A capped trigonal pyramidal molybdenum hydrido complex and an unusually mild sulfur-carbon bond cleavage reaction

Robert H. Morris

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A capped trigonal pyramidal molybdenum hydrido complex and an unusually mild sulfur-carbon bond cleavage reaction

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DFT calculations reveal that a reported molybdenum hydride complex has an unprecedented geometry with the molybdenum in the base of trigonal pyramid defined by three thiolate ligands with a phosphine ligand on the apex and a hydride capping a PS₂ face. This complex reacts with methanol to produce a sulfido complex by a new reaction: the protonation of an ipso carbon of a thiolate ligand by coordinated methanol.

Hydrodesulfurization (HDS) is an important step in the upgrading of petroleum to clean fuels, usually using catalysts based on molybdenum disulfide.¹ There is theoretical evidence for the formation of unstable molybdenum hydrides (MoH) and molybdenum hydrosulfide (MoSH) groups on the surface of the heterogeneous catalyst.^{2, 3} The MoSH groups are thought to be more stable under HDS conditions.³ The mechanism of carbon-sulfur bond cleavage is still under investigation. Inorganic chemists are studying the reactions of well-defined metal complexes to establish the mechanisms of carbon-sulfur bond cleavage.⁴ For example, low valent molybdenum complexes have been shown to cleave C-H and S-C bonds.⁵ The mechanisms of H₂ activation at sulfido-bridged dimolybdenum cyclopentadienyl complexes have been investigated computationally and found to occur either homolytically between sulfur ligands^{6a} or heterolytically across a Mo-S bond^{6b} depending on the complex.

Some of us were involved in the study of homogenous, diamagnetic molybdenum hydridoarythiolato complexes MoH(SAR)₃(PPh₂), R = Me, Et, Ar = 2,4,6-iPr₃C₆H₂ and 2,4,6-Me₃C₆H₂ that underwent a spontaneous S-C cleavage event at a sulfur-aryl bond when their THF solutions were exposed to methanol.^{7, 8} When deuterated methanol (MeO²H) was employed, monodeuterated arene was detected along with non-deuterated free thiol and a dimeric molybdenum complex

Figure 1. The cleavage of sulfur-carbon bonds under mild conditions by reaction of MeO²H with MoH(PMePh₂)(SAR)₃, Ar = 2,4,6-Me₃C₆H₂. The structure of the dimer was determined by single crystal X-ray diffraction^{7,8} and a similar PMe₃ dimer (Mo₂) by DFT calculation (this work). The hydrogens and all carbons except those attached to the donor atoms have been removed for clarity. The level of theory for this calculation and the others shown in this article is M11-L with basis set SDD on Mo and 6-31G(d) on the other atoms with THF solvation applied using the PCM model unless otherwise specified.

(Mo₂) with two bridging sulfido ligands (Figure 1).⁸ The Mo₂ product was characterized by single crystal X-ray diffraction but we were unable to obtain suitable crystals of the starting hydride complex.

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[†] Electronic Supplementary Information (ESI) available: Computational details, coordinates and energies of the structures. See DOI: 10.1039/x0xx00000x

Figure 2. The structure of $\text{MoH}(\text{PMe}_3)(\text{SAR})_3$ with all of the hydrogens on the ligands and all of the carbons apart from the ipso carbons removed. Selected bond distances (Å) and angles ($^\circ$): Mo(1)-H(12) 1.65, Mo(1)-P(6) 2.37, Mo(1)-S(2) 2.34, Mo(1)-S(4) 2.36, Mo(1)-S(8) 2.33; H(12)-Mo(1)-P(6) 54.1, H(12)-Mo(1)-S(2) 73.5, H(12)-Mo(1)-S(8) 84.6, P(6)-Mo(1)-S(2) 115.0, P(6)-Mo(1)-S(4) 84.6, P(6)-Mo(1)-S(8) 91.3, S(2)-Mo(1)-S(4) 112.9, S(4)-Mo(1)-S(8) 121.1, S(8)-Mo(1)-S(2) 121.6.

The molybdenum in $\text{MoH}(\text{SAR})_3(\text{PRPh}_2)$ was proposed to be in a trigonal bipyramidal geometry with the hydride *trans* to the phosphine ligand on the basis of the observation in the NMR spectra of a large $^2J_{\text{HP}}$ coupling constant ranging from 79 to 87 Hz between the hydride, detected at 3.3 ppm for one of the compounds, and the phosphorus nuclei.^{7, 8} However DFT calculations using a slightly simplified structure ($\text{Mo}(\text{PMe}_3)(\text{H})(\text{SAR})_3$, Ar = 2,6-Me₂C₆H₃) now provide strong evidence that the most stable isomer of these complexes has molybdenum in an unprecedented distorted capped trigonal pyramidal (CTP) geometry (Figure 2).

In this diamagnetic, five coordinate complex the molybdenum sits 0.3 Å above the middle of a distorted triangle defined by the three sulfur atoms (Figure 2). The phosphorus is at the vertex of the distorted S₃P trigonal pyramid with the short Mo-P bond (2.37 Å) at a 78° angle to the S₃ basal plane. The hydride ligand caps one PS₂ face of this CTP with a small HMoP angle of 54.1°. Thus the large $^2J_{\text{HP}}$ is associated with this small angle between these nuclei. There are no distortions of the PMe₃ ligand that would indicate bonding favouring 5-coordinate phosphorus. The HOMO is a lone pair with approximately (d_{xz})(Mo) character, out of phase with a (p_z)² lone pair on S8 (see the SI) where the x direction is along the Mo-S8 bond and the z direction is between the Mo-H and Mo-P bonds. None of the 620 five-coordinate complexes containing a terminal hydride found in the Cambridge Structural Database has such a CTP geometry. Two isomers with the hydride approximately *trans* to the phosphorus in a distorted trigonal bipyramidal (TBP) geometry were located as stable minima at 10 and 13 kcal/mol higher in energy and a distorted trigonal bipyramidal complex in the triplet state was located at 5 kcal/mol higher in energy. Even the model complex $\text{Mo}(\text{PMe}_3)(\text{H})(\text{SMe})_3$ with much smaller substituents on the sulfurs adopts this CTP geometry. Apparently molybdenum is large enough to accommodate ligands *cis* to each other, thus avoiding *trans* H-Mo-P and H-Mo-S bond weakening. The $^2J_{\text{HP}}$ (unscaled) were calculated using the gauge-independent atomic orbital method as -70 Hz for the CTP geometry and -31 Hz for the TBP geometry. The former

value agrees better with the range from experiment (79 to 87 Hz, $\pm$ sign not determined).

This CTP geometry explains why the complex $\text{MoH}(\text{PMePh}_2)(\text{SAR})_3$, Ar = 2,4,6-*i*Pr₃C₆H₂ readily reacts with pyridine to give the complex $\text{MoH}(\text{PMePh}_2)(\text{py})(\text{SAR})_3$, Ar = 2,4,6-*i*Pr₃C₆H₂,⁷ now known to have a capped trigonal bipyramidal (CTB) geometry⁹ with the pyridine across from the hydride and the phosphorus at a small angle to the hydride, producing a $^2J_{\text{HP}}$ of 87 Hz (eq 1).

The original proposal for the sulfur-carbon bond cleavage of Figure 1 was that the hydride would attack the carbon,⁸ however this would involve isotope exchange with the hydride

that was not observed and our DFT studies could not find a suitable transition state for the hydride attack. The methanol that is needed to trigger this cleavage reaction (Figure 1) can easily coordinate to give a formally Mo(IV) methanol complex as shown in eq 1. From this experimentally unobserved methanol adduct, the C-S bond is readily cleaved in an

Figure 3. (a) The methanol adduct $\text{MoH}(\text{PR}_3)(\text{OHMe})(\text{SAR})_3$ (Mo(1)-H(22) 1.66, Mo(1)-P(13) 2.39, Mo(1)-O(15) 2.21, Mo(1)-S(2) 2.36, Mo(1)-S(4) 2.33, Mo(1)-S(17) 2.36, O(15)-H(16) 0.97, S(4)-C(5) 1.78 Å; H(22)-Mo(1)-P(13) 52.1, H(22)-Mo(1)-O(15) 148.5, P(13)-Mo(1)-O(15) 158.7, Mo(1)-S(4)-C(5) 113.0°); (b) the hydrogen transfer transition state $[\text{OH}\cdots\text{CSMo}]^\ddagger$ (1635i cm⁻¹; Mo(1)-H(22) 1.66, Mo(1)-P(13) 2.45, Mo(1)-O(15) 2.07, Mo(1)-S(2) 2.37, Mo(1)-S(4) 2.20, Mo(1)-S(17) 2.38, O(15)-H(16) 1.21, S(4)-C(5) 2.14, H(16)-C(5) 1.33 Å; H(22)-Mo(1)-P(13) 54.3, H(22)-Mo(1)-O(15) 146.7, P(13)-Mo(1)-O(15) 157.7, Mo(1)-S(4)-C(5) 107.1°); (c) the sulfido product $\text{MoH}(\text{S})(\text{PR}_3)(\text{OMe})(\text{SAR})_2, \text{HAR}$ (Mo(1)-H(22) 1.65, Mo(1)-P(13) 2.56, Mo(1)-O(15) 1.93, Mo(1)-S(2) 2.40, Mo(1)-S(4) 2.14, Mo(1)-S(17) 2.42 Å; H(22)-Mo(1)-P(13) 54.8, H(22)-Mo(1)-O(15) 145.6, P(13)-Mo(1)-O(15) 155.7° plus HAR (C(5)-H(16) 1.10 Å).

Figure 4. A reaction coordinate diagram for the C-S bond cleavage reaction shown in Figure 1. Calculations were done with M11L/6-31G(d)/SDD on Mo/THF solvation.

unprecedented mechanism: the attack by the hydrogen of the methanol ligand on the ipso carbon of an aryl (Figure 3). The result of this transfer is the formation of a C-H bond in the arene product, consistent with the experimental observation that deuterium from MeO^2H ends up on this carbon (Figure 3b).

The hydrogen of the methanol ligand (Figure 3a) transfers to the aryl carbon 5 via a transition state with arenium character. Indeed the Mulliken positive charges on the carbons of the ring other than carbon 5 increase on going from the methanol adduct to the transition state. Atoms with increased negative charges include carbon 5, sulfur 4, hydrogen 16 and hydrogens on the methoxide methyl. The reaction has characteristics as described for other electrophilic aromatic substitution reactions.^{10, 11} The immediate metal-containing product of this reaction is a formally Mo(VI) CTB sulfido complex $\text{MoH}(\text{S})(\text{PR}_3)(\text{OMe})(\text{SAr})_2$ with a short Mo-S bond of 2.14 Å (Figure 3c). The metal undergoes a formal two electron oxidation in this reaction, paradoxically indicating that the hydrogen transferred as a hydride.

The (OH...CSMo) transition state ($1635i\text{ cm}^{-1}$) is the highest energy point in the overall reaction shown in Figure 1 with a transition state energy of 21 kcal/mol above the energy of the methanol adduct $\text{MoH}(\text{PR}_3)(\text{OHMe})(\text{SAr})_3$ (Figure 4); the same TS energy was obtained for gas phase and liquid phase (THF) calculations. The use of higher basis sets on the central atoms (6-311++G(d,p)) resulted in an energy of 22 kcal/mol and the use of the PBE0 functional with dispersion correction D3 gave 24 kcal/mol. Little is known about the mechanism of protonolysis of carbon-sulfur bonds.^{12, 13}

Another interesting step in the overall reaction involves the transition state for the formal reductive elimination of the Mo(VI) CTB hydridosulfido complex $\text{MoH}(\text{S})(\text{PR}_3)(\text{OMe})(\text{SAr})_2$ to produce the Mo(IV) hydrosulfido complex $\text{Mo}(\text{SH})(\text{PR}_3)(\text{OMe})(\text{SAr})_2$ (Figure 5). This step has a barrier of 15 kcal/mol and is uphill thermodynamically by 7 kcal/mol but is likely driven by subsequent dimerization steps where HSAr is eliminated, a strongly downhill reaction (Figure 4). A similar transition state involving hydride migration to a bridging sulfido ligand in a formal hydride to proton conversion has been reported.^{6b} Molybdenum hydrido sulfido complexes can also readily eliminate dihydrogen.¹⁴

The details of the subsequent steps have not been established. The reaction may proceed via a singly bridged sulfido complex such as $\text{Mo}_2(\mu\text{-S})(\text{SH})(\text{OMe})_2(\text{PMe}_3)_2(\text{SAr})_3$ (Figure 6) which might eliminate a further equivalent of thiol HSAr to give the observed dimeric product $(\text{PMe}_3)(\text{MeO})(\text{ArS})\text{Mo}(\mu\text{-S})_2\text{Mo}(\text{SAr})(\text{OMe})(\text{PMe}_3)$ (Mo_2) of Figure 1 found at the zero energy point of the reaction coordinate diagram, Figure 4.

These unusual reactions and geometries highlight the rich redox chemistry of molybdenum in a sulfur environment. The chemistry has possible relevance to HDS catalysis but also the action of molybdenum enzymes.¹⁵

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Conflicts of interest

There are no conflicts to declare.

Figure 5. (a) Transition state structure $\text{MoH}\cdots\text{S TS}$ ($959i\text{ cm}^{-1}$) for the hydride reductive elimination step ($\text{Mo}(1)\text{-H}(27)$ 1.77, $\text{Mo}(1)\text{-P}(9)$ 2.59, $\text{Mo}(1)\text{-O}(11)$ 1.92, $\text{Mo}(1)\text{-S}(2)$ 2.35, $\text{Mo}(1)\text{-S}(8)$ 2.23, $\text{Mo}(1)\text{-S}(15)$ 2.35, $\text{H}(27)\text{-S}(8)$ 1.59 Å; $\text{H}(27)\text{-Mo}(1)\text{-P}(9)$ 66.0, $\text{Mo}(1)\text{-H}(27)\text{-S}(8)$ 82.7, $\text{P}(9)\text{-Mo}(1)\text{-O}(11)$ 161.3, $\text{S}(2)\text{-Mo}(1)\text{-S}(15)$ 119.8°, $\text{S}(2)\text{-Mo}(1)\text{-S}(8)$ 122.3°) to give the (b) hydrosulfido complex $\text{Mo}(\text{SH})(\text{PR}_3)(\text{OMe})(\text{SAr})_2$ ($\text{Mo}(1)\text{-P}(9)$ 2.52, $\text{Mo}(1)\text{-O}(11)$ 1.92, $\text{Mo}(1)\text{-S}(2)$ 2.30, $\text{Mo}(1)\text{-S}(8)$ 2.39, $\text{Mo}(1)\text{-S}(15)$ 2.29, $\text{H}(27)\text{-S}(8)$ 1.34 Å; $\text{P}(9)\text{-Mo}(1)\text{-O}(11)$ 159.3, $\text{S}(2)\text{-Mo}(1)\text{-S}(15)$ 117.1, $\text{S}(2)\text{-Mo}(1)\text{-S}(8)$ 120.1, $\text{S}(8)\text{-Mo}(1)\text{-S}(15)$ 122.8°).

Figure 6. Structure of a possible intermediate in the reaction shown in Figure 1, a sulfido bridged dimer $\text{Mo}_2(\mu\text{-S})(\text{SH})(\text{OMe})_2(\text{PMe}_3)_2(\text{SAr})_3$.

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A five coordinate molybdenum hydride with an unprecedented CTP structure reacts with methanol, leading to the facile cleavage of a sulfur-carbon bond.

Supplementary Information for:

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Computational details

Density functional theory calculations were performed using the Gaussian09 package¹ and the M11-L functional unless otherwise noted. All of the atoms were treated with the 6-31+G(d,p) basis set (BS1) except for the molybdenum which was treated with the Stuttgart effective core potential (SDD). An ultrafine grid (pruned: 99,590) and the integral equation formalism polarizable continuum model (IEF-PCM) with radii and nonelectrostatic terms from the SMD solvation model for THF (scrf=(smd,solvent=tetrahydrofuran)) were used for all optimizations. Ground states were connected to their transition states by performing intrinsic reaction coordinate (IRC) calculations. A frequency analysis (temperature 298 K) was performed on all geometries and this produced no imaginary frequencies for the ground state structures and only one imaginary frequency for transition states. The geometries of the three structures involved in the OH...CSMo transition state (Figure 3 of the article) were also calculated using a higher basis set 6-311++G(d,p) (BS2) on all of the atoms attached to molybdenum as well as the ipso carbon on the cleaved arene ring. These three structures were also found with the PBE1PBE functional with the same basis set as mentioned in the article. The same transition state structure was located with one imaginary frequency. Similarly the PBE0 functional (Gaussian key word PBE1PBE) with D3 was applied to the calculation of the three structures with comparable results. Three-dimensional visualization of optimized geometries were constructed using ChemCraft.

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Selected Molecular Orbitals of CTP $\text{MoH}(\text{PMe}_3)(\text{SAr})_3$, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_4$

LUMO+4

Approx. d_{yz} oriented between MoS(10) (arene down) (approx. y direction) along Mo-P(24) (approx. z direction). Some Mo-S and Mo-H antibonding.

LUMO+2

Approx. $d_{x^2-z^2}$ oriented along Mo-S(42) (x direction) and between Mo-H(69) and Mo-P(24) (z direction).
Some Mo-S and Mo-P antibonding.

LUMO+1

$d_{xy} + d_{x^2-y^2}$ oriented between Mo-S(10) and Mo-S(42) bond in the MoS_3 plane.

LUMO

d_{xy} - $d_{x^2-y^2}$ oriented parallel to S(10) and S(42) (approx. y direction) in the MoS_3 plane.

HOMO

$(d_{xz})^2$ between bonds Mo-S(42) (arene down) (approx. x direction) and Mo-P (approx. z direction).

HOMO-1 to HOMO-3 were associated with the thiolate ligands (sulfur p and attached arene).

Calculation of $^2J_{PH}$ coupling constants of CTP $\text{MoH}(\text{PMe}_3)(\text{SAr})_3$ and the more stable trans isomer 2, trans- $\text{MoH}(\text{PMe}_3)(\text{SAr})_3$, Ar = 2,6-Me₂C₆H₃ using the GIAO method

	$^2J_{PH}$ (Hz) of CTP $\text{MoH}(\text{PMe}_3)(\text{SAr})_3^a$	$^2J_{PH}$ (Hz) of isomer 2, trans- $\text{MoH}(\text{PMe}_3)(\text{SAr})_3^a$
Fermi Contact (FC) contribution to J	-70.2	-30.7
Spin-dipolar (SD) contribution to J	-0.2	-0.5
Paramagnetic spin-orbit (PSO) contribution to J	-0.8	-0.7

Diamagnetic spin-orbit (DSO) contribution to J	1.7	0.2
Total nuclear spin-spin coupling J	-69.5	-31.9

^a Gaussian input line: # NMR=(MIXED,READATOMS,FOnly) m11/genecp int=(ultrafine,acc2e=11)
 scrf=(smd,solvent=tetrahydrofuran) with 6-31G* on H C S P and SDD on Mo.

Energies (in Hartrees), Structures and Cartesian coordinates

CTP MoH(PMe₃)(SAr)₃, Ar = 2,6-Me₂C₆H₃.

Enthalpy -2654.469362

Free energy -2654.602966

Mo	0.250922	-0.053210	0.388175
S	1.585512	1.000625	-1.219878
C	3.185318	0.267682	-1.382643
C	3.357194	-0.901864	-2.138368
C	2.220618	-1.557259	-2.837628
H	1.684778	-0.853756	-3.497398
C	4.632437	-1.449867	-2.223506
C	5.712270	-0.854437	-1.597901
H	6.709171	-1.299384	-1.681043
S	-0.309576	1.365466	2.191693
C	-1.410925	2.139329	1.045744
C	-0.978719	3.257695	0.300390
C	0.333654	3.906508	0.552694
H	0.402556	4.274515	1.590401
H	0.477550	4.765412	-0.119572
C	-1.839899	3.787922	-0.650895
C	-3.103617	3.257958	-0.848843
H	-3.763854	3.687799	-1.609310
C	-3.544679	2.211035	-0.063079
C	-2.723651	1.642548	0.905157
C	-3.265685	0.584575	1.799418
H	-3.291946	0.931266	2.847113
H	-4.291554	0.316081	1.504473
P	1.439837	-1.290399	2.021110
C	1.658118	-3.053146	1.699347
H	1.464458	-1.948332	-2.132880
H	4.774267	-2.365996	-2.809178
H	1.181979	3.217955	0.409181
H	-1.508241	4.651317	-1.239146
H	-4.557514	1.811822	-0.193821
H	-2.658263	-0.334183	1.796509
H	2.230429	-3.532172	2.510387
H	2.194808	-3.210719	0.750416

H	0.683216	-3.559636	1.623056
C	5.530548	0.311427	-0.877083
C	4.274321	0.894786	-0.758428
C	4.107182	2.137794	0.041295
H	5.069570	2.464650	0.463648
H	3.704341	2.969617	-0.561390
H	3.398323	1.998737	0.877186
H	6.384317	0.791924	-0.384580
S	-1.057087	-1.902434	-0.137156
C	-2.646507	-1.528020	-0.843406
C	-2.818545	-0.660316	-1.932986
C	-1.688177	0.076132	-2.555419
H	-0.804548	-0.561308	-2.721378
H	-1.986775	0.505480	-3.524304
H	-1.354524	0.927752	-1.930893
C	-4.099471	-0.462801	-2.437044
C	-5.196391	-1.096895	-1.886866
H	-6.196927	-0.927044	-2.297893
C	-5.016951	-1.957933	-0.820368
C	-3.754925	-2.196157	-0.290633
C	-3.616591	-3.135119	0.855684
H	-2.955108	-3.986051	0.621775
H	-4.597427	-3.542749	1.144686
H	-3.179185	-2.647192	1.744190
H	-5.878553	-2.473027	-0.378814
H	-4.227800	0.216022	-3.288989
C	3.128055	-0.742233	2.342670
H	3.598770	-1.354405	3.130311
H	3.739358	-0.822513	1.429104
H	3.137295	0.309480	2.670098
H	2.572414	-2.399711	-3.452311
C	0.726437	-1.335050	3.686223
H	-0.321695	-1.672246	3.647787
H	1.293160	-2.032201	4.325923
H	0.744042	-0.343332	4.163018
H	1.522741	-1.067323	0.097938

MeOH

Enthalpy -115.618887

Free energy -115.64534

C	-0.678322	0.018693	0.000000
H	-1.023161	0.224198	1.015409
H	-1.138490	-0.903313	-0.361043
H	-0.959528	0.846298	-0.654365
O	0.754203	-0.127836	0.000000
H	1.157490	0.743347	0.000000

MoH(PMe₃)(OHMe)(SAr)₃, Ar = 2,6-Me₂C₆H₃

Enthalpy -2770.137055

Free energy -2770.254194

Mo	-0.261541	-0.097989	0.329845
S	-1.557720	0.218018	-1.619603
C	-3.265913	-0.106724	-1.302440
C	-4.114644	0.958846	-0.965927
C	-3.607861	2.350416	-0.832073
H	-3.141073	2.716206	-1.762203
C	-5.455922	0.686101	-0.720414
C	-5.952925	-0.601053	-0.807806
H	-7.012891	-0.795832	-0.614395
S	0.626846	-2.203902	0.805806
C	2.118026	-2.547901	-0.097210
C	2.079357	-2.879143	-1.465640
C	0.794510	-2.984415	-2.209641
H	0.123602	-3.729453	-1.748314
H	0.972101	-3.288280	-3.252382
C	3.278847	-3.136031	-2.124528
C	4.486559	-3.095678	-1.454597
H	5.419188	-3.302320	-1.989357
C	4.510108	-2.811418	-0.101372
C	3.341161	-2.541646	0.599724
C	3.405824	-2.295923	2.066355
H	2.893523	-3.095177	2.629414
H	4.450328	-2.260777	2.411361
P	-1.375702	-0.271881	2.432830
C	-2.700224	0.914280	2.748063
O	1.401543	0.150301	-1.106940
H	1.969592	-0.631661	-1.144164
H	-2.829869	2.429183	-0.050851
H	-6.122110	1.515064	-0.453120

H	0.223951	-2.039560	-2.225519
H	3.250429	-3.387462	-3.191388
H	5.463702	-2.802738	0.439685
H	2.914494	-1.356155	2.366628
H	-3.132995	0.779825	3.753582
H	-3.505123	0.786877	2.004682
H	-2.325688	1.947399	2.668454
C	-5.105583	-1.640998	-1.142442
C	-3.757097	-1.418076	-1.397134
C	-2.865948	-2.561843	-1.723603
H	-3.440190	-3.497764	-1.799089
H	-2.326963	-2.412834	-2.674667
H	-2.086505	-2.702841	-0.952083
H	-5.492937	-2.664413	-1.213212
S	0.437267	1.947349	1.270133
C	1.655146	2.749346	0.264978
C	1.246450	3.771123	-0.606486
C	-0.190171	4.104856	-0.796197
H	-0.679671	4.408378	0.144494
H	-0.310533	4.925243	-1.520228
H	-0.759641	3.234454	-1.168402
C	2.213228	4.453167	-1.336676
C	3.554388	4.143185	-1.213470
H	4.302878	4.692420	-1.794202
C	3.945777	3.136807	-0.349149
C	3.014513	2.429247	0.401378
C	3.469673	1.332872	1.293961
H	3.100870	1.450322	2.326836
H	4.568635	1.276117	1.325313
H	3.093026	0.357488	0.941841
H	5.008132	2.885239	-0.244607
H	1.893556	5.247789	-2.021558
C	-2.182974	-1.844416	2.806454
H	-2.630584	-1.833405	3.813570
H	-2.978600	-2.051510	2.072424
H	-1.462172	-2.676444	2.762788
H	-4.423927	3.040694	-0.569292
C	-0.315147	-0.073265	3.891970
H	0.098163	0.944708	3.947271
H	-0.880111	-0.272867	4.818172
H	0.531332	-0.777885	3.845345
C	1.524610	0.845205	-2.322209
H	0.814574	1.681278	-2.304382
H	2.547699	1.241250	-2.434152
H	1.284918	0.190532	-3.178671
H	-1.820127	-0.584685	0.619321

OH..CSMo TS

Enthalpy -2770.10478

Free energy -2770.220971

Mo	-0.283338	0.000257	0.366311
S	-1.517255	-0.283532	-1.640724
C	-3.240396	-0.414344	-1.272965
C	-4.024603	0.749118	-1.232881
C	-3.438357	2.097859	-1.453552
H	-2.961443	2.189530	-2.444030
C	-5.379720	0.624710	-0.945543
C	-5.951031	-0.611216	-0.706420
H	-7.020677	-0.688947	-0.485790
S	0.710540	-1.756988	1.231339
C	2.297277	-2.302903	-0.103567
C	1.974075	-3.462912	-0.841708
C	0.606719	-3.666602	-1.386380
H	-0.063824	-4.103310	-0.624353
H	0.615017	-4.357652	-2.243808
C	2.951900	-4.422999	-1.058656
C	4.223239	-4.273394	-0.531911
H	4.979986	-5.046731	-0.701498
C	4.543555	-3.141362	0.200457
C	3.597585	-2.155475	0.430129
C	3.963862	-0.921540	1.168171
H	3.411804	-0.830392	2.119580
H	5.039484	-0.889262	1.398829
P	-1.444328	0.376880	2.488444

C	-2.781265	1.585948	2.439582
O	1.311535	-0.121255	-0.953396
H	1.841739	-1.159571	-0.614878
H	-2.648690	2.328845	-0.714904
H	-5.996470	1.530632	-0.910576
H	0.137507	-2.721167	-1.702537
H	2.706610	-5.310376	-1.654978
H	5.559225	-3.011766	0.593826
H	3.713799	-0.024226	0.575448
H	-3.253193	1.700341	3.429318
H	-3.553610	1.262214	1.721832
H	-2.410935	2.572378	2.119155
C	-5.166430	-1.748934	-0.748670
C	-3.807751	-1.675641	-1.032958
C	-2.982189	-2.911207	-1.037647
H	-3.606872	-3.803068	-0.877439
H	-2.432684	-3.042164	-1.985207
H	-2.214149	-2.887707	-0.242721
H	-5.613739	-2.731867	-0.558435
S	0.220807	2.293913	0.772431
C	1.604618	2.797745	-0.196309
C	1.415926	3.290009	-1.495341
C	0.060008	3.408421	-2.093761
H	-0.580522	4.101562	-1.521098
H	0.118330	3.782709	-3.127356
H	-0.475619	2.443866	-2.107033
C	2.534265	3.676481	-2.225483
C	3.804727	3.588457	-1.687799
H	4.675167	3.886842	-2.281326
C	3.970862	3.145390	-0.387550
C	2.881117	2.765243	0.386676
C	3.082727	2.382526	1.810768
H	2.661016	3.145251	2.489315
H	4.154570	2.287094	2.044742
H	2.585839	1.435891	2.076098
H	4.973319	3.105197	0.055331
H	2.394312	4.052803	-3.245949
C	-2.239786	-1.072402	3.205503
H	-2.709806	-0.829929	4.172382
H	-3.014761	-1.461462	2.526110
H	-1.503889	-1.875418	3.370357
H	-4.212014	2.877132	-1.377642
C	-0.402865	0.942608	3.854706
H	0.023291	1.934353	3.643472
H	-0.984559	1.000913	4.789919
H	0.431948	0.240466	4.010556
C	1.627194	0.090896	-2.282055
H	0.956375	0.838724	-2.734580
H	2.668059	0.456410	-2.375282
H	1.533821	-0.842734	-2.873282
H	-1.827966	-0.490502	0.726101

MoH(S)(PMe₃)(OMe)(SAr)₂HAr

Enthalpy -2459.508987

Free energy -2459.60867

Mo	-0.503964	-0.072229	0.419373
S	-1.541830	-0.539147	-1.691530
C	-3.286125	-0.680098	-1.458838
C	-4.094524	0.461923	-1.574651
C	-3.520429	1.802627	-1.867568
H	-2.933526	1.810709	-2.801090
C	-5.464065	0.325249	-1.379300
C	-6.025745	-0.903564	-1.083513
H	-7.107177	-0.991442	-0.936514
S	-0.043129	-1.814243	1.578087
C	3.277439	-2.850263	0.392661
C	2.951837	-2.910673	-0.956257
C	1.716280	-3.605583	-1.409050
H	1.477982	-4.477052	-0.778440
H	1.794346	-3.949613	-2.452409
C	3.788151	-2.269866	-1.865544
C	4.894783	-1.565533	-1.426374
H	5.542030	-1.059121	-2.151042
C	5.189229	-1.497975	-0.073979
C	4.383813	-2.145686	0.855049
C	4.673787	-2.075839	2.313736
H	4.851593	-3.075413	2.745042
H	5.561685	-1.460704	2.526314
P	-1.940210	0.655490	2.405735
C	-3.061016	2.010202	2.024757
O	0.998033	0.010090	-0.784613
H	2.632333	-3.363281	1.119007
H	-2.828835	2.139504	-1.073396
H	-6.101043	1.213402	-1.466304
H	0.842553	-2.929007	-1.354001
H	3.554740	-2.313137	-2.936422
H	6.066703	-0.936638	0.270328
H	3.825676	-1.642949	2.873064
H	-3.644778	2.292004	2.916106

H	-3.764864	1.702538	1.233994
H	-2.511770	2.897215	1.674537
C	-5.218435	-2.020928	-0.978067
C	-3.843243	-1.934384	-1.164060
C	-2.995107	-3.145981	-1.019385
H	-3.611352	-4.035710	-0.820743
H	-2.392389	-3.342710	-1.921453
H	-2.271161	-3.042285	-0.190044
H	-5.659546	-2.997417	-0.745559
S	0.321607	2.119447	1.021201
C	1.683049	2.504092	-0.027726
C	1.473741	3.282747	-1.173687
C	0.115639	3.729934	-1.582061
H	-0.398769	4.301241	-0.791636
H	0.164464	4.363009	-2.481027
H	-0.539255	2.869543	-1.813991
C	2.571198	3.599616	-1.966478
C	3.837980	3.148573	-1.646592
H	4.689980	3.404843	-2.284970
C	4.026097	2.372153	-0.517186
C	2.962730	2.041262	0.313263
C	3.189738	1.179106	1.500866
H	2.789960	1.626575	2.426201
H	4.264473	0.988569	1.648003
H	2.686429	0.202882	1.379544
H	5.027603	2.004523	-0.262256
H	2.415225	4.210418	-2.863565
C	-3.043072	-0.638660	2.994251
H	-3.693785	-0.251910	3.795079
H	-3.676578	-1.009577	2.172361
H	-2.468075	-1.488764	3.391045
H	-4.316043	2.557604	-1.959215
C	-1.079923	1.170453	3.903591
H	-0.340771	0.409165	4.197682
H	-0.549306	2.121450	3.755152
H	-1.800638	1.295416	4.728550
C	1.343631	0.082786	-2.095514
H	1.183476	-0.874660	-2.637233
H	0.771260	0.862333	-2.643580
H	2.417720	0.342080	-2.178877
H	-2.136171	-0.304127	0.550760

HAr, Ar = 2,6-Me₂C₆H₃

Enthalpy -310.653597

Free energy -310.69539

C	0.003081	-0.944153	-0.007295
C	-1.214790	-0.275223	-0.003967
C	-2.503785	-1.024881	0.003458
H	-2.349956	-2.104393	-0.152571
H	-3.190246	-0.667015	-0.782420
C	-1.204176	1.119644	0.000324
C	-0.005760	1.810884	0.002158
H	-0.008270	2.907618	0.000845
C	1.200801	1.124862	-0.000391

C	1.220821	-0.265152	-0.004453
C	2.507022	-1.019754	0.003853
H	2.527873	-1.802385	-0.773164
H	3.369986	-0.356396	-0.164663
H	0.006015	-2.043868	-0.015072
H	-3.038518	-0.904377	0.962098
H	-2.155224	1.667760	-0.001637
H	2.148021	1.679159	-0.003035
H	2.671031	-1.533468	0.967497

MoH(S)(PMe₃)(OMe)(SAr)₂

Enthalpy -2459.497059

Free energy -2459.597926

Mo	0.069964	0.539936	0.611381
S	-1.067181	-1.516496	1.037148
C	-2.693357	-1.440989	0.351305
C	-2.918501	-1.956698	-0.935034
C	-1.818742	-2.533437	-1.753831
H	-1.305071	-3.363808	-1.241461
C	-4.204826	-1.889573	-1.458476
C	-5.243881	-1.332704	-0.735750
H	-6.250376	-1.290907	-1.164684
S	-0.201530	2.120131	2.036978
P	-1.006419	2.084855	-1.109725
C	-1.498467	1.242684	-2.620779
O	1.486427	-0.474656	1.437281
H	-1.036640	-1.785357	-1.978106
H	-4.386415	-2.288264	-2.463561
H	-1.948085	1.957090	-3.329444
H	-2.246420	0.465484	-2.392961
H	-0.636709	0.764035	-3.110204
C	-5.009095	-0.835196	0.532435
C	-3.741119	-0.882977	1.101115
C	-3.517285	-0.325766	2.459824

H	-4.465525	0.005940	2.908669
H	-3.055521	-1.060800	3.139356
H	-2.830887	0.540768	2.442653
H	-5.830775	-0.398584	1.112264
S	1.686072	0.676202	-1.170209
C	3.099544	-0.262178	-0.694749
C	3.158880	-1.633018	-0.978850
C	2.020584	-2.353674	-1.605208
H	1.717937	-1.909481	-2.568298
H	2.274764	-3.409638	-1.783424
H	1.125463	-2.326419	-0.957702
C	4.302828	-2.333882	-0.615421
C	5.357593	-1.703003	0.017229
H	6.250872	-2.271451	0.296394
C	5.279802	-0.351093	0.297573
C	4.158301	0.392124	-0.049652
C	4.088502	1.834361	0.301515
H	3.902912	2.472734	-0.578226
H	5.024834	2.169261	0.773050
H	3.263597	2.038437	1.007433
H	6.109895	0.153495	0.806022
H	4.355588	-3.406974	-0.834235
C	-2.536154	2.844903	-0.543608
H	-2.974466	3.464630	-1.342277
H	-3.266755	2.070874	-0.256462
H	-2.352755	3.483303	0.333783
H	-2.203039	-2.912626	-2.712859
C	-0.034404	3.498222	-1.664185
H	0.327036	4.074157	-0.798160
H	0.838934	3.181747	-2.251365
H	-0.657272	4.159405	-2.289076
C	1.733896	-1.627622	2.109390
H	1.108224	-1.739137	3.021492
H	1.567303	-2.531399	1.484447
H	2.797204	-1.644831	2.422478
H	-1.533808	0.605111	0.222362

Enthalpy -2459.482842
Free energy -2459.58393

Mo	0.251911	0.341444	0.607895
S	-1.199814	-1.506935	0.694301
C	-2.872254	-1.170142	0.262003
C	-3.318505	-1.585575	-1.004877
C	-2.425281	-2.302341	-1.956188
H	-2.163313	-3.306044	-1.579167
C	-4.643907	-1.348665	-1.348424
C	-5.519068	-0.756765	-0.455175
H	-6.562200	-0.585813	-0.740177
S	0.201811	1.963523	2.131291
P	-1.173941	1.712547	-1.064383
C	-1.388467	1.108481	-2.751783
O	1.464742	-0.968705	1.320184
H	-1.464994	-1.786317	-2.122166
H	-4.995799	-1.658704	-2.339446
H	-1.751172	1.925070	-3.397738
H	-2.137569	0.303418	-2.778310
H	-0.448538	0.722802	-3.173839
C	-5.078821	-0.404572	0.806522
C	-3.757445	-0.602894	1.192610

C	-3.329460	-0.200253	2.557476
H	-4.202672	-0.024095	3.203400
H	-2.691611	-0.958200	3.039253
H	-2.741062	0.735480	2.553275
H	-5.775724	0.041585	1.525752
S	1.714007	0.592731	-1.209842
C	3.238540	-0.149311	-0.714824
C	3.440923	-1.520209	-0.928266
C	2.380903	-2.385753	-1.506749
H	2.049475	-2.034138	-2.498485
H	2.736325	-3.421302	-1.618641
H	1.479133	-2.402234	-0.868676
C	4.664205	-2.068709	-0.566535
C	5.661916	-1.288582	-0.009541
H	6.621286	-1.739288	0.265276
C	5.446351	0.061008	0.193694
C	4.236897	0.655217	-0.149842
C	4.030777	2.107575	0.095238
H	3.761420	2.652506	-0.824977
H	4.941592	2.568222	0.506743
H	3.209251	2.292618	0.810481
H	6.234087	0.683695	0.633892
H	4.832251	-3.139972	-0.729763
C	-2.856966	2.198952	-0.629297
H	-3.216807	2.975236	-1.325149
H	-3.546286	1.344401	-0.685563
H	-2.898995	2.610597	0.392160
H	-2.917527	-2.434229	-2.931795
C	-0.395645	3.326498	-1.311471
H	-0.344450	3.874880	-0.358017
H	0.630554	3.222541	-1.694448
H	-0.978743	3.929123	-2.027953
C	1.352040	-1.986630	2.220209
H	0.538090	-1.841034	2.961883
H	1.180355	-2.958926	1.711908
H	2.307341	-2.078801	2.772749
H	-1.029232	1.294603	1.369542

Mo	0.246552	-0.700764	-0.339472
S	-1.024467	0.901510	-1.382032
C	-2.642184	1.230148	-0.740411
C	-2.837134	2.302848	0.141580
C	-1.704377	3.133562	0.626969
H	-1.169268	3.628138	-0.201163
C	-4.130111	2.565884	0.579673
C	-5.200537	1.805290	0.147097
H	-6.211920	2.030717	0.500396
S	0.007312	-3.005062	-0.946448
P	-1.307151	-1.359765	1.526793
C	-1.687257	-0.015094	2.676842
O	1.639175	-0.847347	-1.657755
H	-0.950531	2.529939	1.162820
H	-4.291829	3.397034	1.276012
H	-2.238069	-0.408718	3.547846
H	-2.318659	0.747361	2.195745
H	-0.769065	0.471383	3.039964
C	-4.992756	0.765701	-0.740261
C	-3.718548	0.459796	-1.205299
C	-3.526857	-0.668559	-2.153869
H	-4.489401	-1.144290	-2.394412
H	-3.064889	-0.341076	-3.100437
H	-2.855591	-1.445080	-1.745452
H	-5.840028	0.166473	-1.094007
S	1.650075	0.004461	1.330810
C	3.106471	0.721440	0.605295
C	3.157920	2.091759	0.318341
C	1.986378	2.981391	0.529859
H	1.600265	2.926301	1.561609
H	2.245923	4.030209	0.320999
H	1.146174	2.707998	-0.132249

C	4.339542	2.615308	-0.195019
C	5.439642	1.809967	-0.418932
H	6.362411	2.240108	-0.821880
C	5.372906	0.459377	-0.129444
C	4.214815	-0.109957	0.385076
C	4.171422	-1.567568	0.674760
H	3.942459	-1.776973	1.733298
H	5.136456	-2.041839	0.440374
H	3.390843	-2.074541	0.081649
H	6.243368	-0.183614	-0.306047
H	4.387201	3.687113	-0.421240
C	-2.959353	-2.046863	1.248981
H	-3.415799	-2.339078	2.209786
H	-3.614428	-1.299489	0.775265
H	-2.945608	-2.940726	0.605913
H	-2.058873	3.915840	1.314732
C	-0.581498	-2.592971	2.633773
H	-0.405412	-3.543962	2.107268
H	0.391189	-2.243160	3.014696
H	-1.241002	-2.793429	3.494737
C	1.485480	-1.080783	-2.998522
H	1.707836	-2.139654	-3.241108
H	0.467958	-0.845685	-3.376899
H	2.218285	-0.466223	-3.555609
H	-1.111812	-3.422345	-0.330866

Enthalpy -708.800777

Free energy -708.845094

S	-2.087607	0.400223	-0.004067
C	-0.351091	0.093603	0.003638
C	0.026493	-1.257199	0.001181
C	-1.001354	-2.332986	-0.003691
H	-1.651193	-2.286298	-0.897102
C	1.380431	-1.567670	0.000815
C	2.341852	-0.572274	0.004082
H	3.406150	-0.831586	0.005349
H	-1.671411	-2.273440	0.873516
H	1.677707	-2.623910	-0.000463
C	1.949059	0.754304	0.003038
C	0.605781	1.119327	-0.000567
C	0.230085	2.559614	-0.011084
H	1.126452	3.197916	-0.038644
H	-0.386102	2.828409	-0.888758
H	-0.344896	2.855189	0.886208
H	2.705605	1.549212	0.001567
H	-0.534029	-3.329584	0.006812
H	-2.014091	1.730211	0.132125

Mo₂(SH)(S)(OMe)₂(PMe₃)(SAr)₃

Enthalpy -4210.254901

Free energy -4210.410528

Mo	1.791587	0.031621	0.835062
S	-1.814973	-2.512265	0.306305
S	2.720634	2.149130	1.031776
C	1.583811	3.443999	0.625052
C	0.750946	3.966323	1.625403
C	0.721748	3.392158	2.997119
H	0.001910	3.929307	3.633032
H	1.708160	3.437222	3.489104
C	-0.067601	5.043408	1.304274
C	-0.070288	5.586708	0.032200
H	-0.722428	6.435277	-0.200200
C	0.740279	5.045372	-0.948335
C	1.586140	3.976492	-0.671991
C	2.454810	3.418778	-1.742634
H	3.527261	3.525615	-1.504963
H	2.271878	3.927712	-2.701523
P	4.033365	-0.766920	1.740019
C	5.617116	-0.294217	1.009892
O	1.385033	-0.916462	2.446476
C	0.278111	-0.978210	3.250416
H	0.435013	2.324528	2.990603
H	-0.718432	5.461906	2.081159
H	0.732418	5.464281	-1.962159
H	2.283459	2.338145	-1.892618
H	5.665595	0.795355	0.853970
H	5.772118	-0.785981	0.037719

H	6.451687	-0.579912	1.672348
H	0.490613	-0.505410	4.230702
H	0.000934	-2.032882	3.446947
H	-0.601785	-0.461651	2.812536
Mo	-2.189985	-0.305836	-0.541893
S	-0.369533	0.511471	0.363511
S	-3.916538	0.548963	0.796230
C	-4.968924	-0.872851	0.912778
C	-5.820193	-1.224191	-0.144916
C	-5.866062	-0.444935	-1.409929
H	-6.670386	-0.810564	-2.066129
H	-6.038439	0.628612	-1.224941
H	-4.922037	-0.519203	-1.979029
C	-6.634832	-2.340766	0.007436
C	-6.618831	-3.083552	1.172345
H	-7.268951	-3.958447	1.274661
C	-5.784863	-2.714481	2.211970
C	-4.948290	-1.611318	2.107188
C	-4.049627	-1.253330	3.234802
H	-4.227462	-0.230481	3.605893
H	-4.187952	-1.946376	4.078323
H	-2.987309	-1.295133	2.932420
H	-5.774492	-3.297123	3.140491
H	-7.300702	-2.623917	-0.815963
P	-2.381293	1.790299	-1.955084
C	-2.598301	3.348867	-1.078446
H	-3.605893	3.400914	-0.636097
H	-1.868457	3.428125	-0.257127
H	-2.469780	4.217319	-1.745805
O	-2.324451	-0.992180	-2.317471
C	-1.663714	-1.970480	-3.015290
H	-2.239079	-2.221703	-3.926338
H	-0.655468	-1.632907	-3.327197
H	-1.533858	-2.892553	-2.412507
C	4.206606	-2.545002	1.992556
H	5.074386	-2.769704	2.635292
H	3.303435	-2.943129	2.479902
H	4.346046	-3.070487	1.035471
C	4.198459	-0.134035	3.425247
H	3.318921	-0.420224	4.021696
H	5.102263	-0.530121	3.918218
H	4.260031	0.965617	3.424456
C	-3.661246	1.831852	-3.224722
H	-3.630473	0.911574	-3.827895
H	-4.660965	1.912588	-2.771399
H	-3.521575	2.693054	-3.899134
C	-0.866771	2.032907	-2.903464
H	-0.010526	2.131611	-2.218785
H	-0.677440	1.157518	-3.546713
H	-0.912286	2.932373	-3.540964
H	-0.592705	-2.362667	0.862198
S	1.845440	-0.977621	-1.277937
C	3.326889	-1.878873	-1.613680
C	3.331646	-3.267291	-1.399970

C	4.433557	-1.236321	-2.190263
C	4.469749	-3.988898	-1.741026
C	5.548097	-2.000573	-2.519130
C	5.572208	-3.364717	-2.295650
H	4.481214	-5.071445	-1.566486
H	6.416962	-1.501878	-2.965492
H	6.458553	-3.949571	-2.562500
C	2.163786	-3.966556	-0.800388
H	1.911310	-3.570016	0.199860
H	1.249812	-3.845772	-1.407370
H	2.361714	-5.044311	-0.696733
C	4.446073	0.230379	-2.432958
H	5.403854	0.546851	-2.873557
H	3.638994	0.542543	-3.117706
H	4.293921	0.806307	-1.502326

Mo₂

Enthalpy -3501.521858

Free energy -3501.651477

Mo	0.602764	-1.183083	0.092826
S	-1.227673	-0.867627	-1.160935
S	2.603426	-1.293811	-1.132134
C	3.794876	-0.141887	-0.507444
C	4.573231	-0.518042	0.596268
C	4.374486	-1.819873	1.288416
H	5.089681	-1.936627	2.116904
H	4.496952	-2.680392	0.609108
C	5.530400	0.374302	1.065058
C	5.717996	1.603855	0.461535

H	6.479570	2.292227	0.842330
C	4.939607	1.960627	-0.624076
C	3.969336	1.101860	-1.128083
C	3.107594	1.540510	-2.256099
H	3.103507	0.821007	-3.091699
H	3.439597	2.514801	-2.647209
P	0.329761	-3.601506	-0.572111
C	0.251685	-4.045142	-2.315426
O	0.432813	-2.096787	1.765759
C	0.471688	-1.638502	3.061991
H	3.355650	-1.909302	1.709488
H	6.141098	0.087760	1.929541
H	5.079793	2.936224	-1.105047
H	2.057700	1.648228	-1.931447
H	1.147605	-3.682996	-2.844926
H	-0.624826	-3.576745	-2.789632
H	0.185000	-5.136196	-2.459728
H	0.014688	-2.397198	3.726864
H	-0.082721	-0.688915	3.198098
H	1.512030	-1.473799	3.406911
Mo	-0.602720	1.183035	-0.092837
S	1.227720	0.867585	1.160919
S	-2.603354	1.293758	1.132173
C	-3.794891	0.141932	0.507462
C	-4.573249	0.518175	-0.596219
C	-4.374427	1.820007	-1.288344
H	-5.089664	1.936851	-2.116784
H	-4.496763	2.680524	-0.609010
H	-3.355611	1.909347	-1.709481
C	-5.530502	-0.374083	-1.065004
C	-5.718182	-1.603631	-0.461500
H	-6.479827	-2.291932	-0.842283
C	-4.939797	-1.960486	0.624088
C	-3.969443	-1.101809	1.128086
C	-3.107718	-1.540539	2.256086
H	-3.103620	-0.821078	3.091723
H	-3.439749	-2.514841	2.647144
H	-2.057828	-1.648263	1.931431
H	-5.080058	-2.936078	1.105048
H	-6.141200	-0.087473	-1.929464
P	-0.329704	3.601463	0.572082
C	-0.251503	4.045101	2.315390
H	-1.147369	3.682925	2.844962
H	0.625062	3.576737	2.789527
H	-0.184847	5.136158	2.459685
O	-0.432831	2.096744	-1.765779
C	-0.471796	1.638426	-3.061996
H	-0.014926	2.397144	-3.726933
H	0.082695	0.688891	-3.198131
H	-1.512154	1.473609	-3.406815
C	-1.160453	-4.325987	0.136485
H	-1.220849	-5.409680	-0.059342
H	-1.167070	-4.165904	1.225875
H	-2.058827	-3.845311	-0.283177

C	1.652736	-4.637596	0.080710
H	1.782971	-4.449703	1.157719
H	1.438419	-5.709806	-0.062729
H	2.604942	-4.406984	-0.421798
C	-1.652753	4.637525	-0.080635
H	-1.783139	4.449555	-1.157612
H	-2.604889	4.406964	0.422027
H	-1.438402	5.709744	0.062693
C	1.160447	4.325963	-0.136628
H	2.058857	3.845268	0.282935
H	1.166965	4.165916	-1.226024
H	1.220868	5.409650	0.059228

trans-MoH(PMe₃)(SAr)₃, Ar = 2,6-Me₂C₆H₃, isomer

1.

Enthalpy -2654.474901

Free energy -2654.581709

Mo	-0.028475	0.298453	0.448910
S	1.310934	0.520902	-1.442041

C	2.911207	-0.223982	-1.302866
C	3.077206	-1.562388	-1.697868
C	1.928759	-2.388983	-2.156100
H	1.472666	-1.977067	-3.072890
C	4.352243	-2.115938	-1.659555
C	5.447942	-1.363293	-1.278908
H	6.445758	-1.813895	-1.263440
S	0.485009	2.181759	1.835460
C	-0.748915	2.452280	0.622132
C	-0.584979	3.375892	-0.456050
C	0.637497	4.206482	-0.540399
H	0.734809	4.877306	0.330802
H	0.632070	4.828950	-1.447241
C	-1.599400	3.492944	-1.370618
C	-2.780598	2.738916	-1.262570
H	-3.568159	2.859610	-2.013543
C	-2.964164	1.885138	-0.216116
C	-1.964060	1.713372	0.778015
C	-2.385358	1.180797	2.112674
H	-2.411600	2.000241	2.855074
H	-3.393502	0.745469	2.039000
P	1.582868	-1.112894	1.803166
C	1.911081	-2.849862	1.431144
H	1.117369	-2.436162	-1.409134
H	4.481051	-3.164659	-1.953136
H	1.547011	3.583666	-0.553624
H	-1.484438	4.202399	-2.198233
H	-3.910083	1.341269	-0.100482
H	-1.729434	0.411709	2.557216
H	2.423720	-3.327296	2.283212
H	2.559604	-2.950214	0.547948
H	0.978451	-3.402080	1.239223
C	5.278685	-0.036673	-0.928126
C	4.020261	0.553641	-0.932698
C	3.872164	1.974150	-0.524005
H	4.835806	2.392007	-0.195002
H	3.501045	2.603510	-1.351291
H	3.147106	2.091268	0.300610
H	6.144209	0.567748	-0.631520
S	-1.256166	-1.717550	0.365960
C	-2.839996	-1.556710	-0.413018
C	-2.986783	-1.262658	-1.777571
C	-1.841991	-1.153701	-2.722993
H	-0.949654	-1.689172	-2.368729
H	-2.123690	-1.558733	-3.708382
H	-1.536400	-0.104805	-2.888217
C	-4.271769	-1.077170	-2.280995
C	-5.388168	-1.203051	-1.479439
H	-6.388734	-1.049784	-1.896867
C	-5.233900	-1.565865	-0.153111
C	-3.974035	-1.764961	0.395918
C	-3.865011	-2.219950	1.810366
H	-3.373867	-3.205112	1.884902
H	-4.863190	-2.312677	2.265357

H	-3.269660	-1.539563	2.440103
H	-6.115869	-1.714661	0.481417
H	-4.385474	-0.837469	-3.345455
C	3.232359	-0.510315	2.237131
H	3.626094	-1.063650	3.106740
H	3.935366	-0.645356	1.401919
H	3.209525	0.560755	2.494525
H	2.249217	-3.419124	-2.375550
C	0.807164	-1.236940	3.438561
H	-0.183572	-1.713565	3.361830
H	1.425841	-1.839177	4.126566
H	0.669163	-0.239829	3.886906
H	-0.916703	0.447733	-0.920002

trans-MoH(PMe₃)(SAr)₃, Ar = 2,6-Me₂C₆H₃, isomer

2.

Enthalpy -2654.477248

Free energy -2654.587618

Mo	-0.169790	0.019792	0.042929
S	0.308682	-2.222430	0.517958
S	-1.415154	0.370388	-1.912518
S	0.492457	2.075219	0.951467
P	-1.442269	-0.105696	2.115539
C	-2.689682	-1.405281	2.197426
C	-2.367993	1.338769	2.680289
H	-2.270074	-2.379804	1.902781
H	-3.088674	-1.492731	3.222100
H	-3.528510	-1.174095	1.522778

H	-1.724796	2.229651	2.742040
H	-3.201704	1.560604	1.997089
H	-2.792090	1.147407	3.680307
C	-0.371141	-0.457374	3.524627
H	0.429043	0.295228	3.603244
H	-0.955014	-0.442951	4.460247
H	0.095808	-1.447687	3.415992
H	1.476975	-0.048244	0.042528
C	-3.014929	0.039245	-1.231467
C	-3.562860	-1.252468	-1.329972
C	-3.762702	1.114262	-0.716630
C	-4.859657	-1.450611	-0.870799
C	-5.049756	0.856493	-0.258225
C	-5.596118	-0.411941	-0.332030
H	-5.294415	-2.454191	-0.941536
H	-5.639422	1.686530	0.148142
H	-6.615774	-0.590262	0.024656
C	1.892280	2.721504	0.074390
C	1.673989	3.556886	-1.033606
C	3.195799	2.447584	0.517521
C	2.776160	4.078404	-1.701802
C	4.266167	2.990300	-0.183611
C	4.064427	3.795154	-1.289198
H	2.607192	4.728358	-2.568846
H	5.285253	2.771982	0.157701
H	4.920121	4.215038	-1.828039
C	1.892294	-2.692761	-0.129994
C	2.987739	-2.735597	0.747458
C	2.042448	-3.035537	-1.481485
C	4.232384	-3.092553	0.242795
C	3.306212	-3.391408	-1.940306
C	4.396820	-3.415133	-1.091697
H	5.091368	-3.118783	0.924131
H	3.427602	-3.657530	-2.997305
H	5.384390	-3.695872	-1.472116
C	-3.228436	2.501459	-0.681713
H	-3.958913	3.186969	-0.225985
H	-2.284239	2.580263	-0.115251
H	-3.006077	2.873273	-1.696858
C	-2.798476	-2.390979	-1.896617
H	-2.410709	-2.170516	-2.905099
H	-1.919028	-2.637575	-1.275703
H	-3.429383	-3.289812	-1.961785
C	0.891026	-3.037583	-2.423187
H	1.207492	-3.361283	-3.426466
H	0.087226	-3.715288	-2.088194
H	0.427523	-2.040164	-2.521964
C	2.843293	-2.412227	2.192938
H	2.442881	-1.396927	2.358080
H	2.141806	-3.098570	2.698351
H	3.812875	-2.482321	2.709624
C	3.455826	1.589555	1.703061
H	4.525239	1.592126	1.963094
H	2.887279	1.919568	2.588585

H	3.160627	0.541792	1.519613
C	0.303587	3.908025	-1.495428
H	-0.277465	3.017738	-1.791001
H	-0.283336	4.408349	-0.706260
H	0.346138	4.585940	-2.361720

MoH(PMe₃)(SMe)₃ (gas phase calculation)

Enthalpy -1843.881836

Free energy -1843.955261

Mo	0.294052	-0.061456	0.171872
S	0.484624	1.346739	-1.602896
S	2.241630	-0.056067	1.394814
S	-0.271386	-2.250889	-0.188365
P	-2.075462	0.365458	0.247470
C	-2.559215	2.097356	0.433128
C	-3.013332	-0.453636	1.558494
C	2.113942	1.077585	-2.350542
C	2.781894	1.639061	1.686382
C	1.290447	-3.012373	-0.690881
H	-2.131344	2.694978	-0.387053
H	-3.654325	2.225446	0.426622
H	-2.163785	2.504522	1.375640
H	-2.892930	-1.545341	1.478719
H	-2.626989	-0.153459	2.544174
H	-4.088800	-0.213898	1.515092
C	-2.972292	-0.124681	-1.247707
H	-2.874517	-1.208794	-1.409189
H	-4.043474	0.130850	-1.185115
H	-2.539830	0.379252	-2.125736
H	-0.269214	0.764963	1.520739
H	2.347541	1.931809	-3.005199
H	2.118820	0.165884	-2.968342
H	2.897935	0.989277	-1.580300
H	3.817832	1.624263	2.058050
H	2.148376	2.114501	2.450965
H	2.739515	2.246291	0.767529

H	1.860474	-3.336224	0.193872
H	1.918730	-2.305552	-1.259830
H	1.091172	-3.885879	-1.331404

trans-MoH(PMe₃)(SMe)₃ (gas phase calculation)

Enthalpy -1843.872367

Free energy -1843.946669

Mo	0.352735	-0.353168	0.023917
S	1.098982	1.116549	-1.555715
S	1.707577	-0.348975	1.866587
S	-1.146397	-2.108444	0.002020
P	-1.669171	0.992744	0.114367
C	-1.326567	2.687920	0.647610
C	-3.006647	0.490567	1.224834
C	2.609338	0.544601	-2.366317
C	2.617036	1.218505	1.849809
C	-0.401933	-3.658658	-0.533203
H	-0.615089	3.162573	-0.045939
H	-2.243031	3.299846	0.693999
H	-0.866982	2.687853	1.648860
H	-3.369130	-0.511675	0.950834
H	-2.637904	0.431810	2.259907
H	-3.853636	1.195980	1.192026
C	-2.511161	1.198786	-1.467926
H	-2.832912	0.215698	-1.843719
H	-3.397111	1.848245	-1.373623
H	-1.822925	1.632078	-2.208773
H	0.955647	-1.400106	-1.123964
H	3.117046	1.400697	-2.838744
H	2.366070	-0.189942	-3.149605
H	3.295741	0.072826	-1.645002
H	3.213310	1.275961	2.773231
H	1.937540	2.082840	1.818335
H	3.290441	1.269408	0.981933

H	-1.077302	-4.492118	-0.282341
H	0.567569	-3.823513	-0.039174
H	-0.247642	-3.652956	-1.623396