.132336
H   1.699379 -0.664302 -1.239855
H   1.255577  0.280173  0.179593
C   3.178716 -0.688611  0.334391
H   3.649419 -1.637279  0.015526
H   3.200169 -0.695607  1.440203
C   4.000183  0.495558 -0.188271
H   3.972574  0.500326 -1.294590
H   3.521727  1.441322  0.129921
C   5.461184  0.487990  0.278898
H   5.937969 -0.457024 -0.039132
H   5.487646  0.483820  1.383782
C   6.270933  1.676203 -0.250413
H   5.834887  2.633296  0.080463
H   7.314636  1.646279  0.099754
H   6.288607  1.685685 -1.352811
```

Mn(TMSM)C6H11 (Cyclohexane derivative), -1833.9802917, *-1833.743928*

```
Mn  0.272925 -1.302436  0.067466
C  -1.773965 -1.462194 -0.135714
H  -2.030448 -1.886150 -1.126569
H  -2.174070 -2.162117  0.625572
C  -2.131811  1.333567 -1.393757
H  -2.606202  2.324484 -1.306473
H  -1.042198  1.491438 -1.448605
H  -2.452430  0.892163 -2.351495
C  -4.504280  0.090461  0.128785
H  -4.829729 -0.534086  0.976294
H  -4.968027  1.084415  0.242686
H  -4.900711 -0.365106 -0.792822
C  -2.012988  1.020270  1.677914
H  -2.508354  1.989369  1.852101
H  -2.227432  0.374775  2.545631
H  -0.924870  1.208303  1.664143
Si -2.610218  0.210839  0.061597
C   1.889067  1.631278 -0.498865
C   3.017333  1.640637  0.543769
C   3.133729  0.289302  1.265981
C   3.289715 -0.867306  0.264537
C   2.133471 -0.891129 -0.751717
C   2.040576  0.461129 -1.487231
H   3.976565  0.306604  1.977826
H   3.974682  1.854235  0.032266
H   2.862001  2.455659  1.270769
H   0.916875  1.543226  0.030118
H   1.853905  2.593389 -1.037789
H   4.260158 -0.736794 -0.263249
H   3.364727 -1.828582  0.802957
H   2.312891 -1.696504 -1.494589
H   2.957141  0.632277 -2.092320
H   1.202882  0.467127 -2.209624
H   2.217490  0.124923  1.871942
```

Mn(TMSM)C7H7 (Toluene derivative – methyl), -1869.6619213, *-1869.466902*

```
Mn -0.270356 -1.518758 -0.197958
C   1.754745 -1.442581 -0.454209
H   2.261443 -2.207914  0.165031
H   2.006336 -1.671381 -1.509534
C   2.038430  0.657565  1.794852
H   2.451877  1.635982  2.089174
H   0.951062  0.689833  1.976565
H   2.471278 -0.104409  2.463391
C   4.291173  0.411659 -0.294279
H   4.555141  0.211849 -1.345276
H   4.659175  1.419063 -0.038150
H   4.833805 -0.316085  0.330359
C   1.545785  1.562924 -1.112162
H   1.938005  2.575140 -0.920645
H   1.692680  1.344759 -2.182762
H   0.459313  1.589764 -0.920614
Si  2.415819  0.269605 -0.027047
C  -2.213874 -1.992696  0.453731
H  -2.294466 -2.350008  1.488324
H  -2.792862 -2.609361 -0.246554
C  -2.347195 -0.543007  0.273604
C  -2.014396  0.376682  1.316996
C  -2.636238  0.028641 -1.005806
C  -1.987163  1.754660  1.095922
H  -1.793684 -0.019162  2.313171
C  -2.605978  1.408856 -1.214002
H  -2.908144 -0.639562 -1.829345
C  -2.280103  2.286022 -0.168756
H  -1.732634  2.423784  1.922093
H  -2.840937  1.805927 -2.204985
H  -2.251062  3.363902 -0.337974
```

Mn(TMSM)C7H7 (Toluene derivative – ortho), -1869.6523158, *-1869.459442*

```
Mn -0.104964  0.725844 -1.238847
C  -2.153144  0.620129 -1.235186
H  -2.598767  1.634253 -1.266758
H  -2.538291  0.070448 -2.115961
C  -1.880002  0.626648  1.830636
H  -2.208202  0.186816  2.786411
H  -0.779055  0.547384  1.797644
H  -2.143331  1.697087  1.847324
C  -4.559137 -0.283156  0.588563
H  -5.055702 -0.798799 -0.248977
H  -4.838117 -0.802417  1.520377
H  -4.962826  0.740921  0.637204
C  -2.032950 -2.045365  0.306028
H  -2.340122 -2.602579  1.205812
H  -2.418955 -2.588037 -0.572285
H  -0.930843 -2.070847  0.262090
Si -2.676880 -0.260138  0.348040
C   3.195825 -1.871258 -0.208104
C   3.983201 -1.117781  0.667758
C   3.621767  0.202131  0.971192
C   2.477565  0.785665  0.405363
C   1.664488  0.038336 -0.490143
```

```
C   2.050299 -1.291551 -0.772349
H   3.469462 -2.902196 -0.448833
H   4.877540 -1.555005  1.119388
H   1.444072 -1.904688 -1.451594
C   2.109240  2.214548  0.746701
H   1.087199  2.277915  1.161320
H   2.791436  2.651988  1.491245
H   2.140927  2.858344 -0.149447
H   4.241062  0.785168  1.660917
```

Mn(TMSM)C7H7 (Toluene derivative – meta), -1869.6517941, *-1869.459472*

```
Mn -0.279354 -1.287339 -0.572263
C  -2.189240 -0.772531 -1.121411
H  -2.164652 -0.261283 -2.104529
H  -2.832550 -1.666690 -1.240273
C  -1.841378  1.917882  0.346084
H  -2.276522  2.638781  1.057096
H  -0.836096  1.654986  0.716864
H  -1.717024  2.434897 -0.619687
C  -4.697620  0.944786 -0.298933
H  -5.374433  0.081419 -0.401493
H  -5.118410  1.616659  0.467399
H  -4.697092  1.484642 -1.259447
C  -3.014490 -0.514882  1.835887
H  -3.479164  0.116438  2.610536
H  -3.602210 -1.444668  1.764867
H  -2.005636 -0.783055  2.194338
Si -2.944560  0.381466  0.161470
C   3.925277 -1.138028  0.676297
C   4.237797  0.208050  0.454666
C   3.276295  1.093121 -0.063887
C   1.995788  0.583820 -0.343753
C   1.639690 -0.769677 -0.133043
C   2.643122 -1.621196  0.384791
H   4.686386 -1.811180  1.082000
H   5.240798  0.578914  0.688698
H   1.250471  1.287721 -0.740253
H   2.428728 -2.679402  0.570750
C   3.618802  2.540043 -0.326664
H   4.204223  2.972510  0.499943
H   4.224223  2.644209 -1.243196
H   2.712396  3.149716 -0.457825
```

Mn(TMSM)C7H7 (Toluene derivative – para), -1869.6519097, *-1869.459688*

```
Mn -0.398802 -1.239011 -0.400007
C  -2.352238 -0.925782 -0.949432
H  -2.388648 -0.599779 -2.008167
H  -2.948740 -1.856773 -0.879166
C  -2.094192  1.993596  0.006855
H  -2.541895  2.810725  0.595453
H  -1.066705  1.843961  0.380097
H  -2.023383  2.335223 -1.038942
C  -4.917764  0.800103 -0.346297
```

```
H  -5.554333 -0.095937 -0.269500
H  -5.347521  1.578559  0.305683
H  -4.972807  1.160702 -1.385997
C  -3.101075 -0.183704  1.945560
H  -3.570522  0.555659  2.614534
H  -3.646082 -1.134620  2.062525
H  -2.069923 -0.342563  2.305685
Si -3.125990  0.402947  0.137950
C   3.866204 -0.789046  0.544863
C   4.154256  0.515110  0.103592
C   3.112089  1.258002 -0.476279
C   1.827223  0.715050 -0.601772
C   1.515362 -0.593539 -0.160656
C   2.580630 -1.326544  0.416112
H   4.664337 -1.390262  0.993593
H   2.412505 -2.348625  0.774644
H   3.311935  2.273480 -0.834452
H   1.050442  1.339333 -1.062048
C   5.532315  1.105554  0.273455
H   5.644461  1.562142  1.272092
H   6.315041  0.337641  0.177076
H   5.728877  1.892356 -0.470243
```

Mn(TMSM)2 + hexane – reactants association complex, -2284.0521992, *-2283.672122*

```
Mn -0.221240 -0.017217 -1.006206
C   0.973198  1.634302 -1.320559
H   1.820828  1.386486 -1.990445
H   0.352769  2.378510 -1.861056
C   2.998622  1.339656  1.007943
H   3.473358  1.844699  1.864823
H   2.597076  0.380496  1.371854
H   3.789028  1.114501  0.273129
C   2.387607  4.150907 -0.079702
H   1.633114  4.831756 -0.505895
H   2.770136  4.607945  0.848092
H   3.222255  4.088568 -0.796508
C   0.245316  2.630550  1.518141
H   0.598012  3.145536  2.426591
H  -0.591194  3.218096  1.105354
H  -0.161389  1.653939  1.832629
Si  1.643826  2.432922  0.243089
C   0.244912 -2.094409  3.257833
H   0.195054 -3.172393  3.481762
H   1.074888 -1.669292  3.845082
C  -3.412243  1.694402 -0.694024
H  -2.457507  2.183002 -0.434376
H  -3.584142  1.855620 -1.770844
H  -4.211632  2.217355 -0.144299
C  -5.101568 -0.883501 -0.629457
H  -5.360596 -0.779721 -1.695492
H  -5.135542 -1.956606 -0.381122
H  -5.882003 -0.374051 -0.040052
C  -3.028078 -0.348683  1.581350
H  -2.944516 -1.410181  1.866218
H  -2.087571  0.150392  1.867994
H  -3.834847  0.097975  2.184854
```

```
C  -2.017321 -0.990671 -1.272242
H  -0.689908 -1.633911  3.611949
H  -1.952955 -2.062072 -0.998129
H  -2.288682 -0.950336 -2.346603
Si -3.380515 -0.160823 -0.277572
C   0.451848 -1.856274  1.760216
H  -0.413878 -2.247493  1.196034
H   0.469005 -0.761427  1.575139
C   1.741991 -2.469363  1.203935
H   1.737086 -3.560139  1.383375
H   2.609407 -2.071019  1.762176
C   1.935733 -2.198509 -0.290831
H   1.078902 -2.618383 -0.854836
H   1.926363 -1.096574 -0.454850
C   3.242478 -2.736184 -0.884570
H   3.279124 -3.831405 -0.745024
H   4.091135 -2.323451 -0.310509
C   3.403533 -2.391781 -2.368395
H   3.396952 -1.300047 -2.523541
H   4.348939 -2.781388 -2.775711
H   2.581399 -2.816615 -2.967669
```

Mn(TMSM)2 + cyclohexane – reactants association complex, -2282.8577318, *-2282.494592*

```
Mn  0.202152  0.148115 -1.023971
C   2.162511 -0.406185 -1.311956
H   2.230856 -1.490014 -1.534189
H   2.539186  0.124692 -2.209979
C   2.793267 -1.046339  1.651370
H   3.484006 -0.874428  2.492779
H   1.777448 -0.799014  2.000417
H   2.812517 -2.123339  1.417286
C   5.116730 -0.333428 -0.240704
H   5.454948  0.272150 -1.096994
H   5.759948 -0.090028  0.621261
H   5.279722 -1.392725 -0.496976
C   3.095189  1.831097  0.605391
H   3.801562  2.119347  1.400834
H   3.283384  2.484964 -0.261895
H   2.079212  2.051991  0.974520
Si  3.285588 -0.003008  0.141631
C  -1.450672  1.334066 -1.347196
H  -2.343974  0.689749 -1.471149
H  -1.344440  1.912978 -2.285155
H  -0.959746 -2.021601 -1.557297
C  -0.501397  3.967231 -0.057583
H  -0.681840  4.544046 -0.979202
H  -0.595864  4.658791  0.795208
H   0.541985  3.613268 -0.086257
C  -1.415105  1.630172  1.737864
H  -1.608917  2.295746  2.595060
H  -2.071523  0.750800  1.844533
H  -0.371202  1.280492  1.830006
C  -3.492470  3.219988  0.133515
H  -4.230700  2.409576  0.247838
H  -3.627897  3.921693  0.973244
H  -3.728321  3.756791 -0.799306
```

```
Si -1.725801  2.524893  0.083297
C  -0.764361 -2.343817  1.252432
C  -2.268185 -2.410276  1.549120
C  -3.097673 -2.138911  0.285020
C  -2.708112 -3.087679 -0.859635
C  -1.201342 -3.031172 -1.150732
C  -0.361424 -3.285727  0.109343
H  -4.174581 -2.225877  0.504956
H  -2.512242 -3.416394  1.939138
H  -2.532280 -1.694285  2.345330
H  -0.508599 -1.296289  0.971476
H  -0.171249 -2.554134  2.157109
H  -2.978983 -4.123786 -0.581849
H  -3.282001 -2.847453 -1.770011
H  -0.927609 -3.739424 -1.950012
H  -0.510154 -4.331611  0.435847
H   0.712585 -3.175595 -0.115708
H  -2.927779 -1.094459 -0.038088
```

Mn(TMSM)2 + toluene (methyl) – reactants association complex, -2318.5313829, *-2318.206426*

```
Mn  0.017814 -0.280603 -0.687947
C   1.775158  0.711115 -1.124488
H   2.620169  0.043720 -0.863263
H   1.852565  0.927445 -2.207369
C   3.701889  2.959518 -0.041512
H   3.755419  3.908346  0.518061
H   4.345977  2.227335  0.472581
H   4.127777  3.131682 -1.043125
C   0.858473  3.651911 -1.012754
H  -0.182469  3.316131 -1.144218
H   0.839903  4.585948 -0.428182
H   1.259664  3.888528 -2.011797
C   1.281389  2.077856  1.613293
H   1.354660  3.009360  2.198286
H   0.223511  1.761622  1.634457
H   1.868841  1.305809  2.136868
Si  1.915446  2.319925 -0.170267
C  -0.051619 -3.864833 -1.423584
H   0.591922 -4.219034 -2.240959
H  -0.561797 -4.739767 -0.988381
C  -2.741597 -0.186053  1.885400
H  -2.845469 -1.282640  1.938590
H  -1.715288  0.074117  2.195231
H  -3.427727  0.246000  2.632014
C   0.743239 -3.131127 -0.373121
C   2.147835 -3.100459 -0.400673
C   0.082543 -2.460035  0.685864
C   2.881014 -2.444978  0.597765
H   2.674342 -3.601756 -1.217356
C   0.820093 -1.795513  1.685116
H  -1.006744 -2.516179  0.764252
C   2.220320 -1.789111  1.641852
H   3.972383 -2.438466  0.551547
H   0.291460 -1.295233  2.499850
H   2.789414 -1.268893  2.415010
C  -2.838935  2.351666  0.158256
```

```
H  -1.813651  2.606269  0.470808
H  -2.999122  2.787014 -0.841517
H  -3.532159  2.850120  0.855292
C  -4.968559  0.159005 -0.198849
H  -5.254998  0.542715 -1.191396
H  -5.193964 -0.919827 -0.182206
H  -5.609495  0.650206  0.552253
C  -2.010314 -0.344642 -1.131039
H  -2.340655 -1.396833 -1.252486
H  -2.178566  0.148872 -2.109088
H  -0.832009 -3.216435 -1.854485
Si -3.124361  0.475288  0.139571
```

Mn(TMSM)2 + toluene (ortho) – reactants association complex, -2318.5313829, *-2318.206426*

```
Mn -0.017810  0.280603 -0.687949
C  -1.775153 -0.711120 -1.124488
H  -2.620165 -0.043726 -0.863261
H  -1.852561 -0.927449 -2.207369
C  -3.701880 -2.959524 -0.041511
H  -3.755409 -3.908349  0.518070
H  -4.345970 -2.227339  0.472574
H  -4.127764 -3.131698 -1.043124
C  -0.858463 -3.651914 -1.012755
H   0.182478 -3.316129 -1.144225
H  -0.839886 -4.585950 -0.428181
H  -1.259657 -3.888534 -2.011796
C  -1.281380 -2.077860  1.613292
H  -1.354647 -3.009365  2.198285
H  -0.223503 -1.761622  1.634457
H  -1.868834 -1.305817  2.136869
Si -1.915437 -2.319930 -0.170266
C   2.838946 -2.351655  0.158248
H   1.813662 -2.606263  0.470796
H   2.999137 -2.786997 -0.841527
H   3.532170 -2.850109  0.855283
C   4.968562 -0.158983 -0.198842
H   5.255006 -0.542683 -1.191391
H   5.193965  0.919849 -0.182187
H   5.609498 -0.650189  0.552258
C   2.741593  0.186058  1.885401
H   2.845455  1.282645  1.938594
H   1.715285 -0.074122  2.195230
H   3.427725 -0.245992  2.632016
C   2.010318  0.344654 -1.131039
H   1.006733  2.516189  0.764247
H   2.340653  1.396848 -1.252481
H   2.178575 -0.148855 -2.109089
Si  3.124365 -0.475275  0.139571
C  -2.220324  1.789100  1.641857
C  -2.881025  2.444959  0.597771
C  -2.147854  3.100443 -0.400671
C  -0.743258  3.131120 -0.373123
C  -0.082554  2.460036  0.685862
C  -0.820097  1.795512  1.685118
H  -2.789412  1.268880  2.415018
```

```
H  -3.972395  2.438440  0.551556
H  -0.291458  1.295238  2.499851
C   0.051593  3.864830 -1.423590
H   0.831986  3.216435 -1.854491
H  -0.591953  4.219023 -2.240965
H   0.561765  4.739768 -0.988392
H  -2.674366  3.601734 -1.217354
```

Mn(TMSM)2 + toluene (meta) – reactants association complex, -2318.5290003, *-2318.204109*

```
Mn -0.192263 -0.018013 -0.908028
C   1.476407  1.118541 -1.346687
H   2.214271  0.540637 -1.936321
H   1.106199  1.921803 -2.014379
C   3.962853  0.989106  0.513838
H   4.471330  1.431292  1.386188
H   3.771964 -0.071590  0.739741
H   4.658054  1.034234 -0.340119
C   2.746965  3.733771 -0.197510
H   1.828610  4.306963 -0.405528
H   3.244587  4.199607  0.669154
H   3.411260  3.840917 -1.070091
C   1.259807  1.835844  1.691431
H   1.761937  2.309767  2.551336
H   0.300153  2.356825  1.540311
H   1.032193  0.793322  1.972651
Si  2.343359  1.905688  0.126929
C  -2.662680  1.160545  1.600894
H  -1.821216  0.538411  1.949151
H  -2.272323  2.179086  1.440717
H  -3.401464  1.213018  2.417500
C  -4.917108  1.578695 -0.432755
H  -4.589753  2.611665 -0.634504
H  -5.429341  1.210223 -1.336224
H  -5.654767  1.612889  0.386387
C  -4.116556 -1.266606  0.371961
H  -4.566152 -1.710387 -0.531409
H  -3.340846 -1.959553  0.733754
H  -4.901256 -1.220950  1.144770
C  -2.167738  0.406675 -1.379072
H  -1.471357 -2.526466 -0.586919
H  -2.526857 -0.302217 -2.152829
H  -2.126642  1.400729 -1.869287
Si -3.434081  0.471670  0.004437
C   0.857804 -2.165689  1.886536
C   2.024503 -2.294229  1.117420
C   1.960039 -2.445776 -0.276933
C   0.685326 -2.490949 -0.883752
C  -0.495220 -2.399236 -0.113356
C  -0.401483 -2.222650  1.281840
H   0.935076 -2.034411  2.968442
H   3.000585 -2.264750  1.608606
H   0.613208 -2.665209 -1.962367
H  -1.308493 -2.141657  1.883975
C   3.208552 -2.516478 -1.114225
H   3.467248 -1.512646 -1.492448
```

```
H   4.066358 -2.879698 -0.530265
H   3.075298 -3.173923 -1.986196
```

Mn(TMSM)2 + toluene (para) – reactants association complex, -2318.5310214, *-2318.206487*

```
Mn -0.173941 -0.315309 -0.854437
C   1.343043  1.056169 -1.167363
H   2.311045  0.537353 -1.022256
H   1.328905  1.425550 -2.211078
C   2.898308  3.434271  0.183255
H   2.816934  4.298134  0.863919
H   3.670163  2.758519  0.587726
H   3.256406  3.802753 -0.791580
C  -0.054518  3.756300 -0.655779
H  -1.030043  3.268607 -0.811417
H  -0.204792  4.594026  0.044285
H   0.263884  4.178753 -1.622780
C   0.712589  1.961335  1.737266
H   0.640115  2.814369  2.431847
H  -0.271942  1.461611  1.728690
H   1.442199  1.248901  2.155630
Si  1.236986  2.526808 -0.007594
C  -3.421700  1.578868  0.319137
H  -2.449211  1.975964  0.651738
H  -3.680625  2.083984 -0.625672
H  -4.173798  1.868684  1.070917
C  -5.137801 -0.907274 -0.265488
H  -5.516443 -0.469824 -1.203433
H  -5.167240 -2.003641 -0.375034
H  -5.833867 -0.628961  0.543430
C  -2.830960 -1.072922  1.752136
H  -2.759394 -2.171575  1.688869
H  -1.849115 -0.685897  2.073389
H  -3.553638 -0.836284  2.550040
C  -2.158430 -0.760271 -1.266671
H  -0.675688 -2.826521  0.492599
H  -2.254915 -1.844063 -1.484163
H  -2.461416 -0.227452 -2.190256
Si -3.369756 -0.305607  0.092838
C   2.392111 -1.558830  1.330446
C   3.128477 -1.900261  0.183116
C   2.461543 -2.571270 -0.859449
C   1.102264 -2.890187 -0.762587
C   0.372021 -2.536912  0.390163
C   1.031035 -1.868353  1.438495
H   2.891165 -1.034669  2.150264
H   0.478513 -1.597297  2.340937
H   3.015092 -2.842703 -1.762494
H   0.605532 -3.422084 -1.577783
C   4.578175 -1.511387  0.050044
H   4.666846 -0.515826 -0.418194
H   5.073907 -1.458351  1.030454
H   5.131783 -2.221805 -0.581431
```

Mn(TMSM)2 + hexane – products association complex, -2284.0370012, *-2283.662403*

```
Mn -0.343289  0.027999 -0.295807
C  -1.074430  1.765795 -1.145310
H  -0.530002  1.971611 -2.088566
H  -2.147198  1.674956 -1.408637
C   1.002020  3.341556  0.498475
H   1.191079  4.205420  1.156251
H   1.343895  2.437782  1.031496
H   1.635533  3.455468 -0.396373
C  -1.377051  4.878656 -0.719453
H  -2.444873  4.858279 -0.990965
H  -1.223081  5.709076 -0.010422
H  -0.805179  5.103931 -1.634068
C  -1.839844  2.921572  1.612599
H  -1.747247  3.771911  2.307681
H  -2.911348  2.790370  1.388020
H  -1.498505  2.019602  2.148674
Si -0.835081  3.216831  0.024149
C   1.253059 -1.095010  0.383483
H   1.129731 -2.164967  0.116465
H   1.270780 -1.069857  1.493447
C  -2.805672 -1.041444  1.357722
H  -1.790549 -1.349568  1.667360
H  -2.781326  0.013709  1.031681
H  -3.433763 -1.072055  2.263546
C  -5.223397 -1.563467 -0.488380
H  -5.177892 -0.533188 -0.876470
H  -5.662747 -2.199046 -1.273763
H  -5.912390 -1.568396  0.371320
C  -3.599802 -3.946216  0.670711
H  -4.000669 -4.635531 -0.089553
H  -2.603392 -4.313208  0.964772
H  -4.254080 -4.005598  1.555159
C  -2.364268 -2.137990 -1.507784
H  -1.344297 -2.480767 -1.258680
H  -2.740047 -2.806402 -2.300151
H  -2.304530 -1.126280 -1.947650
Si -3.506533 -2.178558  0.008084
C   2.595124 -0.574410 -0.163875
H   2.593724 -0.618856 -1.270479
H   2.715721  0.498009  0.084974
C   3.832273 -1.331526  0.350373
H   3.728118 -2.402694  0.094285
H   3.844742 -1.284076  1.455559
C   5.159422 -0.797703 -0.201094
H   5.141567 -0.844543 -1.306686
H   5.256073  0.274837  0.053876
C   6.391856 -1.551109  0.314840
H   6.294296 -2.622145  0.059841
H   6.409051 -1.503117  1.418919
C   7.711009 -1.007579 -0.243942
H   7.849433  0.052786  0.024685
H   8.578313 -1.565672  0.142459
H   7.734090 -1.074316 -1.344293
```

Mn(TMSM)2 + cyclohexane –products association complex, -2282.844079, *-2282.478919*

```
Mn  0.365760 -0.581298 -0.992942
C   2.042524  0.562342 -1.359674
H   2.645312 -0.017994 -2.089549
H   1.799157  1.524586 -1.850865
C   3.405458 -0.742366  1.088078
H   4.083486 -0.595149  1.944525
H   2.466207 -1.166900  1.481157
H   3.861422 -1.498638  0.428056
C   4.797676  1.626841 -0.293892
H   4.679020  2.585202 -0.824675
H   5.410746  1.810137  0.604236
H   5.360336  0.947463 -0.954398
C   2.225722  2.095526  1.329638
H   2.848441  2.310488  2.213244
H   2.013450  3.052841  0.826995
H   1.266725  1.688072  1.687493
Si  3.106201  0.888921  0.157526
C  -3.012725  0.950285 -1.198336
H  -3.823237  0.320470 -0.798691
H  -3.398386  1.482171 -2.082960
H  -2.220575  0.264274 -1.551333
C  -0.976180  3.203715 -0.646528
H  -1.324291  3.764257 -1.528928
H  -0.581791  3.929116  0.082802
H  -0.135053  2.565329 -0.963062
C  -1.722414  1.224462  1.609718
H  -1.324933  1.916913  2.369067
H  -2.514771  0.620616  2.080057
H  -0.904412  0.531985  1.341606
C  -3.792363  3.302145  0.644988
H  -4.621117  2.720971  1.080115
H  -3.455261  4.026470  1.403717
H  -4.193685  3.872618 -0.207944
Si -2.374413  2.173920  0.102778
C  -0.073260 -3.000336  1.375675
C  -1.584549 -3.260138  1.469803
C  -2.358469 -2.511309  0.373452
C  -1.804265 -2.825438 -1.025021
C  -0.296309 -2.540051 -1.115783
C   0.465401 -3.325094 -0.028061
H  -3.432931 -2.757841  0.428745
H  -1.765505 -4.346092  1.361042
H  -1.961289 -2.978326  2.467858
H   0.119530 -1.930150  1.603490
H   0.467556 -3.578695  2.144017
H  -1.999101 -3.898701 -1.242632
H  -2.362026 -2.255318 -1.788427
H   0.075418 -2.854832 -2.115071
H   0.357806 -4.418303 -0.199049
H   1.552401 -3.124545 -0.071056
H  -2.275153 -1.423327  0.555369
```

Mn(TMSM)2 + toluene (methyl) – products association complex, -2318.5250583, *-2318.202490*

```
Mn  0.567909 -0.230831 -1.513403
C   1.169233  1.722684 -1.421137
H   1.878323  1.945143 -2.242540
H   0.290696  2.378210 -1.585070
```

```
C   3.751675  1.481149  0.251162
H   4.247569  1.698646  1.211007
H   3.757751  0.388549  0.111012
H   4.358569  1.930794 -0.551311
C   2.030275  4.031178  0.519639
H   1.012210  4.453183  0.536920
H   2.514334  4.277035  1.479370
H   2.588907  4.539411 -0.282671
C   1.012731  1.360727  1.659604
H   1.458641  1.624358  2.632909
H  -0.036317  1.698228  1.674591
H   1.015572  0.258922  1.589438
Si  1.978178  2.154901  0.226882
C   0.613667 -2.243234 -2.096952
H   1.408862 -2.455138 -2.825220
H  -0.344696 -2.688681 -2.393547
C  -2.715180 -0.368818  1.770291
H  -3.142194 -1.365879  1.966493
H  -1.623716 -0.482994  1.678300
H  -2.911195  0.259534  2.654067
C   0.988807 -2.443899 -0.690148
C   2.332680 -2.246338 -0.247403
C   0.015250 -2.689743  0.324911
C   2.673454 -2.304307  1.106227
H   3.111745 -2.069274 -0.996064
C   0.366325 -2.744168  1.673863
H  -1.025309 -2.848807  0.027068
C   1.696242 -2.551352  2.079629
H   3.714332 -2.152802  1.403848
H  -0.407802 -2.938535  2.420873
H   1.964019 -2.589929  3.137178
C  -2.679242  2.092560 -0.104400
H  -1.591891  2.005153 -0.258814
H  -3.105651  2.570039 -1.001235
H  -2.839985  2.772690  0.747548
C  -5.335501  0.595317  0.432156
H  -5.798794  1.036481 -0.464961
H  -5.819153 -0.377555  0.615945
H  -5.568082  1.251336  1.286374
C  -3.135593 -0.727624 -1.276288
H  -3.580411 -1.725766 -1.133011
H  -3.553939 -0.301987 -2.202364
H  -2.054357 -0.881840 -1.449479
Si -3.465655  0.400632  0.213224
```

Mn(TMSM)2 + toluene (ortho) – products association complex, -2318.5180085, *-2318.196724*

```
Mn -0.311528  0.224887 -0.340037
C  -2.027494 -0.660165 -1.059350
H  -2.347463 -0.127240 -1.977336
H  -1.857415 -1.716764 -1.347420
C  -3.669418  1.233219  0.738839
H  -4.491967  1.326229  1.466439
H  -2.762046  1.648319  1.210562
H  -3.914356  1.869529 -0.127281
C  -5.066267 -1.240617 -0.454885
H  -4.971937 -2.295959 -0.757653
```

```
H  -5.862227 -1.175774  0.305520
H  -5.394315 -0.668777 -1.337878
C  -2.937512 -1.585977  1.744255
H  -3.749008 -1.582258  2.490041
H  -2.731261 -2.636864  1.482230
H  -2.036317 -1.181574  2.235188
Si -3.415369 -0.574388  0.206911
C   0.993469 -2.131535  1.216356
H   1.106196 -1.090566  1.572055
H  -0.042072 -2.286092  0.865936
H   1.118895 -2.770354  2.106540
C   2.058041 -4.410472 -0.558839
H   1.044548 -4.612773 -0.940914
H   2.776782 -4.717447 -1.335357
H   2.220002 -5.053439  0.321043
C   4.007947 -2.255231  0.542896
H   4.773121 -2.531726 -0.199991
H   4.145869 -1.188478  0.781964
H   4.204017 -2.835164  1.458839
C   1.975811 -1.526929 -1.667185
H   2.138629 -0.451846 -1.470902
H   2.679968 -1.809903 -2.467316
H   0.958949 -1.668479 -2.074533
Si  2.268811 -2.584239 -0.119365
C   2.945104  2.826592  0.984129
C   2.568740  4.093936  0.528321
C   1.363992  4.251168 -0.168814
C   0.522096  3.154674 -0.417537
C   0.883797  1.854041  0.032961
C   2.107102  1.731348  0.732759
H   3.884543  2.691395  1.527736
H   3.211248  4.959538  0.710290
H   2.431210  0.748362  1.097147
C  -0.784969  3.371813 -1.152921
H  -1.644096  3.319732 -0.462371
H  -0.818897  4.353989 -1.648552
H  -0.948699  2.602770 -1.927367
H   1.075467  5.245017 -0.527304
```

Mn(TMSM)2 + toluene (meta) – products association complex, -2318.5178609, *-2318.196976*

```
Mn  0.087628  0.272372 -0.597515
C  -0.171161  2.247579 -1.123813
H   0.296843  2.433397 -2.111189
H  -1.245376  2.500472 -1.228017
C   2.458803  2.935035  0.330717
H   2.970523  3.614823  1.031219
H   2.587236  1.908001  0.712583
H   2.980237  2.998714 -0.638579
C   0.492796  5.221293 -0.317325
H  -0.560572  5.529768 -0.415437
H   0.965008  5.864819  0.443493
H   0.988605  5.417474 -1.281682
C  -0.224203  3.134972  1.833405
H   0.198289  3.810540  2.594884
H  -1.306136  3.338043  1.771675
H  -0.098337  2.102880  2.202075
Si  0.620896  3.384364  0.148326
```

```
C  -2.317259 -0.277533  1.321774
H  -1.351576 -0.783689  1.503233
H  -2.128565  0.772829  1.037234
H  -2.836238 -0.245599  2.294336
C  -5.016231 -0.271340 -0.172765
H  -4.854506  0.766150 -0.506748
H  -5.658448 -0.767746 -0.917695
H  -5.571616 -0.235188  0.778037
C  -3.666936 -2.962201  0.599541
H  -4.277573 -3.517731 -0.130026
H  -2.715268 -3.504108  0.721510
H  -4.193407 -2.987864  1.566979
C  -2.465128 -1.203521 -1.638051
H  -1.509348 -1.755962 -1.586358
H  -3.074877 -1.709576 -2.405119
H  -2.274640 -0.181915 -2.014130
Si -3.373783 -1.183977  0.030202
C   1.721860 -3.637119  0.554356
C   3.100348 -3.440577  0.417389
C   3.608015 -2.202306 -0.014236
C   2.690886 -1.174120 -0.295224
C   1.289481 -1.329072 -0.170087
C   0.831349 -2.595481  0.262690
H   1.343017 -4.606318  0.892932
H   3.792393 -4.256423  0.649568
H   3.101751 -0.209610 -0.623800
H  -0.242478 -2.783964  0.382145
C   5.094020 -1.994817 -0.185226
H   5.659459 -2.404321  0.666822
H   5.463697 -2.500558 -1.093520
H   5.341781 -0.926792 -0.276805
```

Mn(TMSM)2 + toluene (para) – products association complex, -2318.5179441, *-2318.196603*

```
Mn -0.337122  0.293629 -0.625667
C  -2.269519  0.829315 -1.100679
H  -2.285160  1.312156 -2.098263
H  -2.931067 -0.057723 -1.165856
C  -1.798772  3.534911  0.298375
H  -2.192579  4.287753  1.000386
H  -0.796519  3.242330  0.654994
H  -1.674296  4.024208 -0.681717
C  -4.699969  2.654084 -0.263946
H  -5.410786  1.814838 -0.332948
H  -5.078962  3.357875  0.495656
H  -4.701255  3.172557 -1.236317
C  -3.030813  1.186344  1.869881
H  -3.458143  1.858146  2.631984
H  -3.656739  0.279258  1.837045
H  -2.027689  0.887865  2.218548
Si -2.957748  2.033815  0.169185
C  -0.721454 -2.099468  1.353552
H   0.135841 -1.414184  1.484241
H  -1.620440 -1.510850  1.098400
H  -0.913982 -2.545048  2.343811
C  -1.868449 -4.603576 -0.036362
H  -2.774060 -4.051014 -0.334004
H  -1.704603 -5.403334 -0.776178
```

```
H  -2.071195 -5.081842  0.935217
C   1.170636 -4.417928  0.580182
H   1.401065 -5.213373 -0.146419
H   2.050861 -3.758211  0.644888
H   1.034364 -4.892047  1.565283
C  -0.078691 -2.660560 -1.632504
H   0.811772 -2.005971 -1.640303
H   0.100368 -3.436665 -2.395303
H  -0.956553 -2.082487 -1.973424
Si -0.372435 -3.453335  0.068605
C   3.951958  0.187701  0.327184
C   4.364699  1.521969  0.166737
C   3.399008  2.463966 -0.227415
C   2.069228  2.082792 -0.445155
C   1.628903  0.746289 -0.286270
C   2.620556 -0.184611  0.106698
H   4.686740 -0.567760  0.626594
H   2.357682 -1.240802  0.245079
H   3.695814  3.509146 -0.366577
H   1.357588  2.859481 -0.752225
C   5.790960  1.934210  0.436732
H   5.923133  2.228493  1.492373
H   6.493947  1.111244  0.236868
H   6.085772  2.795870 -0.181296
```

Mn(TMSM)2 + hexane – TS, -2283.9976497, *-2283.621878*

```
Mn -0.674982 -0.096392 -0.686293
C  -0.678208  1.832554 -1.360147
H   0.096018  1.967811 -2.141494
H  -1.648639  2.097683 -1.822127
C   1.515050  2.738951  0.608325
H   1.778807  3.404135  1.446434
H   1.701001  1.702272  0.934174
H   2.207507  2.954942 -0.221671
C  -0.541525  4.822571 -0.365159
H  -1.585582  5.016526 -0.659714
H  -0.303171  5.478112  0.488803
H   0.102853  5.116728 -1.209210
C  -1.416680  2.577640  1.548247
H  -1.247965  3.269331  2.389718
H  -2.481825  2.642792  1.271174
H  -1.233737  1.556063  1.925799
Si -0.289721  2.990559  0.068701
C   0.777665 -1.305137  0.524722
H   0.738974 -2.287317  1.029922
H   0.747223 -0.561347  1.350102
C  -4.136300 -0.072632 -0.558551
H  -3.489282  0.794373 -0.344337
H  -4.292403 -0.106725 -1.648843
H  -5.112401  0.120836 -0.084303
C  -4.663773 -3.089407 -0.179709
H  -4.898604 -3.213984 -1.248747
H  -4.276088 -4.050891  0.193399
H  -5.606009 -2.876019  0.351672
C  -3.042045 -1.526666  1.937722
H  -2.565247 -2.435929  2.338174
```

```
H  -2.362944 -0.680949  2.138017
H  -3.966353 -1.350261  2.510853
C  -1.764338 -2.081778 -0.792984
H  -0.511544 -1.752804 -0.171571
H  -1.510023 -3.133837 -0.563244
H  -1.859522 -2.040987 -1.896302
Si -3.401226 -1.700536  0.083444
C   2.071038 -1.176333 -0.292703
H   2.071479 -1.931860 -1.100873
H   2.111786 -0.193881 -0.806687
C   3.359528 -1.327774  0.534962
H   3.347046 -2.312463  1.038256
H   3.354701 -0.572472  1.342856
C   4.642425 -1.184008 -0.291480
H   4.643183 -1.937364 -1.102005
H   4.643425 -0.198057 -0.793819
C   5.926440 -1.329704  0.534630
H   5.924254 -2.314191  1.036893
H   5.923032 -0.576519  1.343348
C   7.201986 -1.181359 -0.301056
H   7.245633 -0.193002 -0.787637
H   8.107511 -1.289583  0.316153
H   7.247134 -1.943195 -1.096791
```

Mn(TMSM)2 + cyclohexane – TS, -2282.8052963, *-2282.439905*

```
Mn -0.053410  0.149190 -0.980785
C  -2.053350  0.327868 -1.355781
H  -2.197541  1.257697 -1.945005
H  -2.400787 -0.505335 -1.999192
C  -2.534210  1.671956  1.408486
H  -3.231691  1.781830  2.254960
H  -1.559875  1.362126  1.821694
H  -2.400368  2.668173  0.955775
C  -4.946203  0.965826 -0.355760
H  -5.385835  0.263612 -1.082415
H  -5.616885  1.013019  0.518245
H  -4.931048  1.963377 -0.824079
C  -3.328779 -1.273991  0.987355
H  -4.033416 -1.228819  1.833833
H  -3.697488 -2.041002  0.286958
H  -2.359452 -1.620426  1.378784
Si -3.194144  0.419692  0.138549
C   1.716582 -1.254746 -1.114154
H   2.806182 -1.147547 -0.958742
H   1.596413 -1.647077 -2.141446
H   1.669380  0.171877 -1.102382
C  -0.432822 -3.398449 -0.474965
H  -0.202095 -3.984575 -1.379173
H  -0.840903 -4.088319  0.280991
H  -1.227629 -2.680238 -0.732884
C   0.734628 -1.635582  1.802823
H   0.435989 -2.357647  2.580292
H   1.617103 -1.088355  2.172421
H  -0.090962 -0.907550  1.710840
C   2.468887 -3.812261  0.513047
```

```
H   3.381029 -3.333220  0.904029
H   2.130779 -4.552189  1.257197
H   2.741296 -4.355406 -0.405757
Si  1.121131 -2.525298  0.165113
C   1.272339  2.458477  1.222295
C   2.793645  2.495267  1.425789
C   3.510324  1.531409  0.468283
C   3.121096  1.795697 -0.996917
C   1.596754  1.726002 -1.199004
C   0.903824  2.723946 -0.246588
H   4.603492  1.610632  0.592403
H   3.153237  3.524887  1.239488
H   3.048264  2.258606  2.472671
H   0.893321  1.461447  1.523968
H   0.772985  3.188576  1.880690
H   3.489588  2.802171 -1.284847
H   3.637873  1.081010 -1.661795
H   1.356973  1.975220 -2.252525
H   1.220987  3.758414 -0.504673
H  -0.196615  2.722138 -0.368173
H   3.238863  0.493108  0.736748
```

Mn(TMSM)2 + toluene (methyl) – TS, -2318.4875551, *-2318.162512*

```
Mn  0.214837 -0.241045  0.971108
C  -0.930787  1.394630  1.415340
H  -1.617466  1.145475  2.248136
H  -0.257070  2.189611  1.790460
C  -3.767126  1.549785  0.180937
H  -4.376796  1.876129 -0.677285
H  -3.854035  0.454805  0.259770
H  -4.201012  1.990465  1.092964
C  -1.847999  3.958466 -0.113239
H  -0.804429  4.288686 -0.246224
H  -2.436059  4.356381 -0.956739
H  -2.227332  4.418306  0.813458
C  -1.340640  1.386341 -1.694844
H  -1.962543  1.761174 -2.525089
H  -0.301253  1.691539 -1.899964
H  -1.385705  0.283970 -1.722620
Si -1.951377  2.063240 -0.022208
C   0.191081 -2.370891  1.905240
H  -0.350859 -2.276316  2.855345
H   0.940963 -3.172580  1.962865
C   2.365153 -0.251993 -1.924838
H   2.703449 -1.292325 -2.060038
H   1.264298 -0.251316 -1.974168
H   2.735966  0.334987 -2.780910
C  -0.665633 -2.449826  0.705802
C  -2.061656 -2.169978  0.738023
C  -0.082681 -2.694501 -0.572296
C  -2.828971 -2.183897 -0.426826
H  -2.534084 -1.960938  1.701905
C  -0.859134 -2.690893 -1.736826
H   0.986221 -2.917504 -0.631760
C  -2.235202 -2.443154 -1.672795
H  -3.902032 -1.986502 -0.366125
```

```
H  -0.381915 -2.885679 -2.700575
H  -2.839848 -2.444955 -2.581880
C   2.448747  2.262942 -0.111261
H   1.352437  2.359476 -0.132915
H   2.799567  2.690635  0.841743
H   2.857757  2.879058 -0.928564
C   4.915902  0.443146 -0.356409
H   5.345941  0.853253  0.571223
H   5.297841 -0.583042 -0.479328
H   5.292030  1.046581 -1.199131
C   2.432603 -0.598952  1.173636
H   3.018781 -1.533810  1.081693
H   2.770538 -0.111131  2.106654
H   1.348250 -1.424738  1.649428
Si  3.018914  0.465265 -0.295500
```

Mn(TMSM)2 + toluene (ortho) – TS, -2318. 481469, *-2318.160578*

```
Mn  0.136228 -0.419311 -0.771095
C  -1.161659 -1.962138 -1.082430
H  -1.602873 -1.891561 -2.096570
H  -0.644732 -2.940017 -1.028864
C  -3.565400 -0.299067 -0.096690
H  -4.402546 -0.230350  0.616871
H  -2.948489  0.606857  0.023685
H  -3.991367 -0.286478 -1.113525
C  -3.695461 -3.377949  0.136533
H  -3.138118 -4.309233  0.327906
H  -4.497233 -3.302387  0.889784
H  -4.168892 -3.470236 -0.854281
C  -1.781906 -1.769028  1.938454
H  -2.560672 -1.807628  2.717559
H  -1.081586 -2.600490  2.121067
H  -1.230342 -0.822706  2.075383
Si -2.540546 -1.870085  0.195935
C   2.266059 -1.817803  1.089338
H   1.460830 -1.321338  1.660113
H   1.800172 -2.582182  0.444239
H   2.886570 -2.353929  1.827198
C   4.760315 -1.552403 -0.686305
H   4.382310 -2.328498 -1.371090
H   5.415820 -0.883609 -1.266211
H   5.375940 -2.050676  0.080717
C   4.009703  0.714931  1.295749
H   4.701965  1.400013  0.780550
H   3.197909  1.323973  1.724500
H   4.557782  0.245754  2.128428
C   2.272494  0.286935 -1.200587
H   1.124492  1.060034 -0.698037
H   2.749727  1.247393 -1.463890
H   2.215010 -0.280939 -2.152284
Si  3.332658 -0.586333  0.099522
C  -0.699816  2.931273  1.900331
C  -1.522718  3.754134  1.121807
C  -1.619266  3.547500 -0.261037
C  -0.908761  2.510614 -0.885260
```

```
C  -0.081298  1.662520 -0.105223
C   0.022465  1.904952  1.280027
H  -0.616467  3.095730  2.977949
H  -2.086605  4.565075  1.589829
H   0.684244  1.278282  1.891199
C  -1.051769  2.259285 -2.369167
H  -1.696109  1.380692 -2.556204
H  -1.505429  3.114566 -2.891497
H  -0.074313  2.052375 -2.835562
H  -2.260171  4.201603 -0.861242
```

Mn(TMSM)2 + toluene (meta) – TS, -2318.4798706, *-2318.159752*

```
Mn  0.334560 -0.402236 -0.880231
C  -0.549543 -2.211918 -1.199423
H  -1.040604 -2.219688 -2.193129
H   0.196457 -3.030343 -1.207463
C  -3.252959 -1.253665 -0.053046
H  -4.035454 -1.417408  0.705705
H  -2.876852 -0.224332  0.067181
H  -3.727968 -1.324324 -1.045368
C  -2.593222 -4.270266  0.017962
H  -1.812772 -5.037970  0.144847
H  -3.357238 -4.432410  0.796405
H  -3.068024 -4.436134 -0.962561
C  -1.071611 -2.314660  1.846411
H  -1.783888 -2.582152  2.643968
H  -0.179980 -2.952089  1.963315
H  -0.767181 -1.267888  2.018166
Si -1.852629 -2.523132  0.123585
C   2.796782 -1.331326  0.928677
H   1.875396 -1.116719  1.498914
H   2.572293 -2.149996  0.224169
H   3.530994 -1.719793  1.654366
C   5.152244 -0.251994 -0.729216
H   5.035935 -1.066275 -1.462359
H   5.594634  0.610204 -1.252940
H   5.869838 -0.588512  0.037258
C   3.726639  1.582299  1.325635
H   4.197076  2.467876  0.869057
H   2.763380  1.902518  1.753872
H   4.371945  1.247809  2.153659
C   2.246940  0.809982 -1.250874
H   0.961219  1.262045 -0.733194
H   2.475117  1.859603 -1.507968
H   2.335486  0.252166 -2.206599
Si  3.485731  0.209038  0.045264
C  -1.460517  2.393464  1.869701
C  -2.446225  3.002395  1.084844
C  -2.416694  2.907258 -0.319398
C  -1.369063  2.180289 -0.909054
C  -0.376483  1.532617 -0.144132
C  -0.430193  1.668177  1.258673
H  -1.496759  2.489813  2.958671
H  -3.249727  3.567547  1.567121
H  -1.337798  2.112594 -2.004491
H   0.339630  1.203189  1.886511
```

```
C  -3.497329  3.544397 -1.158457
H  -4.408478  2.922130 -1.160929
H  -3.780064  4.535104 -0.770209
H  -3.176625  3.664346 -2.203882
```

Mn(TMSM)2 + toluene (para) – TS, -2318.4799334, *-2318.160474*

```
Mn  0.455297 -0.528409 -0.949030
C  -0.257363 -2.436213 -1.057009
H  -0.652865 -2.629278 -2.074488
H   0.545085 -3.179052 -0.881944
C  -3.107505 -1.540889 -0.271789
H  -3.942613 -1.662500  0.437264
H  -2.808997 -0.479601 -0.262953
H  -3.487356 -1.773981 -1.280013
C  -2.268317 -4.465957  0.257925
H  -1.455336 -5.150638  0.549214
H  -3.087090 -4.582994  0.987248
H  -2.642159 -4.791673 -0.726209
C  -1.045468 -2.184799  1.924061
H  -1.809733 -2.400913  2.688390
H  -0.129887 -2.733655  2.198500
H  -0.824621 -1.105136  1.979525
Si -1.651774 -2.669555  0.186452
C   2.798971 -1.018837  1.221995
H   1.803196 -0.826076  1.658981
H   2.724162 -1.934395  0.611378
H   3.474620 -1.242811  2.064423
C   5.233361  0.080660 -0.305769
H   5.279062 -0.828220 -0.926993
H   5.656010  0.910544 -0.894087
H   5.881754 -0.077948  0.571815
C   3.418182  2.002867  1.312410
H   3.854555  2.867953  0.787727
H   2.387311  2.271391  1.593421
H   3.993144  1.846776  2.239248
C   2.327824  0.760423 -1.273665
H   0.968381  1.181136 -0.952041
H   2.514686  1.773916 -1.671078
H   2.558279  0.073251 -2.115012
Si  3.451648  0.459769  0.216114
C  -1.809061  2.446405  1.206321
C  -2.729816  2.930951  0.260125
C  -2.476702  2.678705 -1.101115
C  -1.353735  1.946648 -1.499492
C  -0.440805  1.427529 -0.556403
C  -0.685006  1.717575  0.803190
H  -1.976640  2.648164  2.269421
H   0.015231  1.365815  1.571318
H  -3.171903  3.064002 -1.854390
H  -1.190194  1.773805 -2.569894
C  -3.965261  3.680773  0.691673
H  -4.819555  2.991513  0.806488
H  -3.816413  4.182521  1.659409
H  -4.256563  4.440248 -0.049580
```

Hex-1-ene, -235.5714542, *-235.443248*

```
C    3.016087 -0.389885  0.163722
H    3.129679 -1.040025 -0.719348
H    2.948545 -1.043697  1.048707
H    3.936415  0.207048  0.259243
C    1.776004  0.500902  0.038747
H    1.705534  1.164472  0.919685
H    1.883669  1.167738 -0.836091
C    0.473675 -0.297516 -0.094897
H    0.355689 -0.965075  0.777655
H    0.538863 -0.959086 -0.978811
C   -0.776901  0.593742 -0.216492
H   -0.641906  1.269796 -1.082925
H   -0.862698  1.239285  0.675354
C   -2.042708 -0.194277 -0.396795
H   -2.083994 -0.833904 -1.288919
C   -3.087036 -0.187119  0.442600
H   -3.087684  0.432032  1.345414
H   -3.976837 -0.793659  0.258734
```

Cyclohexene, -234.3738716, *-234.262471*

```
C    0.727673  1.270647 -0.185441
H    1.334706  2.096735 -0.567119
C   -0.615796  1.328121 -0.186743
H   -1.149322  2.203058 -0.569395
C    1.394428  0.033220  0.356536
H    2.472995  0.023359  0.136275
H    1.306771  0.029667  1.461284
C   -1.386890  0.152847  0.355141
H   -1.301877  0.143965  1.460044
H   -2.461965  0.235044  0.132950
C    0.724476 -1.249342 -0.200666
H    1.077142 -2.119742  0.375990
H    1.080671 -1.395981 -1.232778
C   -0.828641 -1.184042 -0.197872
H   -1.199762 -1.306141 -1.227903
H   -1.250856 -2.018667  0.384923
```

Mn(TMSM)C6H13 + H2 – reactants association complex, -1836.3419259, *-1836.085308*

```
Mn   1.061265 -1.615015  0.113891
C    2.486536 -0.507692  1.111489
H    2.026148 -0.072430  2.021257
H    3.341795 -1.126451  1.446473
C    1.614778  1.902371 -0.597907
H    1.935957  2.751076 -1.223360
H    0.921249  1.291895 -1.201798
H    1.042046  2.309469  0.251470
C    4.315326  2.053003  0.881908
H    5.203566  1.505268  1.235626
H    4.657817  2.856985  0.209453
H    3.842412  2.523520  1.758902
C    3.973276  0.137248 -1.510128
```

```
H   4.367041  0.922798 -2.175295
H   4.819482 -0.500923 -1.207503
H   3.284375 -0.484608 -2.107417
Si  3.102855  0.883305  0.006180
C  -0.856684 -1.726551 -0.634661
H  -1.308485 -2.725283 -0.471420
H  -0.845407 -1.577124 -1.733299
C  -1.720795 -0.639157  0.031269
H  -1.739277 -0.786227  1.129358
H  -1.263739  0.358080 -0.122471
C  -3.175037 -0.583915 -0.471189
H  -3.645674 -1.572094 -0.311873
H  -3.167586 -0.424179 -1.565539
C  -4.020222  0.503740  0.201766
H  -4.021153  0.341695  1.296560
H  -3.542159  1.489016  0.042752
C  -5.468668  0.559725 -0.299921
H  -5.944856 -0.425015 -0.141556
H  -5.466807  0.723000 -1.392987
C  -6.302477  1.649760  0.381485
H  -5.866571  2.648133  0.211561
H  -7.336446  1.668288  0.002805
H  -6.348853  1.491598  1.471691
H  -0.308102 -2.753535  2.361944
H   0.315443 -2.515042  2.716204
```

Mn(TMSM)C6H11 + H2 – reactants association complex, -1835.1494996, *-1834.905207*

```
Mn  0.253405 -1.257777 -0.220947
C  -1.791991 -1.366456 -0.490036
H  -2.041567 -1.556219 -1.552090
H  -2.205268 -2.214802  0.092429
C  -2.141663  1.631712 -1.125469
H  -2.598643  2.587121 -0.820678
H  -1.050640  1.783519 -1.167084
H  -2.484801  1.407528 -2.148650
C  -4.508932  0.112979  0.132620
H  -4.831038 -0.673467  0.834122
H  -4.961460  1.064113  0.459059
H  -4.920533 -0.135802 -0.858741
C  -1.992733  0.679398  1.809384
H  -2.470828  1.599236  2.183900
H  -2.212863 -0.126409  2.529234
H  -0.901551  0.850438  1.825101
Si -2.614409  0.229872  0.065339
C   1.905966  1.735829 -0.263813
C   3.027027  1.560285  0.771415
C   3.117809  0.107972  1.264876
C   3.267142 -0.873085  0.089719
C   2.124726 -0.712525 -0.930861
C   2.055902  0.744490 -1.431534
H   3.954005 -0.004102  1.976053
H   3.990842  1.839381  0.305637
H   2.878249  2.248480  1.620696
H   0.929614  1.568932  0.237523
H   1.883254  2.774430 -0.635511
H   4.247422 -0.676656 -0.398084
H   3.320316 -1.910619  0.465692
```

```
H   2.312858 -1.381945 -1.796535
H   2.981338  1.003443 -1.990383
H   1.226215  0.880220 -2.150125
H   2.193066 -0.135030  1.829043
H   0.699926 -2.112365  2.440377
H  -0.050818 -2.176800  2.370148
```

Mn(TMSM)C6H7 (methyl sub.) + H2 – reactants association complex, -1870.8310908, *-1870.627623*

```
Mn  0.287164  1.478741 -0.231282
C  -1.738441  1.407587 -0.513909
H  -2.232928  2.195610  0.087589
H  -1.993069  1.613220 -1.572345
C  -1.938039 -0.680925  1.761434
H  -2.370804 -1.641770  2.084743
H  -0.842988 -0.760424  1.873437
H  -2.298218  0.095684  2.456463
C  -4.314234 -0.369445 -0.173236
H  -4.642148 -0.162300 -1.204632
H  -4.693397 -1.365552  0.109436
H  -4.792547  0.374269  0.484378
C  -1.664391 -1.609532 -1.160280
H  -2.070844 -2.607700 -0.929260
H  -1.876701 -1.398309 -2.221159
H  -0.569198 -1.660748 -1.040014
Si -2.421459 -0.281212 -0.035236
C   2.332962  1.966828 -0.063752
H   2.627987  2.493021  0.853027
H   2.774168  2.417909 -0.962088
C   2.397954  0.502879  0.001392
C   2.251360 -0.203422  1.236931
C   2.424240 -0.297359 -1.184794
C   2.150016 -1.595322  1.276107
H   2.236324  0.368747  2.169317
C   2.326287 -1.688890 -1.131391
H   2.544436  0.202127 -2.151378
C   2.185111 -2.352956  0.096176
H   2.045852 -2.096420  2.242184
H   2.359242 -2.263358 -2.060847
H   2.101022 -3.440597  0.131998
H   0.221369  2.340622  2.475848
H  -0.283194  1.787759  2.580596
```

Mn(TMSM)C6H7 (ortho sub.) + H2 – reactants association complex, -1870.82142, *-1870.620898*

```
Mn  0.107388  0.929863  0.993129
C   2.157809  0.872017  1.043345
H   2.586542  1.874826  0.847161
H   2.533101  0.548594  2.033841
C   1.961575  0.173787 -1.947087
H   2.313532 -0.471117 -2.768595
```

```
H   0.860457  0.095190 -1.920447
H   2.221625  1.214069 -2.203260
C   4.613239 -0.402851 -0.469886
H   5.091702 -0.707455  0.474737
H   4.915927 -1.120423 -1.250418
H   5.014815  0.585863 -0.744276
C   2.088152 -2.075447  0.153770
H   2.418211 -2.821925 -0.586716
H   2.455417 -2.398257  1.141657
H   0.985366 -2.099716  0.178465
Si  2.725571 -0.340991 -0.282483
C  -3.204020 -1.841902  0.567093
C  -3.988204 -1.299560 -0.455780
C  -3.613081 -0.089199 -1.054821
C  -2.458127  0.592890 -0.641243
C  -1.648182  0.062494  0.400771
C  -2.049042 -1.162617  0.980557
H  -3.487796 -2.787254  1.037803
H  -4.890100 -1.817509 -0.792418
H  -1.446216 -1.611354  1.780485
C  -2.071406  1.897987 -1.305740
H  -1.059511  1.840081 -1.744889
H  -2.764163  2.172521 -2.115581
H  -2.066439  2.730643 -0.580347
H  -4.229192  0.328063 -1.858313
H  -1.709285  2.516511  2.133049
H  -1.318955  3.090363  2.438713
```

Mn(TMSM)C6H7 (meta sub.) + H2 – reactants association complex, -1870.8213588, *-1870.620398*

```
Mn -0.270938 -1.556217  0.037528
C  -2.318694 -1.385689  0.118258
H  -2.788261 -1.933473 -0.723187
H  -2.705592 -1.842355  1.051057
C  -2.189808  1.208569 -1.549216
H  -2.487921  2.267034 -1.623349
H  -1.089204  1.170233 -1.612133
H  -2.588972  0.687106 -2.434692
C  -4.724050  0.647272  0.108339
H  -5.145460  0.217015  1.031047
H  -5.003381  1.713367  0.073368
H  -5.205088  0.143066 -0.745202
C  -2.082138  1.341120  1.536520
H  -2.357436  2.408287  1.529453
H  -2.435858  0.911336  2.487968
H  -0.980516  1.282733  1.537521
Si -2.839807  0.422546  0.055635
C   4.072181 -0.947697  0.177503
C   4.181262  0.443323  0.075912
C   3.032163  1.247436 -0.029364
C   1.779799  0.609159 -0.032900
C   1.624698 -0.794565  0.066898
C   2.810598 -1.557942  0.174015
H   4.976777 -1.557868  0.258076
H   5.170094  0.913057  0.077891
H   0.891593  1.250053 -0.119903
H   2.759949 -2.649690  0.254397
```

```
C   3.147311  2.750177 -0.121890
H   3.510880  3.180538  0.826382
H   3.857999  3.051887 -0.908051
H   2.175294  3.213699 -0.346847
H  -0.362595 -1.474296 -2.860809
H   0.338503 -1.328933 -2.614520
```

Mn(TMSM)C6H7 (para sub.) + H2 – reactants association complex, -1870.820875, *-1870.622107*

```
Mn  0.413751  1.216599 -0.363656
C   2.382378  0.933406 -0.878975
H   2.451894  0.679301 -1.955568
H   2.978865  1.854859 -0.727593
C   2.105033 -2.050659 -0.160557
H   2.530842 -2.908228  0.385202
H   1.060734 -1.931523  0.174788
H   2.084703 -2.312469 -1.231260
C   4.933162 -0.821598 -0.289397
H   5.558671  0.068247 -0.113215
H   5.337784 -1.646625  0.320036
H   5.040145 -1.100032 -1.350133
C   3.003832 -0.023458  1.982123
H   3.452467 -0.806631  2.614574
H   3.529687  0.921479  2.195857
H   1.954932  0.096358  2.304435
Si  3.117055 -0.470259  0.137745
C  -3.824466  0.665204  0.647476
C  -4.131503 -0.592749  0.099375
C  -3.109231 -1.282545 -0.574703
C  -1.826063 -0.733697 -0.687975
C  -1.494228  0.530559 -0.143149
C  -2.540030  1.208861  0.528323
H  -4.605834  1.225136  1.172662
H  -2.358152  2.193589  0.975922
H  -3.323972 -2.261550 -1.016340
H  -1.065227 -1.316392 -1.222810
C  -5.506236 -1.194891  0.254987
H  -5.572570 -1.790189  1.182134
H  -6.283613 -0.417737  0.310005
H  -5.749800 -1.866455 -0.582164
H  -0.149633  4.012546 -0.453316
H  -0.810342  3.644353 -0.485411
```

Mn(TMSM)C6H13 β-hydride elimination – products association complex, -1835.151447, *-1834.905602*

```
C  -4.234648 -2.387626 -0.494471
H  -3.413200 -2.805683 -1.098541
H  -4.951940 -1.921725 -1.189753
H  -4.746613 -3.226453  0.001809
C  -3.708354 -1.369349  0.521525
H  -4.544635 -0.988298  1.136147
H  -3.017728 -1.870184  1.224468
C  -2.983089 -0.190966 -0.137280
H  -3.663354  0.320885 -0.842481
H  -2.145535 -0.562457 -0.755892
C  -2.450600  0.827267  0.884393
```

```
H  -1.795292  0.321587  1.616455
H  -3.305541  1.222301  1.469408
C  -1.724805  2.008224  0.292993
H  -2.234989  2.537040 -0.522936
C  -0.576569  2.552893  0.828526
H  -0.127612  2.140892  1.738283
H  -0.199505  3.526717  0.499157
Mn  0.233650  1.209570 -0.843242
H  -0.297745  0.380886 -2.175087
C   2.237431  1.044445 -0.483487
H   2.574050  1.789895  0.261801
H   2.815262  1.200039 -1.412742
C   1.024275 -1.205562  1.263755
H   0.075884 -1.253666  0.697716
H   1.180190 -2.204223  1.704407
H   0.890353 -0.494350  2.095989
C   2.546321 -1.912834 -1.315086
H   3.416982 -1.711651 -1.959809
H   2.609917 -2.959924 -0.977647
H   1.640299 -1.802427 -1.932487
C   4.077296 -0.890096  1.182201
H   4.052904 -0.225803  2.061150
H   4.207053 -1.924288  1.542131
H   4.964554 -0.623454  0.586133
Si  2.495103 -0.711663  0.146783
```

Mn(TMSM)C6H11 β-hydride elimination – products association complex, -1833.9617078, *-1833.732069*

```
C  -1.588415  0.744095  0.932282
H  -0.751883  1.115678  1.535548
C  -2.108529 -0.497468  1.200667
H  -1.696229 -1.081718  2.032812
C  -2.213219  1.706026 -0.056518
H  -2.246818  2.708642  0.404409
H  -1.552289  1.819077 -0.937567
C  -3.349273 -1.030660  0.524378
H  -3.221128 -2.102784  0.304607
H  -4.193243 -0.958845  1.239107
C  -3.620192  1.266529 -0.496624
H  -3.925558  1.828015 -1.393518
H  -4.344947  1.518708  0.297996
C  -3.677253 -0.246007 -0.753860
H  -4.665704 -0.541759 -1.138836
H  -2.945832 -0.516890 -1.541895
Mn -0.294302 -0.867279 -0.345198
H  -0.531093 -2.488464 -0.640887
C   1.213749  0.287394 -1.137704
H   0.905704  1.346820 -1.241145
H   1.468079 -0.085414 -2.148379
C   2.251676  0.647089  1.749298
H   1.519700 -0.061128  2.175995
H   3.130753  0.644497  2.414208
H   1.808005  1.655969  1.789133
C   3.380242 -1.606736 -0.026058
H   3.696108 -1.912696 -1.036556
H   4.246125 -1.718147  0.646609
H   2.601459 -2.315997  0.300155
```

```
C   4.135400  1.335383 -0.577933
H   3.807545  2.387416 -0.563808
H   5.012629  1.244132  0.084156
H   4.459582  1.100804 -1.604528
Si  2.730819  0.175870 -0.035372
```

Mn(TMSM)C6H13 + H2 – products association complex, -1836.3646398, *-1836.101191*

```
C   1.303711  3.007212 -0.178651
H   0.236217  2.725261 -0.142257
H   1.643750  2.891302 -1.221022
H   1.365133  4.075586  0.078317
C   2.132114  2.140881  0.775773
H   3.184100  2.476618  0.772433
H   1.770253  2.268768  1.811587
C   2.078347  0.655590  0.405549
H   2.463507  0.538900 -0.627327
H   1.006645  0.342570  0.413118
C   2.826642 -0.292647  1.348816
H   2.523960 -0.068623  2.387100
H   3.910803 -0.084429  1.288454
Mn  0.164619 -0.154001 -1.719345
H   0.966866  0.275245 -3.127044
C  -1.292568 -1.219951 -0.729483
H  -0.824546 -2.034946 -0.140828
H  -1.920001 -1.711074 -1.501108
C  -1.450601  0.383701  1.929182
H  -0.707388  1.157290  1.677417
H  -2.137795  0.820966  2.671732
H  -0.917553 -0.448149  2.418409
C  -3.054137  1.312023 -0.534867
H  -3.598829  1.018008 -1.446937
H  -3.741808  1.907287  0.087718
H  -2.229631  1.978255 -0.843054
C  -3.908287 -1.214339  1.004948
H  -3.584247 -2.096250  1.580757
H  -4.564540 -0.608913  1.652036
H  -4.510033 -1.574516  0.154983
Si -2.411433 -0.214161  0.399754
C   2.566051 -1.780421  1.060580
H   3.077191 -2.385668  1.828470
H   1.485892 -1.982813  1.182476
C   3.019539 -2.245856 -0.328036
H   2.859928 -3.326914 -0.458145
H   2.471052 -1.742089 -1.144188
H   4.090788 -2.040534 -0.488879
```

Mn(TMSM)C6H11 + H2 – products association complex, -1835.1705392, *-1834.922341*

```
C  -2.453346  0.696801 -1.399369
H  -2.539961  1.203093 -2.375057
H  -1.669917 -0.080621 -1.543356
C  -3.237510  0.337275  1.442751
H  -3.135805 -0.171971  2.415160
H  -4.017955  1.110720  1.571345
C  -3.774149  0.012902 -1.018491
```

```
H  -4.057453 -0.725311 -1.786929
H  -4.579019  0.771723 -1.000321
C  -3.680095 -0.658357  0.359957
H  -4.644546 -1.118026  0.631850
H  -2.946927 -1.489820  0.314825
Mn  0.002657 -1.511902 -0.094414
H  -0.628576 -2.927389  0.539875
C   1.436962 -0.474408 -1.137037
H   0.974745  0.319389 -1.756912
H   1.935754 -1.176506 -1.835375
C   1.923278  1.558772  1.143212
H   1.203846  1.079283  1.827573
H   2.676294  2.071822  1.763153
H   1.378305  2.329435  0.573771
C   3.540268 -1.065899  1.039764
H   4.010638 -1.834678  0.405362
H   4.320057 -0.654357  1.700982
H   2.798858 -1.574702  1.679286
C   4.105754  1.181409 -0.995033
H   3.686012  1.994976 -1.608391
H   4.862978  1.619101 -0.323485
H   4.619354  0.482405 -1.674507
Si  2.740552  0.294512 -0.017640
C  -1.985334  1.685307 -0.321123
H  -1.003395  2.109884 -0.588252
H  -2.694011  2.533032 -0.276742
C  -1.919912  1.024812  1.062442
H  -1.106536  0.257323  1.061067
H  -1.612391  1.753898  1.829936
```

Mn(TMSM)C6H7 (toluene sub.) + H2 – products association complex, -1870.8458326, *-1870.636253*

```
Mn -0.361061 -1.180970  0.049682
C   1.075066 -0.256916 -1.100122
H   1.309529 -0.895884 -1.974318
H   0.677664  0.701351 -1.489597
C   3.418466 -1.607415  0.380016
H   4.339439 -1.463769  0.968160
H   2.715600 -2.198115  0.990932
H   3.674810 -2.214221 -0.503639
C   3.951539  1.029966 -1.128039
H   3.560098  2.017426 -1.422100
H   4.872668  1.190674 -0.543276
H   4.225252  0.492485 -2.050251
C   2.267862  1.047526  1.440111
H   3.187277  1.288571  1.998145
H   1.764236  1.996971  1.195215
H   1.607070  0.483382  2.120410
Si  2.656168  0.052374 -0.137546
C  -2.996453 -0.156231 -0.143636
C  -2.348361 -0.048882  1.114640
C  -2.802512  0.877277 -1.076670
C  -1.548438  1.071747  1.415104
H  -2.524209 -0.815935  1.873979
C  -2.017541  1.999277 -0.770077
```

```
H  -3.282133  0.803726 -2.056427
C  -1.386878  2.098389  0.473555
H  -1.063367  1.143087  2.391385
H  -1.889138  2.789026 -1.513552
H  -0.762196  2.961972  0.709798
C  -3.862601 -1.351422 -0.446964
H  -3.313485 -2.286654 -0.243754
H  -4.761044 -1.354142  0.191570
H  -4.189818 -1.357126 -1.496051
H  -0.808980 -2.711716  0.589450
```

Mn(TMSM)C6H13 β-hydride elimination – TS, -1835.1433696, *-1834.897580*

```
C   2.877367  2.781566 -0.929433
H   1.827554  2.899587 -1.244681
H   3.445050  2.411858 -1.798748
H   3.264034  3.780859 -0.676919
C   2.990324  1.819094  0.256765
H   4.043031  1.747327  0.585031
H   2.427739  2.223366  1.117847
C   2.469247  0.415551 -0.069288
H   3.034793 -0.018317 -0.911634
H   1.423196  0.499172 -0.426730
C   2.505867 -0.544083  1.136971
H   1.934298 -0.108003  1.974179
H   3.552527 -0.640745  1.479930
C   1.969342 -1.906591  0.810290
H   2.565378 -2.516316  0.122845
C   0.795292 -2.395568  1.266609
H   0.174762 -1.830226  1.966450
H   0.468302 -3.412161  1.024801
Mn -0.225405 -1.676199 -1.132733
H   1.176346 -2.109556 -1.969934
C  -1.949796 -1.143093 -0.102835
H  -2.061731 -1.698474  0.846871
H  -2.810039 -1.443317 -0.738221
C  -1.022494  1.225316  1.684667
H   0.043152  1.063993  1.460944
H  -1.155757  2.295326  1.912720
H  -1.265412  0.657051  2.597428
C  -1.601827  1.689144 -1.305613
H  -2.200334  1.402011 -2.185865
H  -1.733647  2.772883 -1.152441
H  -0.540613  1.520362 -1.558630
C  -3.916353  1.186183  0.653804
H  -4.266853  0.652325  1.551857
H  -4.006726  2.268372  0.845446
H  -4.599605  0.931425 -0.172479
Si -2.129010  0.699361  0.232618
```

Mn(TMSM)C6H11 β-hydride elimination – TS, -1833.9611648, *-1833.729732*

```
C  -1.504156  0.615631  1.018764
H  -0.676994  0.846143  1.700099
C  -2.182537 -0.569508  1.167605
H  -1.903220 -1.249908  1.981182
```

```
C  -1.946161  1.714095  0.074951
H  -1.896542  2.676998  0.612794
H  -1.219049  1.811489 -0.753389
C  -3.428367 -0.901027  0.379864
H  -3.412868 -1.963764  0.088700
H  -4.304733 -0.775057  1.046420
C  -3.361728  1.476734 -0.478875
H  -3.539948  2.130562 -1.347004
H  -4.104537  1.758396  0.288730
C  -3.575432  0.002940 -0.852937
H  -4.563259 -0.145105 -1.316603
H  -2.829708 -0.297842 -1.616467
Mn -0.351602 -1.060854 -0.301492
H  -0.716545 -2.651383 -0.627363
C   1.212103 -0.075684 -1.202558
H   0.902335  0.896824 -1.633405
H   1.528213 -0.719478 -2.046840
C   2.321922  1.661718  1.112018
H   1.490095  1.450199  1.803196
H   3.206524  1.896923  1.725855
H   2.060645  2.567125  0.540302
C   2.942032 -1.355482  1.022396
H   3.101276 -2.246741  0.394032
H   3.820221 -1.244383  1.679421
H   2.071767 -1.563243  1.669746
C   4.283251  0.554111 -0.982081
H   4.185000  1.460715 -1.600636
H   5.127493  0.704753 -0.288779
H   4.541324 -0.280822 -1.653335
Si  2.668357  0.194126 -0.047446
```

Mn(TMSM)C6H13 + H2 – TS, -1836.3189412, *-1836.057215*

```
Mn -1.296076 -1.797904 -0.421911
C  -2.364465 -0.267121 -1.232098
H  -1.815614  0.137688 -2.106228
H  -3.344205 -0.618282 -1.609384
C  -0.924081  1.915721  0.412800
H  -1.037753  2.748976  1.125031
H  -0.221311  1.192388  0.857732
H  -0.454925  2.317794 -0.500036
C  -3.785597  2.466723 -0.597315
H  -4.780845  2.047871 -0.817046
H  -3.912665  3.266359  0.151081
H  -3.405411  2.926497 -1.523679
C  -3.314673  0.395183  1.632505
H  -3.511161  1.184562  2.376221
H  -4.264671 -0.131785  1.445412
H  -2.619287 -0.325415  2.097516
Si -2.603056  1.116428  0.021918
C   0.552273 -1.859942  0.845698
H   1.055227 -2.658120  1.419251
H   0.141099 -1.163463  1.606053
C   1.548093 -1.159215 -0.088781
H   1.927078 -1.882944 -0.835196
H   1.044514 -0.363124 -0.675831
C   2.747027 -0.516571  0.633504
```

```
H   3.277993 -1.298559  1.207149
H   2.367447  0.205724  1.379748
C   3.725213  0.189763 -0.311819
H   4.097946 -0.533466 -1.061683
H   3.182956  0.967091 -0.882902
C   4.918240  0.832627  0.406469
H   5.458851  0.055903  0.977258
H   4.543413  1.553925  1.155116
C   5.887444  1.538237 -0.547563
H   5.380418  2.341850 -1.106666
H   6.733142  1.990566 -0.006536
H   6.302441  0.833026 -1.286470
H  -0.293814 -3.069035  0.226869
H  -0.943019 -3.620854 -0.292245
```

Mn(TMSM)C6H11 + H2 – TS, -1835.1251866, *-1834.876648*

```
Mn  0.104189 -1.378213  0.076791
C  -1.831317 -1.312347 -0.537726
H  -1.925818 -1.381821 -1.638459
H  -2.374566 -2.178823 -0.109915
C  -2.130945  1.730533 -1.037741
H  -2.639638  2.659211 -0.732056
H  -1.045952  1.907850 -0.968103
H  -2.373728  1.548677 -2.097253
C  -4.567963  0.137089 -0.025422
H  -4.930025 -0.683059  0.615318
H  -5.049972  1.069071  0.313294
H  -4.908544 -0.067025 -1.053215
C  -2.175168  0.634905  1.844900
H  -2.697935  1.523075  2.236272
H  -2.416575 -0.214015  2.505374
H  -1.091757  0.829483  1.937883
Si -2.675329  0.269427  0.044538
C   1.791745  1.616809 -0.250141
C   3.169004  1.721511  0.420681
C   3.613173  0.373249  1.007122
C   3.582018 -0.742651 -0.052078
C   2.189643 -0.858481 -0.696984
C   1.773391  0.496140 -1.303364
H   4.623473  0.459054  1.440728
H   3.907502  2.048501 -0.335635
H   3.157188  2.497754  1.203945
H   1.026267  1.408332  0.525986
H   1.508811  2.579289 -0.708381
H   4.339136 -0.520741 -0.832122
H   3.883169 -1.702828  0.404145
H   2.205925 -1.647855 -1.476456
H   2.483958  0.768337 -2.115007
H   0.781711  0.446460 -1.793272
H   2.937792  0.099960  1.840241
H   1.717137 -1.537970  0.664980
H   1.250823 -2.008110  1.412911
```

Mn(TMSM)C6H7 (methyl sub.) + H2 – TS, - 1870.8093798, *-1870.601191*

```
Mn -0.377921 -1.309371  0.091646
C   1.291050 -0.886306 -0.998873
H   1.788991 -1.834531 -1.283204
H   1.004450 -0.373686 -1.937888
C   3.027778 -0.736239  1.546637
H   3.755890 -0.148277  2.128868
H   2.161571 -0.937122  2.199547
H   3.493040 -1.706580  1.308204
C   4.071198  0.576317 -1.038504
H   3.817855  1.123543 -1.960896
H   4.774205  1.197290 -0.458714
H   4.597167 -0.346483 -1.331847
C   1.682427  1.816728  0.453744
H   2.384271  2.468795  0.998863
H   1.333220  2.364487 -0.436562
H   0.803710  1.652671  1.099276
Si  2.506440  0.176886 -0.036155
C  -2.640243 -1.851868 -0.449943
H  -3.414869 -2.330396  0.163162
H  -2.671900 -2.190168 -1.492249
C  -2.503537 -0.405707 -0.247274
C  -2.502774  0.131539  1.078671
C  -2.201730  0.496320 -1.311243
C  -2.264749  1.495568  1.305730
H  -2.749403 -0.525935  1.917012
C  -1.977219  1.850341 -1.070471
H  -2.168685  0.108055 -2.332860
C  -2.008360  2.361465  0.238651
H  -2.286745  1.879397  2.328753
H  -1.769241  2.517242 -1.910704
H  -1.823134  3.421681  0.420638
H  -1.617336 -2.532649  0.526337
H  -0.898244 -2.638416  1.226545
```

Mn(TMSM)C6H7 (ortho sub.) + H2 – TS, -1870.801912, *-1870.595566*

```
Mn  0.160926 -1.622038 -0.641954
C   2.037179 -1.318739  0.070435
H   2.116979 -1.771489  1.079462
H   2.794338 -1.821046 -0.561918
C   1.228204  1.305167  1.482175
H   1.438889  2.379376  1.609723
H   0.172864  1.205782  1.179318
H   1.346502  0.823092  2.466610
C   4.186845  0.883334  0.694190
H   4.890417  0.464409 -0.043216
H   4.377963  1.966797  0.767010
H   4.419755  0.431784  1.671962
C   2.056198  1.348416 -1.486995
H   2.319247  2.418637 -1.470789
H   2.644105  0.871204 -2.288123
H   0.988820  1.278804 -1.758648
Si  2.388480  0.529490  0.196415
C  -2.739151  1.607166 -1.192399
C  -3.268555  1.773321  0.093134
```

```
C  -3.038568  0.806104  1.081234
C  -2.265505 -0.332474  0.807430
C  -1.708133 -0.500890 -0.486556
C  -1.979305  0.466056 -1.475794
H  -2.928091  2.354486 -1.967552
H  -3.872055  2.654066  0.326918
H  -1.593124  0.323905 -2.493381
C  -1.979879 -1.352440  1.885876
H  -0.940542 -1.255678  2.250037
H  -2.642686 -1.231852  2.755468
H  -2.101597 -2.381173  1.507474
H  -3.465485  0.942183  2.080203
H  -1.522199 -1.899451 -1.125274
H  -1.081945 -2.725858 -1.522609
```

Mn(TMSM)C6H7 (meta sub.) + H2 – TS, -1870.8005262, *-1870.595762*

```
Mn  0.492247  1.821824 -0.525266
C   2.294952  1.213186  0.176212
H   3.130848  1.617075 -0.426317
H   2.427114  1.595743  1.208449
C   1.917545 -1.361628 -1.492509
H   2.015194 -2.459245 -1.520078
H   0.875664 -1.120776 -1.765125
H   2.576088 -0.946989 -2.273128
C   4.083420 -1.314397  0.696433
H   4.381032 -0.945233  1.691024
H   4.107288 -2.416443  0.722778
H   4.843173 -0.976489 -0.026626
C   1.093559 -1.318435  1.479914
H   1.113877 -2.419276  1.531391
H   1.305781 -0.932455  2.490279
H   0.069076 -1.011703  1.212667
Si  2.359895 -0.671384  0.224708
C  -3.018012  0.373720  1.598293
C  -3.322449 -0.786521  0.875819
C  -2.766766 -1.016182 -0.396398
C  -1.896760 -0.043489 -0.917146
C  -1.539865  1.114538 -0.195690
C  -2.135490  1.321428  1.065972
H  -3.473915  0.536364  2.579164
H  -4.011047 -1.523237  1.300733
H  -1.481848 -0.205355 -1.921783
H  -1.908502  2.223835  1.644911
C  -3.078199 -2.278145 -1.162847
H  -2.445471 -3.112698 -0.815395
H  -4.126698 -2.585249 -1.028725
H  -2.892416 -2.150948 -2.239674
H  -0.531906  2.948560 -1.634728
H  -1.109649  2.313843 -1.112388
```

Mn(TMSM)C6H7 (para sub.) + H2 – TS, -1870.8005326, *-1870.595558*

```
Mn  0.725026  1.877096  0.004897
C   2.414245  0.951450 -0.631601
H   2.443666  0.981921 -1.739623
```

```
H   3.326754  1.464457 -0.272355
C   0.976698 -1.766612 -0.937170
H   0.948856 -2.826530 -0.636166
H   0.001871 -1.318149 -0.684715
H   1.087896 -1.732465 -2.033273
C   4.033706 -1.734695 -0.481927
H   4.882536 -1.243104  0.020162
H   4.011706 -2.788056 -0.156766
H   4.231806 -1.718665 -1.565718
C   2.127092 -0.931922  1.800866
H   2.185180 -1.968631  2.170732
H   2.883785 -0.340191  2.341518
H   1.131578 -0.543691  2.076842
Si  2.400748 -0.851927 -0.080165
C  -2.684222 -0.533118  1.192524
C  -3.365861 -0.775296 -0.013852
C  -3.050206  0.025888 -1.127142
C  -2.068367  1.018193 -1.043461
C  -1.350565  1.240957  0.151831
C  -1.704861  0.462214  1.274123
H  -2.931477 -1.129305  2.076957
H  -1.206895  0.632265  2.237077
H  -3.585106 -0.132989 -2.069294
H  -1.856090  1.623062 -1.933050
C  -4.393293 -1.874205 -0.117681
H  -3.925727 -2.813501 -0.460101
H  -4.865988 -2.079068  0.854428
H  -5.184118 -1.621333 -0.839851
H  -0.135240  3.400920  0.699904
H  -0.787307  2.655520  0.514132
```

Mn(TMSM), -1598.948629, *-1598.854509*

```
Mn -2.197452  0.000000 -0.005204
C  -0.517523  0.000059 -1.045618
H  -0.583045 -0.897694 -1.691578
H  -0.583042  0.897883 -1.691480
C   1.126064 -1.549806  1.086376
H   2.075751 -1.602304  1.643475
H   0.301573 -1.557837  1.817329
H   1.041809 -2.464481  0.477558
C   2.565748  0.000047 -1.156304
H   2.567957  0.890089 -1.805436
H   3.504631  0.000014 -0.578283
H   2.567947 -0.889932 -1.805522
C   1.126078  1.549702  1.086523
H   2.075762  1.602135  1.643634
H   1.041841  2.464436  0.477791
H   0.301582  1.557676  1.817471
Si  1.058666  0.000000 -0.000051
```

SiC4H11 radical, -448.1853208, *-448.091235*

```
C   0.000010 -0.305433  1.884289
H  -0.919024 -0.380736  2.475998
H   0.919050 -0.380726  2.475990
```

```
C  -1.555188 -0.782812 -0.714912
H  -1.592813 -0.600939 -1.801141
H  -1.582558 -1.871605 -0.552501
H  -2.466956 -0.351873 -0.271125
C  -0.000016  1.852633 -0.312990
H   0.890256  2.339260  0.114810
H  -0.000025  2.035227 -1.400463
H  -0.890290  2.339246  0.114822
C   1.555195 -0.782788 -0.714923
H   1.592808 -0.600917 -1.801153
H   2.466960 -0.351833 -0.271144
H   1.582584 -1.871580 -0.552509
Si  0.000000 -0.013795  0.044259
```

2 x Mn(TMSM)2 – primary condensation product, -3645.6472933, *-3645.330689*

```
Mn  2.557627  0.270358  0.627229
C   3.256012 -1.573817  0.016634
H   3.846960 -1.478539 -0.915580
H   3.928800 -2.016192  0.777389
C   0.645171 -1.925791 -1.573606
H  -0.216277 -2.568603 -1.813725
H   0.245388 -0.959029 -1.215681
H   1.184903 -1.715994 -2.511344
C   2.284902 -4.444234 -0.891970
H   2.941183 -4.946963 -0.163657
H   1.399602 -5.082263 -1.049423
H   2.832114 -4.381164 -1.846174
C   0.815508 -2.915603  1.340474
H  -0.073300 -3.553316  1.210546
H   1.441014 -3.362660  2.130340
H   0.464503 -1.939129  1.727261
Si  1.794691 -2.716879 -0.280372
C   1.038991  1.559455  0.998249
H   1.156358  2.054305  1.989330
C   2.287387  4.193259 -0.137827
H   3.298659  3.757760 -0.189079
H   2.211038  4.969131 -0.917638
H   2.187394  4.687891  0.841819
C   1.210947  2.020862 -2.051311
H   0.414617  1.289561 -2.266136
H   1.196286  2.770225 -2.859716
H   2.175859  1.487864 -2.121040
C  -0.736271  3.730964 -0.420360
H  -0.959894  4.222421  0.540407
H  -0.761287  4.500993 -1.209647
H  -1.552911  3.018413 -0.626980
Mn -0.712192  0.523495  1.084887
C  -2.738619  0.364898  1.349794
H  -2.986973 -0.166577  2.289211
H  -3.142822  1.393352  1.444549
C  -3.099258 -2.346685 -0.067049
H  -2.006757 -2.480104 -0.116807
H  -3.451422 -2.829398  0.859090
H  -3.542384 -2.888278 -0.918418
C  -2.965506  0.253250 -1.730096
H  -3.163070  1.337360 -1.762796
```

```
H  -1.881296  0.106367 -1.875110
H  -3.472176 -0.203604 -2.595886
C  -5.464113 -0.367064 -0.048057
H  -5.928292 -0.891284 -0.899920
H  -5.867513 -0.803615  0.879709
H  -5.781471  0.687519 -0.086237
Si  0.955914  2.856059 -0.357392
Si -3.570862 -0.507734 -0.093722
```

2 x MnTMSM – primary condensation product, -3196.7585786, *-3196.569764*

```
Mn -0.098033  1.633384 -0.161099
C   1.118338  0.476260  0.785695
Si  2.796626 -0.094603  0.253977
H   0.824809  0.357762  1.847785
C   2.555721 -1.497004 -1.087666
C   3.747148 -0.894438  1.682421
C   3.862434  1.213694 -0.600510
H   3.184164 -1.740987  2.105029
H   3.909609 -0.162688  2.489263
H   4.732774 -1.261892  1.353798
H   1.911861 -2.360231 -0.787769
H   3.545509 -1.959055 -1.245960
H   2.239535 -1.135928 -2.085710
H   3.320113  1.645980 -1.456542
H   4.816003  0.799641 -0.967514
H   4.088064  2.033096  0.099963
H  -3.890976 -1.797263 -1.541960
H  -1.513369  0.459513 -1.924487
C  -3.644227 -1.851588 -0.469266
Mn  0.276543 -0.797948 -0.581228
H  -2.931386 -2.681071 -0.333156
H  -4.504057  1.294953 -1.065556
C  -1.363458  0.247877 -0.842158
H  -4.568520 -2.099971  0.078978
Si -2.889953 -0.213376  0.135349
C  -4.231448  1.126035 -0.011148
H  -5.147512  0.841389  0.532970
C  -2.428988 -0.410343  1.968396
H  -1.651477 -1.180417  2.101992
H  -3.872801  2.083964  0.398678
H  -3.305000 -0.705868  2.568472
H  -2.036638  0.531913  2.384767
```

2 x Mn(TMSM)2 – associated reactants, -4094.5090418, *-4094.062047*

```
C  -1.143496  2.565503 -1.900221
H  -1.061728  2.354947 -2.986834
H  -1.834446  3.425495 -1.796377
C   1.817020  1.705492 -1.758128
H   2.593436  1.530455 -0.994072
H   1.340243  0.742932 -2.038413
H   2.351903  2.012400 -2.672997
C   1.204957  4.699232 -1.948545
H   0.552501  5.536330 -1.651799
H   2.220592  4.915013 -1.576810
```

```
H   1.240564  4.679274 -3.049692
C   0.516010  3.214775  0.632767
H   1.472503  3.598708  1.022152
H  -0.282485  3.907521  0.945340
H   0.321684  2.256586  1.146079
Si  0.538290  3.058906 -1.262653
C  -0.730791 -1.105674 -1.491420
H  -1.708988 -1.492721 -1.139846
C  -0.856231 -3.745995 -3.153217
H  -1.099901 -3.186572 -4.070303
H  -0.327000 -4.667096 -3.447991
H  -1.804465 -4.038289 -2.674824
C   1.822909 -2.237167 -2.841394
H   2.513546 -1.694896 -2.174218
H   2.351908 -3.140619 -3.185844
H   1.638444 -1.599842 -3.721207
C   0.582658 -3.714207 -0.420888
H  -0.334249 -3.922260  0.153295
H   1.040545 -4.679189 -0.692978
H   1.285177 -3.197997  0.254677
Mn  0.626849 -0.297189 -0.067557
C   1.408113 -0.499614  1.805913
H   0.945858  0.229066  2.499425
H   1.087681 -1.501920  2.156668
C   3.804693  1.455818  1.977784
H   3.494950  1.991569  1.066809
H   3.350710  1.976212  2.836432
H   4.899012  1.550691  2.066241
C   4.107111 -1.201805  0.442185
H   3.773004 -2.246179  0.326138
H   3.877090 -0.668350 -0.496191
H   5.204363 -1.215364  0.546233
C   3.926842 -1.216121  3.511861
H   5.022734 -1.129837  3.596341
H   3.480084 -0.764772  4.412139
H   3.670977 -2.288024  3.513816
Si  0.198911 -2.701508 -1.978313
Si  3.283464 -0.367109  1.941398
C  -2.514192 -1.894522  1.753240
H  -3.029531 -2.654307  1.142615
H  -1.495206 -1.772891  1.349201
H  -2.413973 -2.295548  2.774895
C  -3.785456  0.337105  0.004184
H  -4.304513 -0.470553 -0.550938
H  -4.484357  1.196309  0.037413
C  -5.063077 -0.503158  2.758158
H  -4.849451 -0.835132  3.787917
H  -5.642792  0.432276  2.817272
H  -5.705263 -1.262195  2.282795
C  -2.398225  1.032185  2.677985
H  -2.863446  2.031168  2.659444
H  -2.241512  0.750206  3.731925
H  -1.401535  1.124453  2.213142
Si -3.466517 -0.245546  1.758563
H  -0.877708 -0.595530 -2.468450
Mn -2.063574  0.909228 -0.999489
```

2 x MnTMSM – associated reactants, -3197.9227999, *-3197.717351*

```
Mn -3.265821 -1.731307 -0.342151
C  -1.657209 -0.644990  0.226901
Si -2.027276  1.216266 -0.039057
H  -0.958650 -1.158585 -0.508646
H  -1.619260 -1.051306  1.280170
C  -2.106946  1.517983 -1.901069
C  -0.693681  2.348778  0.701556
C  -3.665905  1.642486  0.803873
H   0.285601  2.226909  0.211847
H  -0.556487  2.177761  1.781486
H  -1.003343  3.399981  0.565330
H  -1.159661  1.230831 -2.384849
H  -2.283236  2.584822 -2.113831
H  -2.917441  0.935522 -2.366876
H  -4.508653  1.108862  0.335703
H  -3.863870  2.725051  0.736279
H  -3.644864  1.369964  1.871146
H   3.808062 -2.521793 -0.561029
H   2.747029 -1.079449  1.974426
C   3.445522 -1.687140 -1.183185
Mn  0.424170 -0.635080  0.911009
H   2.434588 -1.949251 -1.536165
H   5.671749 -0.387751  0.875331
C   2.357981 -0.254427  1.344671
H   4.105798 -1.611681 -2.062755
Si  3.418061 -0.065903 -0.195441
C   5.213774  0.388210  0.240796
H   2.403962  0.668570  1.955949
H   5.835389  0.496292 -0.663671
C   2.733919  1.313291 -1.313616
H   1.728562  1.057406 -1.688184
H   5.255795  1.339364  0.795963
H   3.385753  1.479076 -2.187141
H   2.658736  2.268873 -0.768531
```

2 x Mn(TMSM)2 – associated products, -4094.5136031, *-4094.067504*

```
Mn -1.093430  1.914872  0.662100
C  -1.481072  1.589217  2.667732
H  -1.101743  2.436414  3.272890
H  -2.570985  1.526959  2.855950
C   1.226789  0.153171  2.926878
H   1.775835 -0.739706  3.264951
H   1.436772  0.281950  1.849526
H   1.651362  1.030539  3.440901
C  -0.925948 -0.394158  5.068751
H  -2.000162 -0.510758  5.284656
H  -0.416946 -1.327799  5.360281
H  -0.543243  0.415729  5.710349
C  -1.285311 -1.457132  2.201447
H  -0.823544 -2.409204  2.508068
H  -2.378612 -1.566143  2.292011
H  -1.058303 -1.314370  1.128594
Si -0.642992  0.008282  3.236113
C  -0.017604  1.606710 -1.030605
```

```
H  -0.668943  1.649223 -1.933682
C   0.712183  4.536938 -1.826508
H  -0.031623  4.965150 -1.134898
H   1.528374  5.268907 -1.944917
H   0.223770  4.414417 -2.806839
C   2.165385  3.154942  0.521596
H   2.636764  2.234973  0.903760
H   2.951267  3.925242  0.455489
H   1.438501  3.493074  1.280822
C   2.748468  2.298892 -2.357013
H   2.351666  2.095632 -3.365023
H   3.537301  3.064170 -2.450655
H   3.226261  1.372526 -1.995185
Mn  0.753424 -0.279092 -0.992490
C   1.945833 -1.790766 -1.705128
H   1.327359 -2.643844 -2.047201
H   2.480036 -1.402678 -2.596308
C   2.278722 -3.221185  1.001787
H   1.574570 -2.523139  1.482251
H   1.698282 -4.090203  0.650875
H   2.978810 -3.575377  1.775835
C   4.192274 -0.917120  0.223173
H   4.700652 -0.382259 -0.595910
H   3.547293 -0.190883  0.745815
H   4.964398 -1.242045  0.939495
C   4.427500 -3.651957 -1.162189
H   5.147018 -3.995695 -0.400486
H   3.900707 -4.536706 -1.554622
H   5.000202 -3.209056 -1.993001
Si  1.360853  2.871078 -1.181337
Si  3.197622 -2.395715 -0.441734
C  -2.067927 -1.763006 -1.965977
H  -1.556730 -0.952864 -2.514349
H  -1.475689 -2.016576 -1.069227
H  -2.064043 -2.653034 -2.614873
C  -3.718627  0.365412 -0.471507
H  -3.179598  1.139802 -1.045469
H  -4.713924  0.764409 -0.220083
H  -3.188910  0.183389  0.480145
C  -4.843569 -0.930487 -3.043020
H  -4.913250 -1.842328 -3.657506
H  -5.869417 -0.615534 -2.793358
H  -4.391650 -0.140885 -3.664601
C  -4.617578 -2.592287 -0.426771
H  -5.632153 -2.306588 -0.106111
H  -4.696632 -3.537831 -0.986722
H  -4.019486 -2.787009  0.478001
Si -3.823954 -1.238474 -1.480595
```

2 x MnTMSM – associated products, -3197.9362555, *-3197.736603*

```
Mn  0.000002 -1.247382  0.000002
C   1.222530  0.112277 -0.786769
Si  2.931876  0.017633 -0.021646
H   1.140118  0.089339 -1.894197
C   2.717291  0.049714  1.868371
```

```
C   4.023130  1.477659 -0.550333
C   3.824775 -1.588851 -0.502525
H   3.587597  2.433171 -0.217441
H   4.117266  1.517865 -1.647336
H   5.037460  1.392968 -0.125896
H   2.219274  0.974152  2.207812
H   3.691427 -0.007551  2.380629
H   2.108049 -0.803159  2.214333
H   3.272246 -2.467889 -0.133504
H   4.844681 -1.623047 -0.084552
H   3.905116 -1.679824 -1.597670
H  -4.117274  1.517838  1.647353
H  -1.140121  0.089334  1.894198
C  -4.023136  1.477647  0.550350
Mn -0.000002  1.447334  0.000000
H  -3.587606  2.433165  0.217470
H  -3.905118 -1.679846  1.597647
C  -1.222530  0.112274  0.786771
H  -5.037465  1.392957  0.125909
Si -2.931875  0.017632  0.021646
C  -3.824772 -1.588860  0.502504
H  -4.844675 -1.623055  0.084525
C  -2.717291  0.049736 -1.868371
H  -2.219280  0.974182 -2.207802
H  -3.272239 -2.467893  0.133476
H  -3.691427 -0.007529 -2.380630
H  -2.108043 -0.803129 -2.214344
H   0.272452 -2.877075  0.370567
H  -0.272434 -2.877074 -0.370578
```

2 x Mn(TMSM)2 – TS, -4094.4712351, *-4094.027203*

```
C  -1.336210  2.811729 -1.071581
H  -1.574568  3.075335 -2.122112
H  -2.039565  3.387697 -0.438756
C   1.615796  2.392204 -1.860142
H   2.672659  2.609142 -1.638662
H   1.477862  1.293523 -1.809286
H   1.428119  2.670522 -2.910486
C   0.752667  5.184086 -0.938061
H   0.113687  5.782297 -0.268502
H   1.802934  5.443149 -0.724419
H   0.530353  5.492143 -1.972423
C   0.858297  2.905565  1.105165
H   1.868624  3.254139  1.372222
H   0.142861  3.385736  1.793383
H   0.828846  1.820795  1.318698
Si  0.424928  3.327998 -0.700231
C  -0.565298 -1.068549 -1.219831
H  -2.056352 -0.924266 -0.989092
C  -1.829781 -3.750033 -2.206406
H  -1.523693 -3.557700 -3.247330
H  -1.863100 -4.842357 -2.060465
H  -2.851041 -3.357824 -2.081752
C   1.090637 -3.741411 -1.288322
H   1.833475 -3.429182 -0.534013
H   1.020295 -4.841499 -1.239745
```

```
H   1.489514 -3.471569 -2.279534
C  -1.131788 -3.337961  0.790336
H  -2.131778 -2.939039  1.021554
H  -1.156023 -4.426564  0.959764
H  -0.423485 -2.906815  1.518509
Mn  1.082479 -0.585598 -0.043320
C   2.413453 -0.887367  1.482528
H   2.182780 -0.284502  2.380832
H   2.334460 -1.952860  1.780693
C   4.501992  1.334340  0.980974
H   3.785213  1.890884  0.357064
H   4.408693  1.711782  2.012027
H   5.516685  1.573636  0.623982
C   4.374011 -1.103887 -0.898603
H   4.129895 -2.172830 -1.014097
H   3.719616 -0.536248 -1.584843
H   5.408849 -0.959538 -1.250576
C   5.475058 -1.431124  1.955146
H   6.496809 -1.208552  1.605535
H   5.404073 -1.129154  3.012328
H   5.332582 -2.522925  1.909051
Si -0.613315 -2.940542 -0.993889
Si  4.172341 -0.531445  0.907959
C  -2.216050  0.354728  2.169771
H  -1.562988 -0.533232  2.145768
H  -1.629612  1.223345  1.816671
H  -2.453414  0.559981  3.227210
C  -3.405695 -0.548050 -0.566133
H  -3.608079 -1.633848 -0.581388
H  -4.064120 -0.108515 -1.337212
C  -4.850593 -1.209521  2.121377
H  -5.096321 -0.857462  3.136630
H  -5.795405 -1.420395  1.595825
H  -4.300639 -2.159591  2.219798
C  -4.756677  1.719674  1.079401
H  -5.734309  1.591499  0.588252
H  -4.933332  2.139177  2.082899
H  -4.182333  2.460149  0.499438
Si -3.825912  0.075531  1.178634
H  -0.344926 -0.882949 -2.298195
Mn -1.592691  0.781853 -0.832823
```

2 x MnTMSM – TS, -3197.8944711, *-3197.697692*

```
Mn -1.378928  2.062415  0.336725
C  -1.594904  0.456781 -0.830509
Si -2.339056 -1.014410  0.101908
H  -2.057709  0.548845 -1.840386
C  -2.064241 -2.655243 -0.810293
C  -4.203329 -0.727587  0.274123
C  -1.545620 -1.110155  1.821545
H  -4.681814 -0.625883 -0.712946
H  -4.397265  0.197298  0.838846
H  -4.684552 -1.568913  0.799380
H  -2.502518 -2.619524 -1.820493
H  -2.541005 -3.487087 -0.265760
H  -0.993357 -2.885936 -0.916051
```

```
H  -0.462799 -1.297333  1.744396
H  -1.990370 -1.924316  2.416344
H  -1.689934 -0.175819  2.391287
H   4.429249 -2.267613 -0.290976
H   1.184869 -2.013603 -0.685250
C   4.485351 -1.174603 -0.409922
Mn  0.343688  0.412623 -1.252583
H   4.634665 -0.953740 -1.477605
H   2.544800 -1.816661  2.244623
C   1.457073 -0.948528 -0.772716
H   5.368038 -0.814543  0.143830
Si  2.917761 -0.334530  0.247899
C   2.683495 -0.735894  2.085292
H   3.562262 -0.414802  2.668784
C   3.070107  1.546210  0.038149
H   3.250291  1.822735 -1.014067
H   1.800731 -0.215301  2.488278
H   3.922807  1.926365  0.625318
H   2.174296  2.085964  0.395153
H  -2.728250  2.647077  0.996706
H  -0.090896  2.956098  0.895743
```

2 x MnH2 – product, -2303.804499, *-2303.813095*

```
Mn  1.370529  0.000000  0.000000
H   0.000000 -1.248089  0.000000
Mn -1.370529  0.000000  0.000000
H   3.013578  0.000000 -0.000003
H   0.000000  1.248088  0.000000
H  -3.013578  0.000000 -0.000002
```