Supporting Information

ACID-FACILITATED PRODUCT RELEASE FROM A MO(IV) CENTER: RELEVANCE TO

OXYGEN ATOM TRANSFER REACTIVITY OF MOLYBDENUM OXOTRANSFERASES

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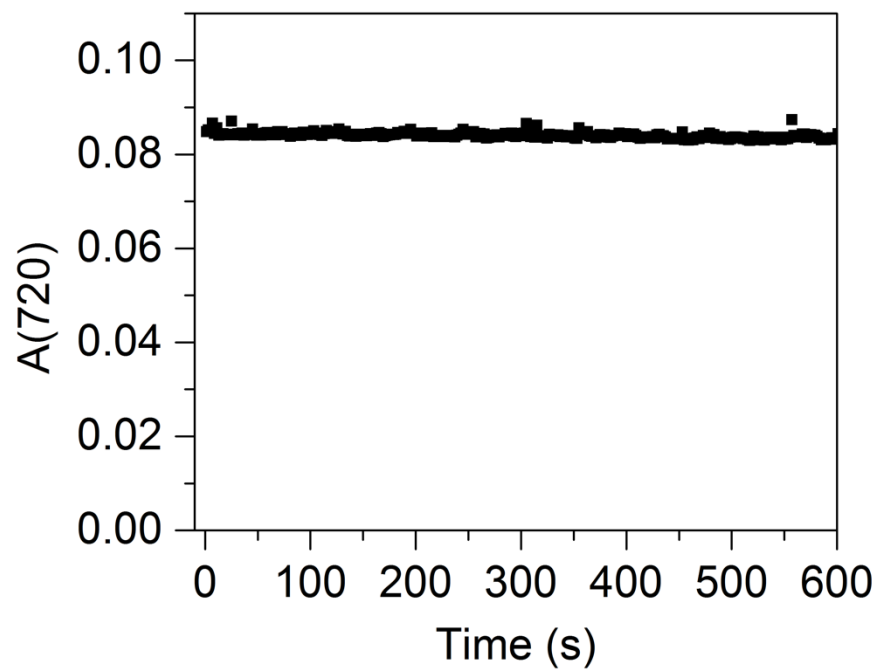
Figure S1. UV-visible spectra monitored at 720 nm after the addition of 10 equiv. pyridinium triflate to 1.0 mM [Tp*Mo^{IV}OCl(NCCH$_3$)] (**2**) in acetonitrile at 10 °C as a control experiment.
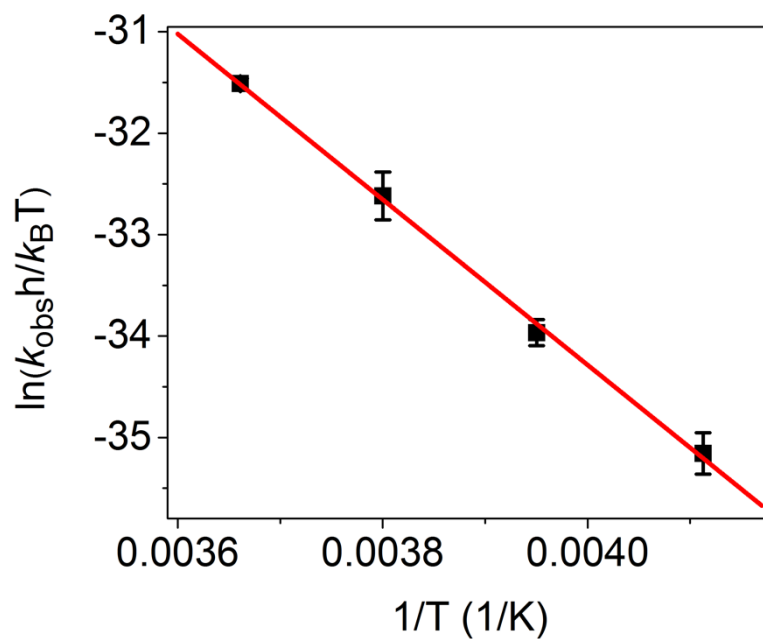
Figure S2 The Eyring plot for the conversion of 1.0 mM [Tp*Mo^{IV}OCl(OPMe$_3$)] (**1**) to **2** in CH$_3$CN in the presence of 10 equiv. 3-bromopyridinium tosylate. Temperature range: −30 to 0°C. $\Delta H^{\ddagger}$ = 68(2) kJ/mol. $\Delta S^{\ddagger}$ = −14(7) J/mol. Error bars show one standard deviation from at least three independent measurements.

Computational results for non-competitive I_a pathways in the absence of HPyr[+]

An acetonitrile molecule can approach the molybdenum atom from the octahedral face formed by the chlorine and two Tp* nitrogen atoms, denoted as the I_a-NNCl pathway (Figure S3). The relaxed scan calculations showed that decrease of the distance between the acetonitrile molecule and the central molybdenum atom leads to the gradual lengthening and eventual dissociation of the Mo-Cl bond. The $\Delta G^{\ddagger}$ for this process was found to be ~12 kJ/mol higher than that for the I_a-NNO pathway presented in Figure 6. For this reason of higher activation energy, as well as the lack of the experimentally observed products associated with this pathway, we conclude that this reaction pathway does not play a major role in the solvolysis of **1**.

A

B
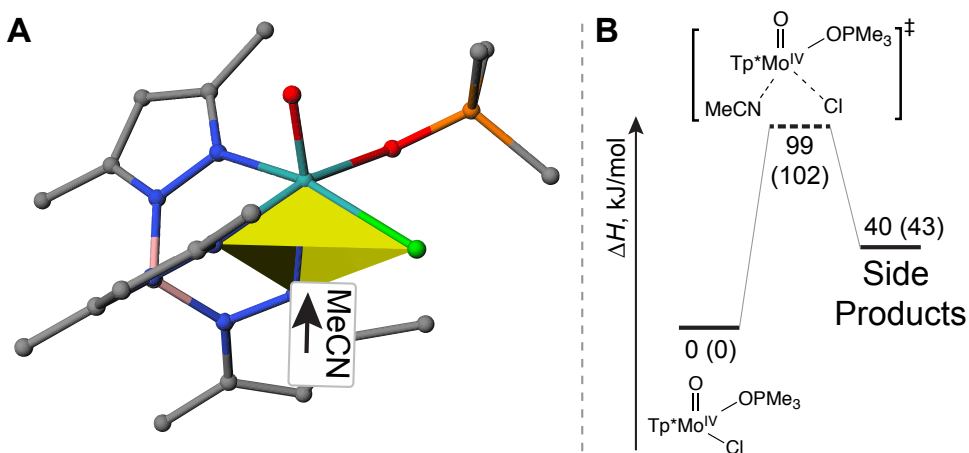
Figure S3. The I_a-NNCl mechanism that leads to the side products.

We also investigated the reaction pathway in which an acetonitrile molecule approaches the molybdenum atom from the octahedral face formed by two Tp* nitrogen atoms and the oxygen atom of the Mo=O moiety, denoted as the I_a-NNOxo route (Figure

S4). This direction of MeCN attacking led to the dissociation of one of the Tp*–Mo

bonds. Due to the high energetic cost of more than 100 kJ/mol (estimated using relaxed
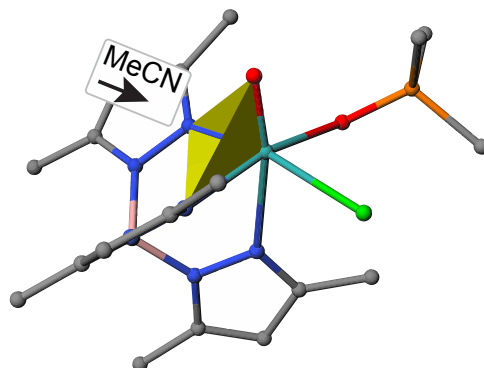
scan along the MeCN$\cdots$Mo bond), this reaction channel was not further considered in

this study.

Figure S4. An illustration of the direction of CH_3CN attack in the I_a-NNOxo mechanism.

As one of the Mo–N bonds in complex **1** is significantly longer than the other two

Mo–N bonds (i.e. 2.5 vs 2.2 Å), we evaluated the bond energy of this weak bond and

found that its dissociation requires 61 kJ/mol, which is significantly lower than the

activation energy needed for the dissociation of the Mo—$OPMe_3$ bond. Accordingly, we

inspected if such a formation of penta-coordinated Mo complex might be involved in

facilitating the formation of the final products. We found that dissociation of the Me_3PO–

Mo bond in the complex shown in Scheme S1 (denoted as the I_a-penta route) leads to the

formation of the less stable product ($\Delta H = 104$ kJ/mol, $\Delta G = 104$ kJ/mol), as compared

with the initial pre-reaction complex. Therefore, this pathway is expected to be

noncompetitive with the dominant I_a-NNO mechanism shown in Figure 6.

Scheme S1.

0 (0)

61 (47)

81 (82)

104 (100)

28 (23)

6
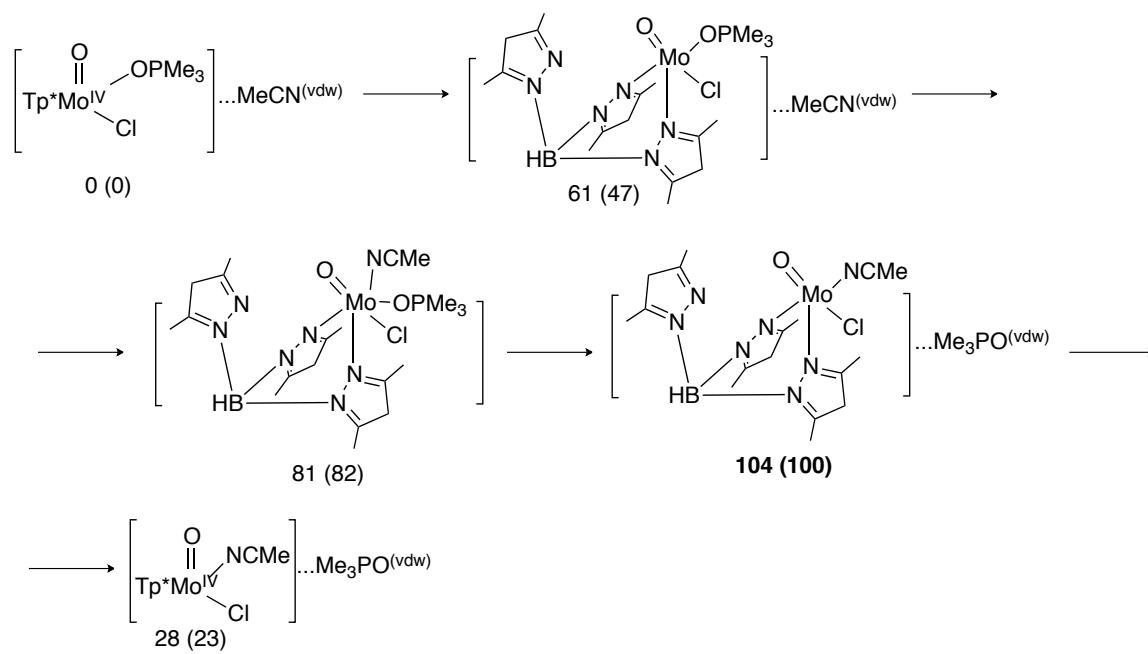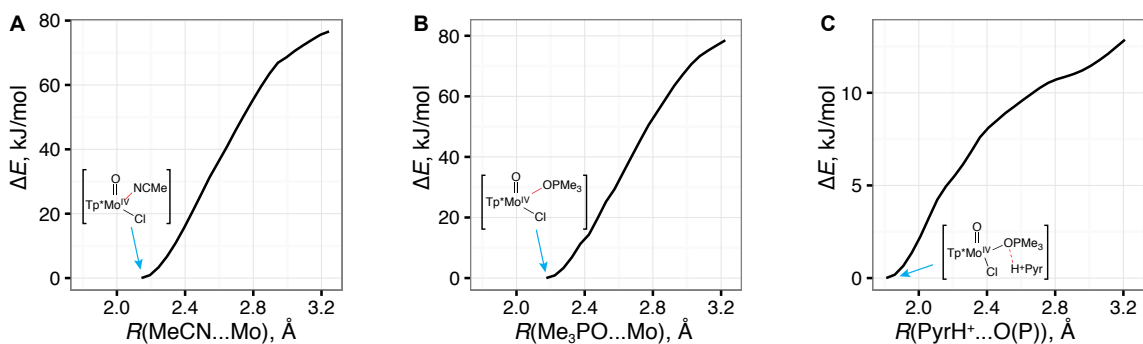
Figure S5. Electronic energy profiles for the dissociation of the MeCN⋯Mo bond in [Tp*MoOCl(MeCN)] (**A**), Me₃PO⋯Mo bond in [Tp*MoOCl(Me₃PO)] (**B**), and HPyr⁺⋯O(PMe₃) bond in [Tp*MoOCl(Me₃PO)(HPyr⁺)] (**C**), calculated using the relaxing scan technique at the M06L/def2-SV(P)+PCM(MeCN) level of theory.

Computational details for alternative mechanisms in which HPyr⁺ binds to the oxo ligand
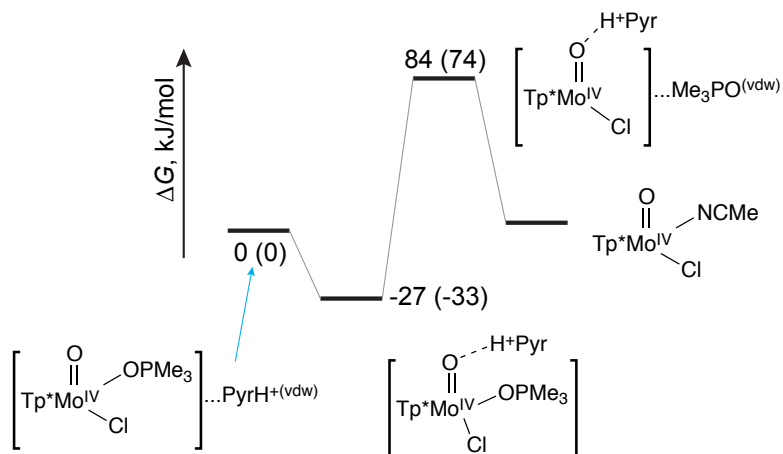
Figure S6. Alternative I_d mechanism in which HPyr⁺ is coordinated to the oxygen atom of the oxo ligand.
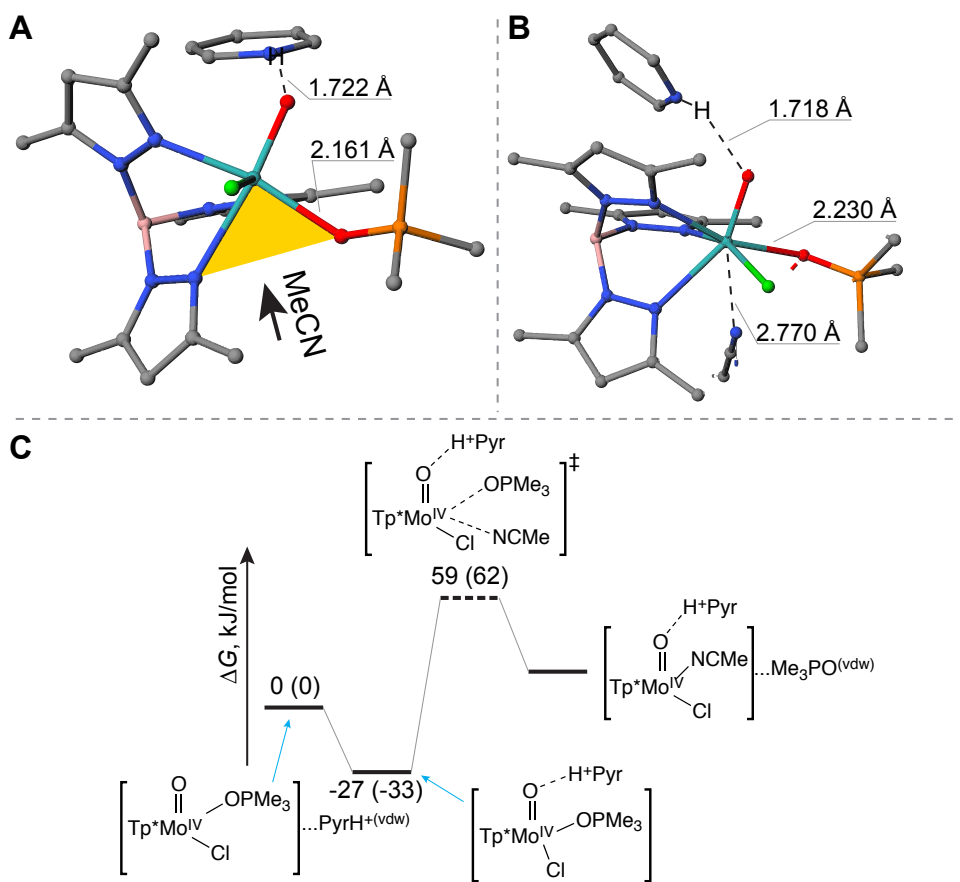
Figure S7. Alternative I_a mechanism in which HPyr[+] is coordinated to the oxygen atom of the Mo=O moiety.

Archive entries from the calculation files

The archive entries, formerly intended for the Browse Quantum Chemistry Database System, are organized as a simple list of data fields separated by backslash symbols, which is wrapped in 70-char text lines. The script 'Parse.Archive.pl', written in Perl, converts archive entry into human readable format. To use this script,

1. Check if Perl interpreter is installed on the system. To do this, run the command 'perl –v' in console. If console returns a message like 'command not found', please obtain and install a Perl interpreter (www.perl.org/get.html; Perl is Open Source software licensed under GNU GPL).
2. Save the script code, listed below, as a file named 'Parse.Archive.pl'.
3. Select an archive entry of interest and save it as another file (e.g. 'B-Xb.txt').
4. Run the command 'perl Parse.Archive.pl B-Xb.txt > B-Xb-parsed.txt' in console. The parsed archive entry will be stored in the file 'B-Xb-parsed.txt' in this example. In some cases, absolute path to the Perl interpreter might need to be provided.

```
# --- Parse.Archive.pl ---

# Merge all strings in one line
my $s='';
while (<>) {chomp;$s .= $_}
$_ = $s;

# Some PDF viewers (like Mac OS's Preview) might substitute
# 'end of line' symbols by the white space symbols,
# To remove these extra white spaces, please uncomment the following lines:
# my $str_length = 70;
# my $index = $str_length;
# while (length($_) > $index) {
#     substr $_,$index,1,'';
#     $index += $str_length;
# }

# Replace all backslashes by new-line symbols
s:\\:\n:g;

# Print the resulting output
print;

# --- END ---
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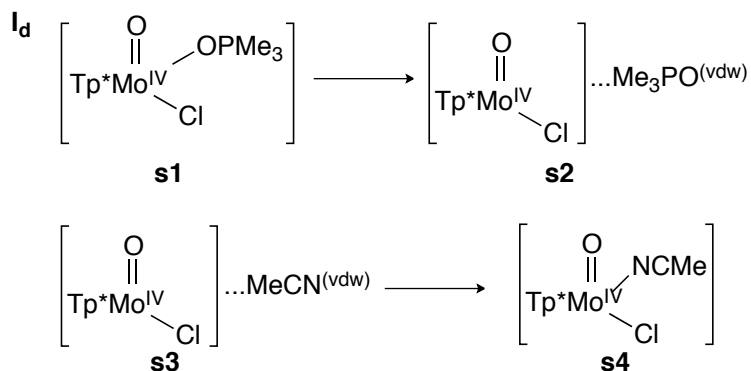
Dissociative pathways

Scheme S2

s1

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s2

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s3

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s4

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7.1942633605\C,0,4.3331299854,3.7618922568,7.963128825\C,0,9.002560120
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\C,0,5.3357307265,0.3123568822,2.0454377867\C,0,4.3425603337,1.2131696
336,2.4547013688\C,0,2.8912363187,1.1833141856,2.1378628805\C,0,7.9053

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142904,2.9600474381\H,0,4.3779951293,6.6361468656,1.2219749635\N,0,2.8
126020291,4.4440493787,2.7353330122\C,0,2.1402610692,4.7820235993,1.84
83801739\C,0,1.3163276982,5.1749734787,0.7382652232\H,0,1.1116105936,4
.3131843012,0.0808970006\H,0,1.8332828145,5.948462057,0.1469548675\H,0
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6493,-8.237051,-44.4714158\PG=C01 [X(C17H25B1Cl1Mo1N7O1)]\\@

Scheme S3
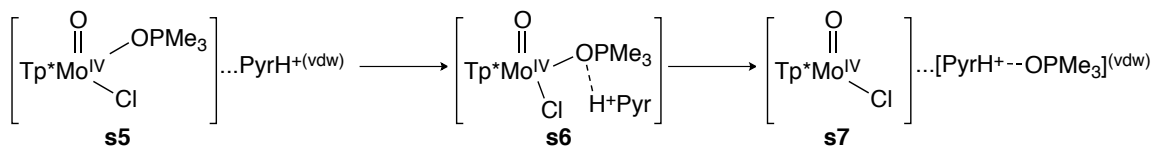
I_d (HPyr⁺)

s5

1\1\GINC-JOKER-C5\Stability\RM06L\Gen\C18H31B1Cl1Mo1N6O2P1\SOFIBALI\10
-Feb-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(r
ead) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine
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0746913764,5.3898107621\N,0,5.0151245871,2.320682547,2.9077883715\N,0,
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6985721116\C,0,0.6083895315,4.9444184304,3.1340845946\C,0,1.1462503758
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C,0,7.8020351545,6.0427938322,2.048760024\C,0,6.4197462767,6.024310665
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\C,0,6.4261278824,3.1354880505,7.5821968078\C,0,5.2849527342,3.6440776
635,6.9459155271\C,0,4.0089498832,4.0877909995,7.5594794227\C,0,8.6817
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5\H,0,3.5843858871,4.9544906728,7.0272201808\H,0,3.2498982185,3.284365
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8851222043\H,0,0.9650716029,5.3588540152,4.0913840928\H,0,0.5039924686
,3.8517796895,3.2373989065\H,0,0.199158479,5.2020609136,0.0455770236\H
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67\PG=C01 [X(C18H31B1Cl1Mo1N6O2P1)]\\@

s6

1\1\GINC-JOKER-C8\Stability\RM06L\Gen\C23H37B1Cl1Mo1N7O2P1(1+)\SOFIBAL
I\16-Feb-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gue
ss(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultra
fine)\\Title\\1,1\Mo,4.1131166495,3.9622748587,3.9770983771\O,2.846415
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\C,6.6476710092,5.4555621974,-1.5405596206\C,7.6593948068,4.4979379878
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162707,-12.6340139,-35.0902095\PG=C01 [X(C23H37B1Cl1Mo1N7O2P1)]\\@

s7

1\1\GINC-COMET-05-59\Stability\UM06L\Gen\C23H37B1Cl1Mo1N7O2P1(1+)\TALI
POVM\29-Jul-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
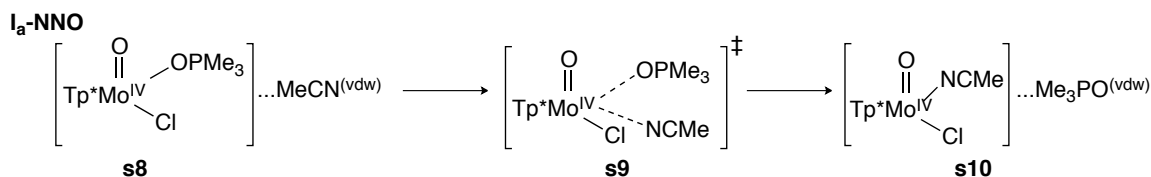trafine)\\Title\\1,1\Mo,0,5.4391395537,4.7230462506,3.3031189536\O,0,3

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Associative pathways

Scheme S4

I_a-NNO

$$\left[\text{Tp*Mo}^{IV} \overset{\overset{O}{\|}}{\underset{Cl}{}} \text{OPMe}_3 \right] \text{...MeCN}^{(vdw)} \longrightarrow \left[\text{Tp*Mo}^{IV} \overset{\overset{O}{\|}}{\underset{Cl}{\cdots}} \begin{matrix} \text{OPMe}_3 \\ \text{NCMe} \end{matrix} \right]^{\ddagger} \longrightarrow \left[\text{Tp*Mo}^{IV} \overset{\overset{O}{\|}}{\underset{Cl}{}} \text{NCMe} \right] \text{...Me}_3\text{PO}^{(vdw)}$$

s8   s9   s10

<u>s8</u>

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1\1\GINC-COMET-06-44\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\29-Jul-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,4.1175793682,3.9234240796,3.8893834586\O,0,2.895
7301589,2.9633711078,4.5859591877\O,0,3.1736386338,4.5181886965,2.0103
904747\P,0,1.795913565,5.1759628345,1.734941843\B,0,7.2892362774,2.857
442713,3.8327253276\Cl,0,3.5663054744,6.2523308114,4.6262246877\N,0,6.
1371938063,4.9037155532,2.9446663682\N,0,7.2954021929,4.2034076267,3.0
891091696\N,0,5.5381775391,3.59338445,5.5090709791\N,0,6.7754340979,3.
0679517177,5.2734359191\N,0,5.0429316619,2.2038615658,2.8934917242\N,0
,6.3539756354,1.8862468747,3.0794862752\C,0,1.8750759555,6.9506251359,
1.4614786738\C,0,0.6266220684,4.8738386517,3.0656156016\C,0,1.09631389
71,4.4653230567,0.2387960472\C,0,8.3257587173,4.8499888496,2.496001785
9\C,0,7.811746716,6.0188203634,1.9467051442\C,0,6.4413976244,6.0164097
189,2.2528419145\C,0,5.437022798,7.0513380776,1.90400905\C,0,9.7147640
455,4.3245771537,2.4849416281\C,0,7.4080797464,2.8277443519,6.44550986
89\C,0,6.5386918298,3.1877364384,7.4701066377\C,0,5.3775635474,3.66315
64205,6.8446612184\C,0,4.1087283792,4.1129424395,7.4684734791\C,0,8.78
69074575,2.2831116477,6.5254773497\C,0,6.6449959027,0.7233650488,2.452
3921757\C,0,5.4702734332,0.2632278218,1.8638700862\C,0,4.4890095276,1.
2186904488,2.1609692234\C,0,3.0511040906,1.2234293613,1.7957679289\C,0
,8.0054770754,0.1292451681,2.4432360024\H,0,5.3440441236,-0.653193477,
1.285921912\H,0,7.9981433492,-0.8256567887,1.8949917534\H,0,8.74346643
53,0.7919457416,1.9573612478\H,0,8.3777751728,-0.0683413703,3.46398777
32\H,0,2.855461171,0.5262335177,0.9651010877\H,0,2.7287773259,2.234770
307,1.500337683\H,0,2.4143666643,0.91745467,2.6462981278\H,0,6.7268371
239,3.1153498639,8.5421401075\H,0,4.276349021,4.4223680781,8.512979519
6\H,0,3.6611006732,4.9514670277,6.9101477082\H,0,3.3605779305,3.298626
4981,7.4813653929\H,0,8.3629221798,6.7803513356,1.3928282199\H,0,10.37
83864136,5.0184303428,1.9456402174\H,0,10.1178502817,4.1966175758,3.50
51119335\H,0,9.7822161001,3.3396439592,1.9898740228\H,0,0.8652155964,7
.3440209348,1.2526243052\H,0,2.2829348836,7.4414648581,2.3599437108\H,
0,2.5266951707,7.1576928596,0.5960113187\H,0,-0.3598658959,5.304796533
5,2.8242505056\H,0,1.0124840037,5.3280042548,3.9932584101\H,0,0.520053
4154,3.7870736555,3.2204170202\H,0,0.1200087408,4.9250263826,0.0114830
686\H,0,1.7823751787,4.6472207196,-0.6049910974\H,0,0.9558132217,3.379
0615759,0.3615054272\H,0,8.4063054554,2.3964201155,3.8656543752\H,0,9.
0824665443,2.1564752309,7.5786587182\H,0,9.5245618387,2.9502965637,6.0
454693882\H,0,8.8742280073,1.3007835514,6.0283756587\H,0,5.7241861635,
7.5755645192,0.9771077615\H,0,5.3392568781,7.8097868949,2.7021288505\H
,0,4.4462744574,6.5991891774,1.7647098236\C,0,5.5385940772,3.778839794
8,-0.1807930298\C,0,4.7460958338,4.8726483416,-0.6888408256\N,0,4.0976
730582,5.7502231749,-1.0950767204\H,0,6.6086268461,4.0480406994,-0.166
1339304\H,0,5.4096143533,2.8828226432,-0.8117183794\H,0,5.2204659823,3
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743,-23.7649848,-21.7408895,-24.1516539,-6.5671204,-24.0229411\PG=C01
[X(C20H34B1Cl1Mo1N7O2P1)]]\\@

s9 (Imaginary frequency: 46.0*i* cm⁻¹)

1\1\GINC-C01\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\SOFIBALI\13-Mar-
2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(read)
geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)\\Ti
tle\\0,1\Mo,0,4.229505219,4.1147417681,3.4586312716\O,0,3.0631250524,3
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0,1.1372275192,4.9415943584,2.0262812628\B,0,7.3399185553,2.8200955548
,3.8686360661\Cl,0,3.657759224,6.5006766152,3.9829589259\N,0,6.5424158
475,5.0628431205,3.0753460752\N,0,7.5739083006,4.1893748676,3.21269557
82\N,0,5.4883334754,3.7295515126,5.2913233022\N,0,6.665416158,3.055809
6897,5.2277401981\N,0,5.1807126893,2.3372661841,2.6074489406\N,0,6.440
7055385,1.9457000924,2.9590268518\C,0,1.1451682125,6.6384408527,1.4169
955932\C,0,0.4170704781,4.9766037201,3.6773012738\C,0,-0.0277602898,4.
0380362445,0.9875480873\C,0,8.7290402082,4.7210189617,2.7454831125\C,0
,8.426575342,5.9939940504,2.2807610016\C,0,7.0493763414,6.1688426942,2
.5050861908\C,0,6.2545040156,7.3751309604,2.1536456951\C,0,10.02972051
18,4.0042726489,2.7803242023\C,0,7.1287131834,2.7924480549,6.473891651
\C,0,6.1985065791,3.3011863761,7.3715877272\C,0,5.1822534767,3.8791280
089,6.5899661118\C,0,3.9274871826,4.5245539382,7.0537433679\C,0,8.4159
521093,2.0958621526,6.7258595697\C,0,6.7534121372,0.7825492388,2.34577
62002\C,0,5.6518412772,0.4030543526,1.5833452121\C,0,4.6895573813,1.40
24196138,1.7702744555\C,0,3.3283007028,1.4752714228,1.1836865671\C,0,8
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.9718922132\H,0,8.0583364592,-0.851582496,1.945041124\H,0,8.9036299646
,0.7020219393,2.1549723277\H,0,8.264613139,-0.1505323165,3.5713715443\
H,0,3.1161927119,0.5610970894,0.6057678806\H,0,3.2152551049,2.34977227
66,0.5210397115\H,0,2.5541950489,1.5900400798,1.9613945748\H,0,6.25055
51124,3.2623667608,8.4608383947\H,0,4.0528069448,4.9268339385,8.073089
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98145\H,0,0.3454566795,4.0136432672,-0.0499956281\H,0,-0.1144870463,2.
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6.3415254884\H,0,8.4531072326,1.1028332412,6.2435128054\H,0,6.84168294
79,8.0262658917,1.484219721\H,0,5.9811132764,7.9671626203,3.0438549361
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671756,4.6969774622,0.9460515138\H,0,5.6572255446,4.5152874672,-2.1382
967451\H,0,5.6106087497,2.8436744792,-1.5065119794\H,0,7.0524755861,3.
866515873,-1.2271364932\\Version=ES64L-G09RevE.01\HF=-2209.8054511\RMS
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653,-19.0746061,-18.9788592,-26.818744,-32.9969849,-42.9858886\PG=C01
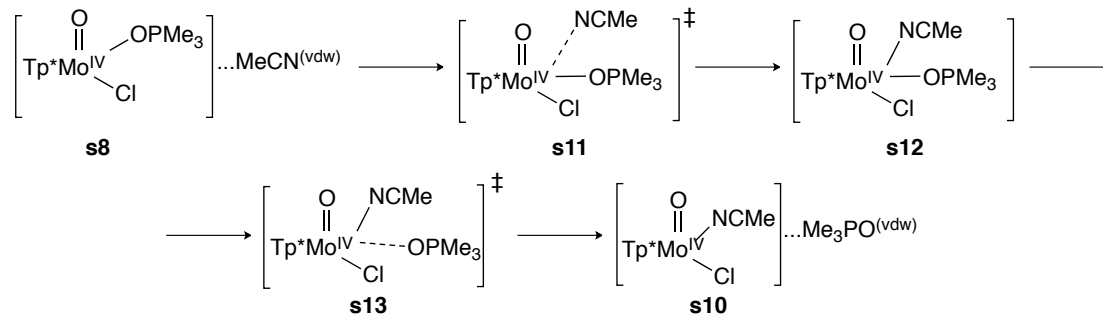[X(C20H34B1Cl1Mo1N7O2P1)]]\\@

s10

1\1\GINC-COMET-06-54\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM

\28-Jul-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,4.7175835799,3.7788132059,3.2570325832\O,0,3.295
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40403328,4.1582023043\Cl,0,4.1442854554,6.1409385486,3.8462029823\N,0,
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97,1.2308105479\C,0,0.5187513256,4.9908978965,3.2608286439\C,0,-1.1934
584558,5.5985459918,1.0300632543\C,0,9.1372478817,4.6028026095,3.03882
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80414515,2.1010884444\C,0,6.5867085349,6.6084561098,1.2977594455\C,0,1
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0,5.8509012436,3.1606333414,8.4924530057\H,0,3.4726167885,4.2891643547
,7.7267589046\H,0,3.4090862297,4.9449774102,6.0580182602\H,0,2.9342296
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54\H,0,11.2553094884,4.8041838479,3.1587765311\H,0,10.5192909724,4.081
9393389,4.6122881779\H,0,10.6959021756,3.113427341,3.1375727691\H,0,0.
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917181976\H,0,1.4235967478,7.0750024821,0.1596614563\H,0,-0.0026465665
,5.8135692337,3.7802094367\H,0,1.5569151835,4.9360964673,3.6305891452\
H,0,0.0093641203,4.0405921235,3.4949446022\H,0,-1.6033358946,6.4459654
662,1.6052892415\H,0,-1.2578129221,5.8337344448,-0.0457938412\H,0,-1.8
111332236,4.7051484922,1.2234401477\H,0,8.7972512599,2.2372969748,4.52
43733718\H,0,8.3974860995,2.2180232775,8.2976819652\H,0,9.2590079773,2
.9335652212,6.9114830959\H,0,8.6369188236,1.2764805682,6.8029907998\H,
0,6.4455679797,6.2328384016,0.266737814\H,0,7.0774635008,7.5922734631,
1.2137552805\H,0,5.5883464571,6.7491127017,1.7417889675\C,0,3.51163684
74,4.9117065869,-1.1644917782\C,0,3.9503300466,4.6011959606,0.16696889
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783,-1.2021809086\H,0,4.0216887069,4.28021412,-1.9116335037\H,0,3.7061
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PG=C01 [X(C20H34B1Cl1Mo1N7O2P1)]\\@

Scheme S5

I_a-ClOO

[structures: s8, s11, s12, s13, s10 — chemical scheme]

s11 (Imaginary frequency: 36.4*i* cm⁻¹)

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1\1\GINC-COMET-07-19\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\12-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,3.1747406155,5.290165763,4.8058500876\O,0,2.2537
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25989\P,0,5.9441192405,3.7294449698,6.6602006728\B,0,1.1947449554,6.99
910625,6.9861847196\Cl,0,5.1771089553,6.2488536147,3.6090668993\N,0,3.
668196021,7.0146051897,6.6120396928\N,0,2.6267469792,7.3388426141,7.42
09533875\N,0,1.834519529,7.1011482687,4.5583700372\N,0,1.0108964324,7.
5224238889,5.5525535994\N,0,1.7473003307,4.6081121954,6.3278628132\N,0
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,7.1653693631\C,0,6.1182753501,7.4933876531,6.5598213351\C,0,2.1174690
423,8.5765020693,9.5317508494\C,0,0.1696609128,8.4819589529,5.09562742
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9985395594\H,0,-1.5298187772,4.6654615021,9.1831399434\H,0,-0.41360027
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58643,6.5082772345\H,0,3.051872885,2.1703026591,6.1324580451\H,0,-0.03
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30871\H,0,3.198810048,7.2505692729,2.2400718612\H,0,1.6368626969,6.730
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6860049887,9.0912713263,10.322526877\H,0,1.3814668908,9.2944771192,9.1
266552677\H,0,1.5395883546,7.7640561124,10.0069056725\H,0,8.1325589928
,3.2937579421,5.7354077591\H,0,6.8883472739,3.4859156158,4.4514151758\
H,0,7.5282811225,4.9238347111,5.2817423874\H,0,6.6128124218,1.47178479
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614,1.8119272457,7.7022587136\H,0,7.5334990724,3.7319875265,8.49746047
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795061,9.8771403478,5.3664583383\H,0,-0.3515086335,9.7213592696,6.7851
738896\H,0,-1.5312976739,8.448013118,6.4259864303\H,0,6.8930807638,7.6
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N7O2P1)]\\@

s12

1\1\GINC-JOKER-C8\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\SOFIBALI\13
-Apr-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(r
ead) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine
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67033,6.9893749164\Cl,0,5.1392582529,6.2301160226,3.5386005424\N,0,3.6
751446394,7.0062470743,6.5578261079\N,0,2.652346006,7.311604141,7.3969
614216\N,0,1.8059420228,7.1090329584,4.5560511205\N,0,0.9986924264,7.5
185076704,5.5671211875\N,0,1.7452682539,4.584524361,6.3039512732\N,0,0
.9792240258,5.4481683438,7.0329723512\C,0,7.2419300756,3.8637614556,5.
388168871\C,0,5.6872436358,1.9868941544,6.9337800909\C,0,6.6825652339,
4.3636154368,8.1799647313\C,0,3.0874927331,8.0352759191,8.457319517\C,
0,4.4555125855,8.2032965629,8.2936795179\C,0,4.7793472824,7.5516971094
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7.9899752321\H,0,-1.4897307428,4.6419423154,9.2067845723\H,0,-0.364570
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5\H,0,6.8715250136,3.4714534388,4.4281878655\H,0,6.6270383833,1.496765
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3105552,1.8540493185,7.7369851959\H,0,7.5729219094,3.7777941248,8.4635
193921\H,0,6.9719143223,5.4205164314,8.0654343485\H,0,5.9355209133,4.2
929145863,8.9881781571\H,0,0.4321016256,7.5069448348,7.7486153787\H,0,
-1.429651982,9.8799855882,5.4509657938\H,0,-0.3418282077,9.7013016592,
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371,2.7307548346\C,0,4.5452047328,2.3267937123,3.4719648939\N,0,4.1057
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4B1Cl1Mo1N7O2P1)]\\@

s13 (Imaginary frequency: 86.0*i* cm⁻¹)

1\1\GINC-COMET-08-48\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\04-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,2.9987176572,5.4269799377,4.4860061135\O,0,1.998
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126519\P,0,5.9012712895,3.5772764143,6.9877240347\B,0,1.2223317364,7.0
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7.1721549226\N,0,1.5818873507,7.2108393881,4.4211772334\N,0,0.87176924
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\N,0,1.0136471133,5.4888468285,6.9083313849\C,0,7.3411390929,3.7731661
51,5.902283199\C,0,5.6152325501,1.791248602,7.078844114\C,0,6.48241300
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332,6.7836722266\C,0,6.1410076036,7.2007370225,6.122575632\C,0,2.42072
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7.4593257674\H,0,5.3664915979,1.386015532,6.0836970082\H,0,4.766979907
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02502\H,0,-1.5640541879,8.472201502,6.6865296207\H,0,6.9523678192,7.21
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,3.3331538871\\Version=ES64L-G09RevD.01\HF=-2209.8029913\RMSD=2.359e-0
9\Dipole=1.9783315,-4.1732047,3.2044765\Quadrupole=27.1841915,-78.4025
701,51.2183786,-30.9416398,39.3340387,-0.0866711\PG=C01 [X(C20H34B1Cl1
Mo1N7O2P1)]\\@

Scheme S6

I_a-NNO (HPyr+)

s14 ... MeCN(vdw) ⟶ s15 ‡ ⟶ s16 ...[PyrH+--OPMe_3](vdw)
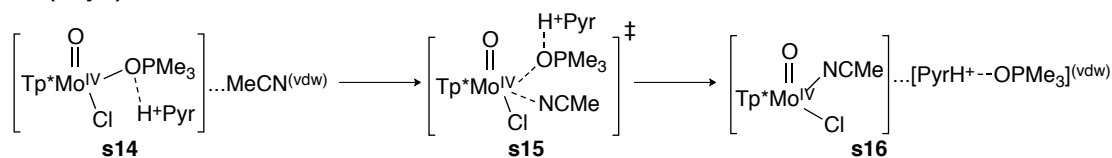
s14

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1\1\GINC-COMET-02-67\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
POVM\13-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
trafine)\\Title\\1,1\Mo,0,3.4874753297,5.0514265611,5.5845282804\O,0,2
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46\H,0,0.3907203812,7.9330033299,2.2560032549\H,0,2.1444325817,6.06723
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5\H,0,5.0563131236,1.7896044691,5.2467794145\H,0,7.4178597211,1.563161
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17883,1.5248466829,8.0862546202\H,0,0.4332308803,7.9538553769,7.269821
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26\H,0,4.2473313714,2.7638611988,9.6720057339\H,0,1.81689194,4.5472083
262,12.7797376479\H,0,4.3243436922,4.8100531026,8.61193923\\Version=ES
64L-G09RevD.01\HF=-2458.3641848\RMSD=1.838e-09\Dipole=-0.7772614,-3.68
30202,7.1719683\Quadrupole=-122.2818146,-99.2327233,221.5145379,-4.474
8972,120.1448604,158.7555745\PG=C01 [X(C25H40B1Cl1Mo1N8O2P1)]\\@

s15 (Imaginary frequency: 77.0*i* cm⁻¹)

1\1\GINC-COMET-04-59\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
POVM\20-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
trafine)\\Title\\1,1\Mo,0,3.2261540761,5.8242894285,6.4914493915\O,0,2
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8300146984\P,0,5.8465760814,3.4688593026,7.1979787832\B,0,0.5417315682
,7.8696266113,6.5026661197\Cl,0,5.4321447425,6.6006272222,5.6269593647
\N,0,2.9613415346,8.2174185645,7.0685480441\N,0,1.6930581858,8.7065544
901,7.0803130054\N,0,2.0437247334,6.6986109167,4.8602832911\N,0,0.9230
297874,7.4372629019,5.0772229829\N,0,1.31773188,5.7094530645,7.5700369
782\N,0,0.3195855633,6.6167259725,7.3807447505\C,0,7.4949376794,4.1825
159678,7.3055173722\C,0,5.5815209556,3.0337501733,5.4759658133\C,0,5.8
994399897,1.9108738834,8.1037299221\C,0,1.6524665469,9.9355995518,7.64
61657676\C,0,2.9529195102,10.2520695795,8.0183693163\C,0,3.7409349703,
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2,3.9000036\C,0,1.0847349828,7.155398035,2.8919509742\C,0,2.1522162895
,6.5073263481,3.532786411\C,0,3.2264275172,5.6864394762,2.919519927\C,
0,-0.9006396341,8.5699691116,3.8084718491\C,0,-0.7721959778,6.26140983
95,8.096993004\C,0,-0.469602622,5.075520234,8.7591469861\C,0,0.8496634
981,4.7631628003,8.4045951771\C,0,1.665509849,3.5899839862,8.801422861
6\C,0,-2.0264178406,7.055766331,8.1146181293\H,0,-1.1301643581,4.50730
10693,9.4152817693\H,0,-2.7820046445,6.553441998,8.7385505343\H,0,-1.8
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s16

1\1\GINC-COMET-10-01\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
POVM\29-Jul-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
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45781\C,0,9.4953720743,5.3271558089,3.0166516811\C,0,8.1725182616,5.79
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\C,0,7.82737178,0.6890944351,6.4686520941\C,0,6.5177278841,0.910947699
,1.8142476195\C,0,5.4679564407,1.070304909,0.9161603346\C,0,4.83672073
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25

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51,-2.5133179215\H,0,3.7068433159,5.3210363914,-2.2085256508\N,0,1.813
552649,4.6208801323,-1.7417099637\C,0,0.767618579,3.8208422514,-1.9977
052769\H,0,-0.0768780685,3.8887739888,-1.3068504006\H,0,1.9686237562,2
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Scheme S7
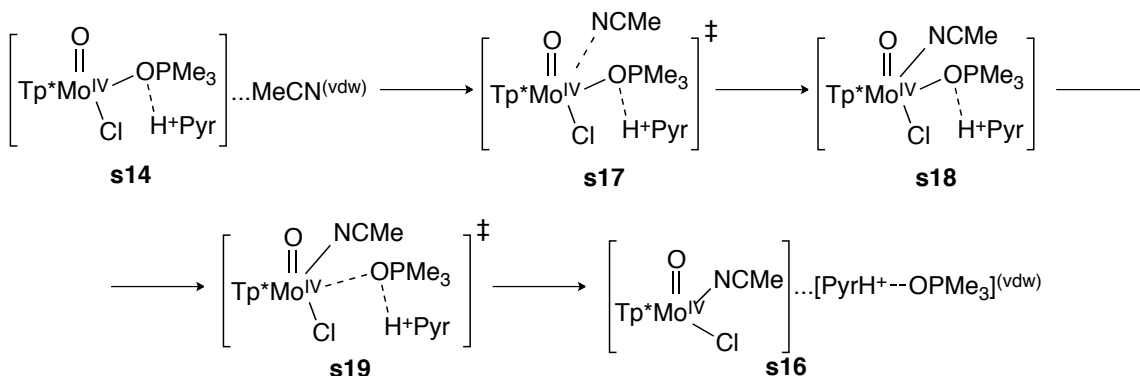
s17 (Imaginary frequency: 67.0*i* cm⁻¹)

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1\1\GINC-COMET-05-15\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
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guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
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s18
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guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
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28

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074014,3.4638598733,8.1186176029\H,0,7.1419177966,5.0359592767,8.18571
49157\H,0,6.4560101281,3.5972650933,9.0053287452\H,0,0.3797679321,7.41
56856557,7.8481260665\H,0,-1.7000615365,9.532041095,5.4458370601\H,0,-
0.6688599083,9.4853033906,6.8954073678\H,0,-1.6783115554,8.0859319269,
6.4868331609\H,0,6.8571609755,7.5291002373,7.5403291895\H,0,6.37180714
98,8.0307155061,5.9042132751\H,0,6.2737717364,6.3266787059,6.337289144
8\C,0,4.979735589,1.2570511485,2.7687240397\C,0,4.4783881014,2.3727708
078,3.5301486128\N,0,4.0845915577,3.2638914845,4.1632026452\H,0,6.0492
638807,1.0958442026,2.9846164362\H,0,4.8703240877,1.4502612004,1.68916
45625\H,0,4.4280392495,0.3350643414,3.016631422\\Version=ES64L-G09RevD
.01\HF=-2458.3395892\RMSD=2.888e-09\Dipole=2.1385974,-6.0064892,6.6366
878\Quadrupole=-64.8010885,-130.3395801,195.1406685,20.3892075,127.561
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## s19 (Imaginary frequency: 25.1*i* cm⁻¹)

1\1\GINC-COMET-08-12\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
POVM\10-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
trafine)\\Title\\1,1\N,0,3.4482420241,4.2857669329,9.0035900462\H,0,3.
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470323602\H,0,2.7498331127,2.3426509007,8.8047049966\C,0,3.5604269186,
5.4215620832,9.7124865925\C,0,2.1013930128,3.2860157931,10.6692082976\
H,0,4.182167016,6.2072592908,9.2699441225\C,0,2.9285314165,5.538030428
,10.939072068\C,0,2.1849410656,4.4580938916,11.4199768477\H,0,1.536553
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73671\H,0,1.6771000929,4.5276165453,12.3873601117\Mo,0,3.0388868332,5.
3215625629,4.719101993\O,0,2.0601901071,4.8727109419,3.4096230324\O,0,
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\C,0,7.2543838121,3.8623746464,5.3734571611\C,0,5.9463792087,1.6345274
36,6.7386779417\C,0,7.0910069151,3.7806978954,8.2539734121\C,0,3.03204
20196,8.2913223057,8.2448785327\C,0,4.4070542291,8.3932148383,8.089890
303\C,0,4.7535052491,7.4571304367,7.0977708298\C,0,6.1244633073,7.1948
674763,6.5932156878\C,0,2.1206123728,9.0321465603,9.1536704506\C,0,-0.
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,7.5013836284\C,0,1.3090765036,3.3071131341,6.5378961164\C,0,1.8906765
809,2.1159131105,5.8726338377\C,0,-0.7883511224,5.2771122744,8.8432244
449\H,0,-0.2420868336,2.4861145259,7.9175498642\H,0,-1.336630535,4.481
4343007,9.3718162893\H,0,-0.2505944974,5.8793689298,9.5960548269\H,0,-
1.5322686041,5.9443495612,8.3737034022\H,0,1.7503598518,2.1419938221,4
.7777343053\H,0,1.4173968354,1.1976406422,6.2555084919\H,0,2.977595012
1,2.0520858367,6.0533380283\H,0,-0.3136489946,9.3632403383,3.260181002
4\H,0,1.8105596679,8.6529316176,1.630268916\H,0,3.0563533096,7.5584761
362,2.3172108385\H,0,1.5496553243,6.893094684,1.6602335495\H,0,5.08234
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8913525,9.7810287546\H,0,7.8807478269,4.7275452918,5.6461813326\H,0,7.

29

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,7.4330467122,7.851522618\H,0,-1.7484070486,9.6262798922,5.5703626117\
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118,6.5933209045\H,0,6.8588194971,7.2890457878,7.4124055379\H,0,6.4146
993437,7.918129058,5.8107749724\H,0,6.1992666983,6.1975197296,6.144897
9618\C,0,5.2037656065,1.4594557302,2.8932314888\C,0,4.5895590492,2.555
6367593,3.5975013535\N,0,4.0961125486,3.4348316247,4.1751525759\H,0,6.
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.0491084,130.8600003\PG=C01 [X(C25H40B1Cl1Mo1N8O2P1)]\\@

Alternative/non-competitive pathways

Scheme S8
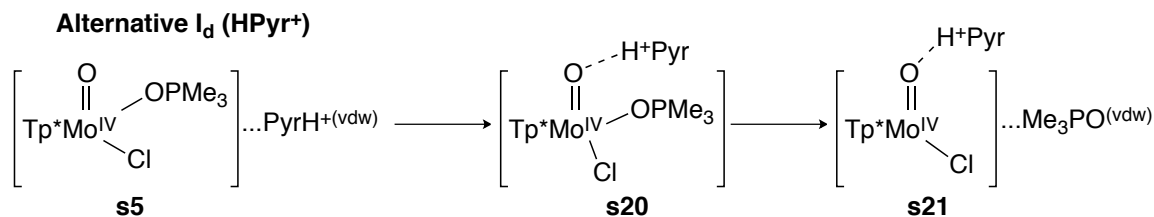
<u>**s20**</u>

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1\1\GINC-COMET-04-17\Stability\RM06L\Gen\C23H37B1Cl1Mo1N7O2P1(1+)\TALI
POVM\01-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
trafine)\\Title\\1,1\Mo,0,4.1377592072,4.1255636854,4.1426994885\O,0,2
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2691218401\P,0,1.7643461822,5.1745968081,1.9779506078\B,0,7.1877019895
,2.8042263995,4.2795846623\Cl,0,3.7701565274,6.5431743657,4.5694835915
\N,0,6.1557498356,4.7546417418,3.0768272128\N,0,7.2702380215,4.0191659
981,3.3442135292\N,0,5.5292583628,3.9182416468,5.8195027962\N,0,6.7186
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6142462\C,0,7.8888047249,5.592611572,1.9252585283\C,0,6.5209474937,5.7
17748338,2.2100192378\C,0,5.5726981587,6.7244996587,1.6729588338\C,0,9
.6899652386,3.9028338515,2.7511092487\C,0,7.3104635477,3.0980898139,6.
8790945967\C,0,6.4606328899,3.6434174897,7.8377523024\C,0,5.3565338986
,4.149981201,7.1369462379\C,0,4.1193478129,4.7607516174,7.6813602995\C
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.4353261308,0.2050953298,2.9277403748\H,0,7.9263649415,-0.2066493049,4
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\H,0,6.6261268128,3.6748751791,8.9152135196\H,0,4.3027481959,5.1883530
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4665488,7.1029729878,0.6987588781\H,0,5.4674354409,7.5912902289,2.3495
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,-1.6722930496,5.5480460535\H,0,5.0983776057,1.6123485092,6.669105247\
C,0,5.3085535961,-0.5675616171,6.5963633629\C,0,4.6784546039,-1.739858
7427,6.1779080237\H,0,2.9140485873,-2.5733026762,5.2145471855\H,0,6.27
81345806,-0.5866941818,7.101423745\H,0,5.1558152091,-2.7103397234,6.34
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26.3078488,-17.4526267,71.2703384,-27.2605289\PG=C01 [X(C23H37B1Cl1Mo1
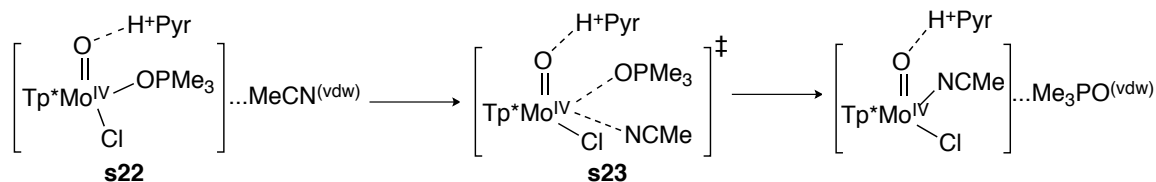N7O2P1)]]\\@

s21

1\1\GINC-COMET-03-43\Stability\UM06L\Gen\C23H37B1Cl1Mo1N7O2P1(1+)\TALI
POVM\05-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
trafine)\\Title\\1,1\Mo,0,4.6244129361,4.1280037949,3.6541587891\O,0,3
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8,2.6861030653,4.4131284183\Cl,0,4.4043161359,6.5545342203,3.799675837
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15781\N,0,6.5594143497,1.676592895,3.7258320928\C,0,-0.0365232265,3.38
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\H,0,8.8451653831,-0.0681345118,3.446558869\H,0,8.037139002,-0.3316279
06,5.0026950005\H,0,3.5475083753,0.5028037993,0.8918430654\H,0,3.55943
12124,2.2648492379,1.186362028\H,0,2.7191063544,1.1807579793,2.3066608
221\H,0,6.1140849649,4.0449227673,8.75431901\H,0,3.8383611216,5.373907
3989,8.0117054831\H,0,3.771831328,5.8753093207,6.2902917381\H,0,3.0607
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8618\H,0,0.8488422406,6.8709298939,3.9067157247\H,0,2.3484419793,4.888
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24101896\H,0,8.4808897472,2.7171601627,8.5191617186\H,0,9.2899686263,3
.0723110643,6.969195878\H,0,8.4277480858,1.5370934342,7.1824476137\H,0
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32

321633\C,0,5.0954676422,-0.3802911879,6.5649586519\C,0,4.5516487522,-1
.596547142,6.1506617005\H,0,2.9971327031,-2.5432888887,4.9581928298\H,
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64,6.5006473258\\Version=ES64L-G09RevD.01\HF=-2325.670426\S2=0.014414\
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17\Quadrupole=51.8421564,-101.2641446,49.4219882,24.6292978,106.672961
6,-8.6281416\PG=C01 [X(C23H37B1Cl1Mo1N7O2P1)]\\@

Scheme S9

<u>s22</u>

1\1\GINC-COMET-05-03\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
POVM\05-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
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9\Mo,0,4.1161579271,4.1642926484,4.2107978807\O,0,2.8993734886,3.29054
78122,5.0691694012\O,0,3.136678894,4.530152844,2.3259282924\P,0,1.7939
065507,5.2446879955,1.9985596439\B,0,7.1613620863,2.8225078648,4.30871
71455\Cl,0,3.7481768691,6.5763621893,4.6652099937\N,0,6.1450598242,4.8
155471265,3.163950346\N,0,7.2487338406,4.0499271121,3.3892610071\N,0,5
.5172371529,3.9297350219,5.8752056104\N,0,6.7004062989,3.2686495017,5.
7113509565\N,0,4.8767582189,2.2737728344,3.3938216633\N,0,6.129481618,
1.8375442008,3.7053137609\C,0,2.000022275,6.9403083196,1.4441540217\C,
0,0.671161267,5.2469395391,3.4011089354\C,0,0.973254084,4.3573376044,0
.6702873987\C,0,8.3140110163,4.5380838846,2.7131086784\C,0,7.879721888
6,5.6630656695,2.0211904244\C,0,6.5187774903,5.8044315304,2.3298425012
\C,0,5.5837655741,6.8473928506,1.8421387921\C,0,9.65962744,3.913301739
9,2.764481686\C,0,7.30159021,3.0835550855,6.9093437467\C,0,6.464679631
3,3.6243819007,7.8814666489\C,0,5.3584034733,4.1476311442,7.1964715279
\C,0,4.1307334101,4.7623548747,7.7575768761\C,0,8.61533971,2.409487658
2,7.0579859604\C,0,6.299835406,0.5661341458,3.2766460361\C,0,5.1066607
897,0.1659021061,2.6793772917\C,0,4.2438107939,1.2665669254,2.76042940
52\C,0,2.8574809014,1.3883456377,2.2417218416\C,0,7.5679226526,-0.1838
21755,3.4534385496\H,0,4.8930013064,-0.8063957242,2.2333542826\H,0,7.4
439779977,-1.2234280814,3.1123280412\H,0,8.3953656054,0.2648716189,2.8
754258162\H,0,7.891841743,-0.2068816831,4.5086533344\H,0,2.4449069173,
0.394387272,2.0043296692\H,0,2.8340323074,1.9905382775,1.3155556989\H,
0,2.1842889301,1.8867162657,2.9606572336\H,0,6.6403855524,3.642516252,
8.9575943116\H,0,4.3257649545,5.1789696179,8.7588054381\H,0,3.74195703
43,5.5593997163,7.1035134781\H,0,3.3267091617,4.0100580603,7.864008561
4\H,0,8.4766816223,6.3019773565,1.3690132023\H,0,10.3662055031,4.48223
34301,2.1406038708\H,0,10.0621303487,3.8849373985,3.7924493746\H,0,9.6
464512688,2.871764451,2.3975677116\H,0,1.0165178849,7.3779353834,1.200
7984409\H,0,2.4775018134,7.5321752993,2.2419102281\H,0,2.6322298818,6.
9534777583,0.5405077408\H,0,-0.2991458869,5.6882822108,3.1169697551\H,
0,1.1125285253,5.8296467064,4.2259746333\H,0,0.5097194798,4.2110742999
,3.7431758206\H,0,0.0379556839,4.8687540562,0.3875977\H,0,1.6389480752
,4.3156666074,-0.2075112286\H,0,0.7328417425,3.3312831344,0.9929143383
\H,0,8.2367077666,2.2779420026,4.3889285763\H,0,8.9038793613,2.3724529
657,8.1196991551\H,0,9.4134849265,2.9369060098,6.5066607908\H,0,8.5937
589979,1.373571419,6.6752866668\H,0,5.9021585716,7.222067453,0.8550653
376\H,0,5.5400516701,7.710623162,2.5305714567\H,0,4.5637739174,6.44823
13385,1.7584724178\N,0,3.4510960226,0.6995308706,5.7732485184\H,0,3.04

0229118,1.6471260164,5.5834233582\C,0,2.8120689062,-0.4069078347,5.355
8459668\H,0,1.8415957228,-0.2575130966,4.8767663069\C,0,4.6514557199,0
.6615787236,6.3762497347\C,0,3.3951045005,-1.648257763,5.5434339389\H,
0,5.0678740864,1.6239181576,6.6867675896\C,0,5.2799274886,-0.554647059
3,6.584761311\C,0,4.6462336592,-1.7223503449,6.1586660742\H,0,2.871956
6931,-2.5456497804,5.2048540727\H,0,6.2551046543,-0.5789370735,7.07864
4068\H,0,5.1262014595,-2.694376192,6.3100129991\\Version=ES64L-G09RevD
.01\HF=-2458.3648302\RMSD=5.637e-09\Dipole=-1.3126534,-7.2923907,1.349
2689\Quadrupole=44.1953405,-69.7285373,25.5331968,-18.1123002,77.08701
63,-19.8925164\PG=C01 [X(C25H40B1Cl1Mo1N8O2P1)]\\@

s23 (Imaginary frequency: 61.3*i* cm⁻¹)

1\1\GINC-COMET-02-52\Stability\RM06L\Gen\C25H40B1Cl1Mo1N8O2P1(1+)\TALI
POVM\05-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check)
guess(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ul
trafine)\\Title\\1,1\Mo,0,4.1023663292,4.0628912577,3.6361827214\O,0,3
.0364406315,3.1741709703,4.6567696145\O,0,2.3886777666,4.0598039201,2.
2092775589\P,0,1.2564896691,4.9979627644,1.7770577041\B,0,7.1956252772
,2.7860148107,4.0358490826\Cl,0,3.4715483805,6.4169280444,4.1077283548
\N,0,6.3220654947,4.9899813808,3.1902261234\N,0,7.3794042858,4.1488427
549,3.354325242\N,0,5.4152487726,3.7725098288,5.4779075559\N,0,6.55504
23098,3.0386955838,5.4104732921\N,0,5.0540052031,2.2992404984,2.748756
6255\N,0,6.2956746734,1.8896440629,3.1502053146\C,0,1.8065297244,6.508
1286197,0.9655779731\C,0,0.1676449038,5.474785515,3.1299584412\C,0,0.2
372450745,4.1262611014,0.5753032742\C,0,8.524584218,4.7164024996,2.906
9720555\C,0,8.1907818586,5.975750893,2.4293650239\C,0,6.8059510495,6.1
113867573,2.6242125686\C,0,5.9962509734,7.3018622052,2.2554092995\C,0,
9.8456350439,4.040608767,2.9674125709\C,0,7.0627167691,2.8336601483,6.
6502393629\C,0,6.2017183496,3.4522258759,7.5497046636\C,0,5.1791822615
,4.0283550565,6.7750004694\C,0,3.970246694,4.7480538283,7.2507681582\C
,0,8.3144757703,2.075082028,6.8967484599\C,0,6.6179861698,0.7199937932
,2.5563601998\C,0,5.5415786166,0.3511249914,1.7534101873\C,0,4.5855138
99,1.3642904301,1.8922864252\C,0,3.2474008698,1.4215216332,1.254054143
6\C,0,7.9064864533,0.0170908401,2.7786719452\H,0,5.4597578877,-0.54769
14164,1.1410517793\H,0,7.9052799094,-0.9478597433,2.248211825\H,0,8.76
6022339,0.6039531765,2.4100105949\H,0,8.0919669239,-0.1808235744,3.848
9573417\H,0,3.0839090941,0.5139253314,0.6511852267\H,0,3.1394035253,2.
3055023864,0.6048984471\H,0,2.4403507913,1.500397481,2.0016326167\H,0,
6.2992900999,3.4790760709,8.6362192694\H,0,4.1473143808,5.1834926368,8
.2478121229\H,0,3.6755816313,5.5494368857,6.5544755211\H,0,3.098446468
6,4.0721723439,7.3398842081\H,0,8.8665416961,6.7133353438,1.9934332143
\H,0,10.6187550002,4.6816968335,2.5155240112\H,0,10.1538800784,3.82350
92384,4.0058214356\H,0,9.8472677852,3.0778262832,2.4265629099\H,0,0.93
99416197,7.1034037573,0.6303760751\H,0,2.4118355421,7.0999291027,1.670
5356721\H,0,2.4260078928,6.2500317978,0.0909756528\H,0,-0.6826029414,6
.0758033626,2.7652667923\H,0,0.743694859,6.0582080287,3.8664431593\H,0
,-0.2197529659,4.565823501,3.6202664763\H,0,-0.6090815445,4.7469212479
,0.2368378646\H,0,0.85408355,3.8550377128,-0.2979428908\H,0,-0.1542603
958,3.1994069102,1.0267230593\H,0,8.2647522788,2.2413769128,4.17916806
99\H,0,8.478769388,1.956698559,7.9794573265\H,0,9.1994350975,2.5856496
139,6.4761908685\H,0,8.2824546514,1.0671092095,6.4459155295\H,0,6.5798
740992,7.9493580699,1.579745041\H,0,5.7188275807,7.9020054667,3.138799
2076\H,0,5.0556692867,7.0263865538,1.7540807716\C,0,5.4706744001,3.883
4502254,-1.3553551897\C,0,5.0401840026,4.3333339297,-0.0533732731\N,0,
4.6889385559,4.6763295189,0.9998981416\H,0,4.7607400315,4.2083207598,-
2.1329458071\H,0,5.5298560183,2.7824039052,-1.3756428942\H,0,6.4655979
135,4.2900707311,-1.5978019448\C,0,4.5745343037,0.163576196,5.20514207

35

64\C,0,5.3325561638,-0.8954950301,5.6722260201\N,0,4.067665602,1.06044
65601,6.070220537\H,0,4.3366065903,0.321967291,4.1490924914\C,0,5.5564
334752,-1.0107044661,7.0460427901\H,0,5.7377604947,-1.6210434326,4.961
7613399\C,0,4.2632384281,0.9756347596,7.3966777488\C,0,5.0107386217,-0
.0688798106,7.9175164615\H,0,6.1541427016,-1.8397205294,7.4381010406\H
,0,5.1625362745,-0.1343636782,8.9976248512\H,0,3.8003564433,1.75071811
99,8.0104451411\H,0,3.5421101468,1.8764917393,5.6631558704\\Version=ES
64L-G09RevD.01\HF=-2458.3351309\RMSD=2.264e-09\Dipole=-0.5823554,-5.37
55555,-0.764663\Quadrupole=38.7477218,-70.0261523,31.2784305,-7.675547
3,66.0647514,-30.7706044\PG=C01 [X(C25H40B1Cl1Mo1N8O2P1)]\\@

Scheme S10

I$_a$-NNCl

s14	s24	s25
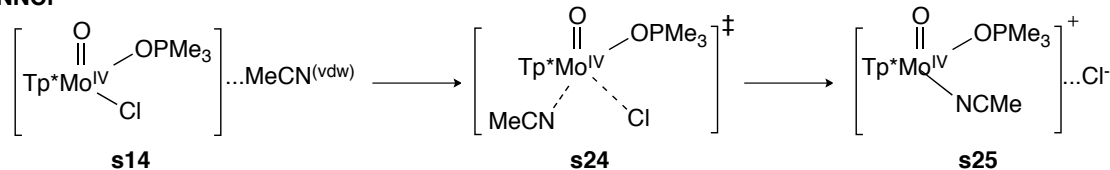
s24 (Imaginary frequency: 58.9i cm^{-1})

1\1\GINC-COMET-03-20\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\04-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,3.0606865517,4.9573413013,5.4468563716\O,0,2.264
8293646,3.5123701624,5.0460316459\O,0,4.747672892,4.2010433841,6.56822
67271\P,0,5.882077815,3.1763215066,6.3377356251\B,0,1.0238068447,7.206
5236687,6.9603779871\Cl,0,4.6141511576,4.338693873,3.3349847305\N,0,3.
4995357087,6.8395653593,6.9742113575\N,0,2.4589375144,7.6458803133,7.2
992048526\N,0,1.5678146112,6.3355728163,4.6199621992\N,0,0.8270779271,
7.1569103398,5.4249381737\N,0,1.6679498763,4.8124568054,7.2393481893\N
,0,0.8150979372,5.8127297991,7.5702977803\C,0,7.3161486991,3.841400780
4,5.4807370841\C,0,5.3344675854,1.7087146416,5.4580087113\C,0,6.458309
1327,2.6336263906,7.9548455002\C,0,2.8898861617,8.7493522949,7.9567568
706\C,0,4.2726860078,8.6491836696,8.0507798422\C,0,4.6134057665,7.4392
602525,7.4208535495\C,0,5.9783133452,6.8854514937,7.2231826485\C,0,1.9
734812937,9.8063579191,8.4560343747\C,0,-0.0201579562,7.8983871788,4.6
765897356\C,0,0.1679579891,7.5344797581,3.3462848418\C,0,1.1708784714,
6.5582629431,3.3516802111\C,0,1.7425860457,5.8339570258,2.191275764\C,
0,-0.9597915894,8.8968403724,5.2475806914\C,0,-0.0209376618,5.41532282
88,8.5604892102\C,0,0.3017386645,4.0977727253,8.8625383388\C,0,1.36869
65151,3.7574950345,8.0111525288\C,0,2.091662677,2.4640889927,7.9078207
735\C,0,-1.0451763743,6.3109600789,9.1557223126\H,0,-0.1723660873,3.46
29616775,9.6128049413\H,0,-1.6513901551,5.7597507934,9.8917937042\H,0,
-0.5901783565,7.1744673502,9.6742092062\H,0,-1.7295028752,6.7236026424
,8.3931946509\H,0,2.0480853533,1.9139559336,8.8626200466\H,0,3.1469461
886,2.6280543781,7.63840187\H,0,1.6581795193,1.811737064,7.1280453785\
H,0,-0.3640543037,7.9279957011,2.478976106\H,0,1.3035911888,6.21083241
07,1.2531123499\H,0,2.8400344825,5.9336139092,2.1471683234\H,0,1.54477
80932,4.748816684,2.2504637955\H,0,4.9520971038,9.3635511954,8.5189978
722\H,0,2.5501555133,10.6117501098,8.937716395\H,0,1.376283699,10.2593
009719,7.644983856\H,0,1.2553264143,9.4160180982,9.1994454886\H,0,8.07
56102638,3.0536292247,5.3385847007\H,0,6.9862911781,4.2246432842,4.501
0887411\H,0,7.7615297795,4.6609634302,6.0681565707\H,0,6.1432540256,0.
9597783198,5.4114269912\H,0,5.0323345074,2.007950237,4.4408604774\H,0,
4.4660566211,1.270102549,5.9773987236\H,0,7.2818844182,1.9066194445,7.
8595344565\H,0,6.8151363606,3.5013467851,8.5338068077\H,0,5.6293341144
,2.1630861833,8.5089154397\H,0,0.2311545052,7.9888458733,7.4323170444\
H,0,-1.5541914459,9.3561063206,4.4421775004\H,0,-0.4338991938,9.706930
9711,5.7822505382\H,0,-1.6610569899,8.4416208229,5.968976441\H,0,6.736
1804889,7.6627757833,7.4165253389\H,0,6.1132039558,6.5136008696,6.1941
028345\H,0,6.1856688365,6.0418162211,7.9048917624\C,0,4.2558659857,9.2
361023277,2.9818460091\C,0,4.3051602471,8.0423861763,3.7914151324\N,0,
4.3215164201,7.0682551455,4.4247742123\H,0,3.2672417862,9.3222948075,2
.5004104606\H,0,5.0249334925,9.2042431841,2.1932100236\H,0,4.422492809
9,10.1347373327,3.5974423217\\Version=ES64L-G09RevD.01\HF=-2209.803249

8\RMSD=3.097e-09\Dipole=1.509195,2.1501372,1.7177356\Quadrupole=-10.65
75578,23.1526178,-12.4950601,12.0293749,31.2732212,21.9000695\PG=C01 [
X(C20H34B1Cl1Mo1N7O2P1)]\\@

s25

1\1\GINC-COMET-08-18\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\03-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,2.91272706,5.29756692,5.5504150368\O,0,2.3596355
267,4.011645325,4.5844554634\O,0,4.5217585299,4.3951096417,6.658973392
3\P,0,5.7701406057,3.531469189,6.3328755936\B,0,0.7566724234,7.2514985
539,7.1747008501\Cl,0,5.4276724187,3.536929265,2.0850881642\N,0,3.2600
29126,7.2250243067,6.9370625694\N,0,2.1578810055,7.8339154725,7.452618
6635\N,0,1.3970268158,6.6831409342,4.8063689406\N,0,0.5098944832,7.279
1544356,5.6503266009\N,0,1.6047655467,4.872482901,7.2425566611\N,0,0.7
137770908,5.7981066767,7.6964412715\C,0,6.9806332354,4.3025564644,5.25
1196667\C,0,5.3274722534,1.9968010028,5.5168251833\C,0,6.5746229715,3.
156438791,7.8938720159\C,0,2.5118249217,8.9182953706,8.1811059726\C,0,
3.8986757185,9.0118227663,8.132703859\C,0,4.3274478669,7.9338154193,7.
3437974082\C,0,5.717010307,7.5679166194,6.9685864\C,0,1.5265569626,9.7
850524197,8.8754123755\C,0,-0.4088546361,7.9736015396,4.9406878625\C,0
,-0.1109700767,7.8002898333,3.5924376817\C,0,1.0341800976,6.9931452211
,3.5474157614\C,0,1.7841647406,6.5257458342,2.3526195154\C,0,-1.498444
1408,8.7556378735,5.5764179603\C,0,-0.0539396302,5.261791288,8.6713575
777\C,0,0.3462233649,3.938431816,8.8364046559\C,0,1.3916291261,3.73276
88551,7.9278628985\C,0,2.1698308593,2.4931102364,7.6807759423\C,0,-1.1
08948282,6.0254716695,9.3832160653\H,0,-0.0741018413,3.2100458288,9.53
08457263\H,0,-1.633509969,5.3707253178,10.0961142026\H,0,-0.691673041,
6.876010492,9.9505861803\H,0,-1.8587134104,6.4416159495,8.6878155102\H
,0,1.6617179506,1.62418658,8.1278385828\H,0,3.1802209707,2.5545113785,
8.1214489735\H,0,2.2932708529,2.3048242362,6.6009027157\H,0,-0.6603933
454,8.2107445376,2.7443727717\H,0,2.5767910428,7.2435804149,2.07096968
6\H,0,2.2694811999,5.5502176472,2.5178522706\H,0,1.1115245939,6.435545
1943,1.4843206091\H,0,4.521121456,9.7658362168,8.6164830331\H,0,2.0446
648383,10.6003767635,9.4037024846\H,0,0.8084410319,10.2415875301,8.171
8013825\H,0,0.9329561777,9.2243350855,9.6186908271\H,0,7.913288342,3.7
118882043,5.2837527128\H,0,6.5919787591,4.2841218439,4.2109898928\H,0,
7.2086352303,5.3332777452,5.5683406682\H,0,6.2082871716,1.3339866761,5
.4648199119\H,0,5.0090360022,2.2310257611,4.4823746297\H,0,4.522604529
7,1.4785044862,6.0618192736\H,0,7.4572628519,2.5147423901,7.7390708763
\H,0,6.8944736723,4.0943597408,8.3778861105\H,0,5.8675637769,2.6403972
93,8.563869519\H,0,-0.0871985673,7.9093166479,7.7360435455\H,0,-2.1718
257189,9.1620154802,4.8059483007\H,0,-1.1084600318,9.6058661978,6.1636
189572\H,0,-2.1013142182,8.1397487159,6.2662612602\H,0,6.4341302921,7.
9271280747,7.7244440574\H,0,6.0163778959,8.0131758073,6.0012160752\H,0
,5.8206288573,6.4760270039,6.8780138258\C,0,6.1387465215,6.8925869083,
2.5196035842\C,0,5.1692856044,6.5158740649,3.5063957146\N,0,4.38908955
93,6.1801261231,4.3015287028\H,0,5.7993247336,7.7587105358,1.926656372
5\H,0,6.2714115531,6.0073003234,1.8669579008\H,0,7.1021683833,7.137170
1617,2.9989241422\\Version=ES64L-G09RevD.01\HF=-2209.8192296\RMSD=3.23
7e-09\Dipole=0.2667258,3.2500503,5.2504851\Quadrupole=-37.6823952,9.68
41729,27.9982222,18.9370728,44.1509562,60.9162336\PG=C01 [X(C20H34B1Cl
1Mo1N7O2P1)]\\@

Scheme S11

I$_a$-penta (Tp-open)

s12   s26   s27

s28   s10
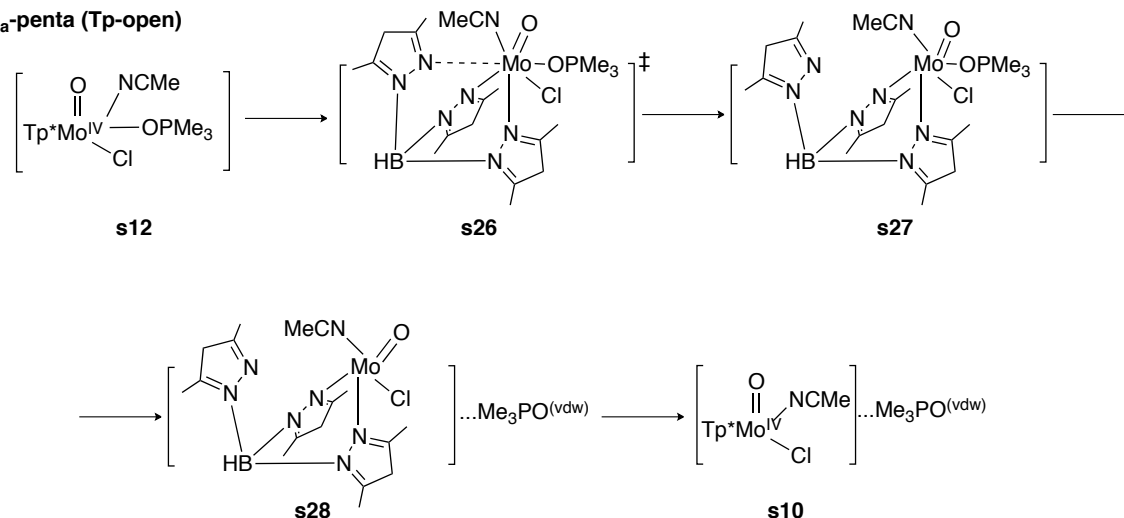
s26 (Imaginary frequency: 20.6*i* cm^{-1})

1\1\GINC-COMET-08-38\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\02-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,3.0429415947,5.1648619411,4.5502496431\O,0,2.081
5370353,4.5672916715,3.2830580061\O,0,4.522367266,4.9060233485,6.22694
14091\P,0,5.7842979088,4.1598781224,6.6733117271\B,0,1.3484275791,7.00
83008464,6.8874439668\Cl,0,5.0111206128,6.1422032566,3.3455608346\N,0,
3.7412985536,7.6224478348,6.374104712\N,0,2.8073456861,7.2856849536,7.
2957676723\N,0,1.7959445926,6.9927768684,4.4066852076\N,0,1.1295704055
,7.5310843865,5.4625498269\N,0,1.6811080271,4.5726480415,6.1739031773\
N,0,1.0185503024,5.487840813,6.9415565533\C,0,7.0820180827,4.096995135
5,5.4255437396\C,0,5.4409125808,2.4651395416,7.1909261883\C,0,6.535214
078,4.9349254717,8.1127088738\C,0,3.3284474386,7.2896550488,8.54989754
15\C,0,4.6627749058,7.6580280153,8.4287714485\C,0,4.8702400183,7.84413
14747,7.047987733\C,0,6.1334495826,8.1818077721,6.3362966328\C,0,2.528
5367783,6.9449253138,9.7525624455\C,0,0.3812790831,8.5841310517,5.0563
889791\C,0,0.5591045138,8.7123987363,3.6844615774\C,0,1.4508200666,7.6
935717167,3.3131136562\C,0,1.9289044322,7.3559911515,1.9486472042\C,0,
-0.4474452281,9.3970945865,5.9822002136\C,0,0.0990156047,4.8642280008,
7.7136590205\C,0,0.1718742425,3.5025515477,7.435645615\C,0,1.173045077
2,3.3600542228,6.4686980512\C,0,1.6240296154,2.10710354,5.812560667\C,
0,-0.8140639879,5.5706946892,8.6486016168\H,0,-0.4364732993,2.71102496
02,7.8754008258\H,0,-1.468411375,4.8417980036,9.1524228085\H,0,-0.2710
679603,6.1324098177,9.4277582238\H,0,-1.458657015,6.2978590767,8.12410
18687\H,0,1.5726643337,2.1778093349,4.7124863906\H,0,0.9928512104,1.26
32485743,6.1341152227\H,0,2.6689126737,1.8613797344,6.0695840302\H,0,0
.0941962551,9.4509120545,3.0297187268\H,0,1.7814303602,8.2108253984,1.
2681960498\H,0,2.9956966445,7.0776089124,1.9511760618\H,0,1.3739837093
,6.49643698,1.5303185508\H,0,5.3868663842,7.7702458927,9.2393885823\H,
0,3.1344033065,7.0554121231,10.6664281223\H,0,1.6378501865,7.591280641
4,9.8608759188\H,0,2.1628400452,5.9009029411,9.7231209138\H,0,7.423715
3673,5.1204932983,5.2022361265\H,0,7.9361846142,3.5029043166,5.7927029
568\H,0,6.703352071,3.6602288529,4.489072648\H,0,6.3438977258,1.997363
7733,7.6179588389\H,0,5.0902740338,1.8509840523,6.3475961675\H,0,4.651

9207989,2.4806378118,7.9620558226\H,0,7.4054354066,4.3446974679,8.4475
833644\H,0,6.8657461037,5.9565488661,7.8672131306\H,0,5.8007870303,4.9
955942309,8.9321093333\H,0,0.5819323359,7.5665038974,7.6478109839\H,0,
-0.9742912863,10.1861664249,5.4227036988\H,0,0.1605219586,9.8855420311
,6.7640501007\H,0,-1.2061522223,8.7874987351,6.5044634007\H,0,6.928376
3014,8.4763055593,7.042062322\H,0,5.9945254748,9.0090909096,5.61752973
8\H,0,6.4967410915,7.3214628554,5.7432397489\C,0,5.1376146333,0.983776
0565,3.2090484304\C,0,4.5452098057,2.1892875279,3.7293953824\N,0,4.074
7172929,3.1549106701,4.1728665626\H,0,5.092032863,0.9779786609,2.10787
08193\H,0,4.6087674391,0.0928340631,3.5866157547\H,0,6.1960812524,0.91
88903921,3.5117774322\\Version=ES64L-G09RevD.01\HF=-2209.80482\RMSD=4.
602e-09\Dipole=2.0253002,-5.1088322,3.0016223\Quadrupole=35.5608042,-9
0.3244368,54.7636326,-34.1316687,41.1571902,-16.6489849\PG=C01 [X(C20H
34B1Cl1Mo1N7O2P1)]\\@

s27

1\1\GINC-COMET-05-10\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\06-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,-1.2653635185,-0.8018019992,0.5732841715\O,0,-1.
9271090555,-2.3188285178,0.9738157192\O,0,-0.7830692717,1.1575878984,-
0.3221246652\P,0,-1.02763577,2.6703422225,-0.1355067916\B,0,2.13108827
67,-0.9318300651,-0.4693374911\Cl,0,-2.1000620486,0.6342730069,2.47733
80799\N,0,3.0154617383,1.2227702639,0.3406434201\N,0,2.2999357853,0.60
3230416,-0.633874664\N,0,0.6279666029,-1.146467524,1.615490113\N,0,1.8
460867826,-1.2779311642,1.0040182266\N,0,-0.2707666925,-1.4867093506,-
1.2634096269\N,0,1.0876615259,-1.5553317898,-1.4214276342\C,0,-2.75113
00191,3.100007309,0.1605104227\C,0,-0.5972920019,3.5810365342,-1.62526
58664\C,0,-0.0291553905,3.3103366611,1.2114461071\C,0,2.1558336877,1.4
105794422,-1.7194042973\C,0,2.801932985,2.6062359651,-1.422884756\C,0,
3.319405807,2.4368532699,-0.1229315764\C,0,4.0742596106,3.4081073087,0
.716645202\C,0,1.3990774755,1.0559509856,-2.9502842094\C,0,2.775087236
4,-1.6760942147,1.90001366\C,0,2.1347149124,-1.8470151418,3.1213658542
\C,0,0.7949828153,-1.515664203,2.9081840148\C,0,-0.2937137046,-1.62287
00818,3.9131665685\C,0,4.2125463575,-1.8585992793,1.5804579562\C,0,1.3
826292327,-2.2135586098,-2.5692563963\C,0,0.1839613229,-2.5820198481,-
3.1650039553\C,0,-0.8266410926,-2.1121332818,-2.3203853996\C,0,-2.2906
553852,-2.2726696123,-2.5117044313\C,0,2.7633749221,-2.4622255839,-3.0
5664184\H,0,0.0583053025,-3.1348011223,-4.0967230721\H,0,2.7262142987,
-2.9408785083,-4.0482373704\H,0,3.3554567347,-1.5353521784,-3.14667857
88\H,0,3.3255175286,-3.1288644149,-2.3794466829\H,0,-2.7931873887,-2.6
375969494,-1.6006383547\H,0,-2.484624957,-2.9909446274,-3.3242741527\H
,0,-2.7730460834,-1.3195146202,-2.7901867148\H,0,2.584844091,-2.186994
1297,4.0549512529\H,0,0.0389877318,-2.2668949646,4.7439256396\H,0,-0.5
716394841,-0.6417345604,4.3308997161\H,0,-1.2130198471,-2.0519231906,3
.4833240708\H,0,2.8689877866,3.4854785159,-2.0686520553\H,0,1.32578714
71,1.9370793894,-3.6096112784\H,0,1.8802385575,0.2559327041,-3.5414626
362\H,0,0.3729992276,0.7189986226,-2.7173473899\H,0,-3.1411015953,2.53
2642693,1.019861136\H,0,-2.8351074665,4.1822596331,0.3584866425\H,0,-3
.343713701,2.8653525068,-0.7393764759\H,0,-0.8785711548,4.6417813206,-
1.5118614793\H,0,-1.1450853963,3.1588918185,-2.4843235071\H,0,0.484237
5742,3.5148561124,-1.8193991401\H,0,-0.0894410893,4.4097065424,1.27697
76792\H,0,-0.3787280331,2.8600024069,2.1551035081\H,0,1.0185265408,3.0
061776632,1.0387072196\H,0,3.1876109477,-1.4704628066,-0.7425189833\H,
0,4.7670354588,-2.1251192471,2.4945475496\H,0,4.6485798101,-0.93372531
8,1.1655876634\H,0,4.3782926584,-2.6579999975,0.8375238965\H,0,4.97201
9159,3.793148606,0.2003273262\H,0,4.4005059575,2.932893085,1.656557571

4\H,0,3.4629783429,4.2909768363,0.9828440806\C,0,-5.5624817,0.41672763
58,-1.159155648\C,0,-4.2479145809,0.0459457942,-0.7050653556\N,0,-3.18
25149508,-0.2569227478,-0.3543990872\H,0,-5.5942262945,0.4825847859,-2
.259484687\H,0,-5.8580944128,1.3914458864,-0.7368534085\H,0,-6.2975757
817,-0.3368799733,-0.8332705795\\Version=ES64L-G09RevD.01\HF=-2209.814
4616\RMSD=5.140e-09\Dipole=-2.8118384,2.7258087,-3.7339735\Quadrupole=
10.8869331,1.1525728,-12.0395059,-15.8034064,17.7575597,-0.0974232\PG=
C01 [X(C20H34B1Cl1Mo1N7O2P1)]\\@

s28

1\1\GINC-COMET-05-11\Stability\RM06L\Gen\C20H34B1Cl1Mo1N7O2P1\TALIPOVM
\05-Aug-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gues
s(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultraf
ine)\\Title\\0,1\Mo,0,-1.0659325857,-1.1029643413,0.6015838789\O,0,-1.
9466855227,-2.3694074761,1.2741287018\O,0,-2.7530945321,5.9176348499,-
0.8732903154\P,0,-2.2924329287,4.6054065225,-0.2828594786\B,0,2.155841
7756,-1.2129771304,-0.558239518\Cl,0,-1.1836779159,1.0050782235,1.8499
016069\N,0,2.5673573794,1.0156479903,0.4124493505\N,0,1.9495486284,0.3
243982809,-0.5819744136\N,0,0.8185989184,-1.5124744175,1.5674136099\N,
0,1.996216618,-1.6873041068,0.9022724345\N,0,-0.2079148162,-1.97359456
9,-1.1796826792\N,0,1.1318172263,-1.9429456771,-1.4573411395\C,0,-3.54
32668916,3.7862590529,0.7370805436\C,0,-0.837223155,4.750279847,0.7832
18476\C,0,-1.8241844237,3.3754067233,-1.5288222741\C,0,1.394869603,1.1
761503572,-1.4967048107\C,0,1.6580496098,2.4651881742,-1.0523274609\C,
0,2.3916834727,2.3082513652,0.1423163448\C,0,2.9173317271,3.3575851687
,1.0586896851\C,0,0.6720936931,0.7636670449,-2.7313317545\C,0,2.963323
7502,-2.0457506881,1.7736645277\C,0,2.3814980822,-2.1425361091,3.03516
01154\C,0,1.0374961603,-1.7930681397,2.8690194749\C,0,-0.0505033648,-1
.7871889153,3.8775021921\C,0,4.37979598,-2.2424350327,1.3791743265\C,0
,1.36807632,-2.5798767085,-2.6261670551\C,0,0.1503121153,-3.0516391902
,-3.1054470587\C,0,-0.8159440293,-2.6489484981,-2.1803722095\C,0,-2.27
74443013,-2.9097980583,-2.2273343783\C,0,2.7159958171,-2.6968843881,-3
.2350729232\H,0,-0.0136814564,-3.6272540477,-4.0168247775\H,0,2.647160
9555,-3.2211380923,-4.2007896019\H,0,3.1754950267,-1.709169763,-3.4141
53272\H,0,3.4130524568,-3.258927172,-2.5897517268\H,0,-2.7267063022,-2
.9689389943,-1.2233119748\H,0,-2.4758950074,-3.8606887135,-2.747486896
2\H,0,-2.8111730806,-2.1223700465,-2.789403752\H,0,2.8761939314,-2.431
1898433,3.9632289922\H,0,0.367751226,-1.7795608818,4.8965415172\H,0,-0
.7087928213,-0.9102802087,3.7597295242\H,0,-0.688020893,-2.68603315,3.
787336255\H,0,1.3591558341,3.3937532114,-1.5438683602\H,0,0.4133535756
,1.6576540681,-3.3218769747\H,0,1.2775333142,0.1067392755,-3.381568852
7\H,0,-0.2725453689,0.2258293289,-2.5238452102\H,0,-4.4536051358,3.617
5355967,0.1364754703\H,0,-3.1764711454,2.8200260174,1.1276004428\H,0,-
3.8119291365,4.4387906558,1.5854706884\H,0,-0.5188951951,3.7641483512,
1.1638946399\H,0,-1.0671799682,5.4111031116,1.6366398422\H,0,-0.006916
0323,5.2011004342,0.2128142222\H,0,-1.4454959102,2.4487014172,-1.06146
97383\H,0,-2.6935738854,3.1437027299,-2.1682229016\H,0,-1.0346936943,3
.7957110825,-2.1749628794\H,0,3.2675181346,-1.5227910088,-0.9390871683
\H,0,4.9697134213,-2.5806684552,2.2453275353\H,0,4.8275935453,-1.30438
10105,1.0064059804\H,0,4.4886728269,-2.9917205151,0.5764365129\H,0,3.4
439500968,4.1588467558,0.5107785022\H,0,3.6202588977,2.9190415964,1.78
60469076\H,0,2.1093573005,3.8472501659,1.6340116107\C,0,-4.5842722805,
0.6820117404,-2.0519594513\C,0,-3.5102054099,0.1998467642,-1.228034314
7\N,0,-2.64271058,-0.230172386,-0.5839683139\H,0,-5.3673520356,-0.0917
291896,-2.1178262419\H,0,-4.2213393919,0.8925013815,-3.0717232162\H,0,
-5.0337793928,1.5971804327,-1.6332131778\\Version=ES64L-G09RevD.01\HF=
-2209.7948469\RMSD=1.237e-09\Dipole=-1.7579996,-3.3134385,-3.1631419\Q

uadrupole=19.0541519,-33.528267,14.474115,5.9842029,13.0801052,11.4440
198\PG=C01 [X(C20H34B1Cl1Mo1N7O2P1)]\\@

Scheme S12

$$Me_3PO \ + \ PyrH^+ \ \longrightarrow \ Me_3PO(H^+) \ + \ Pyr$$
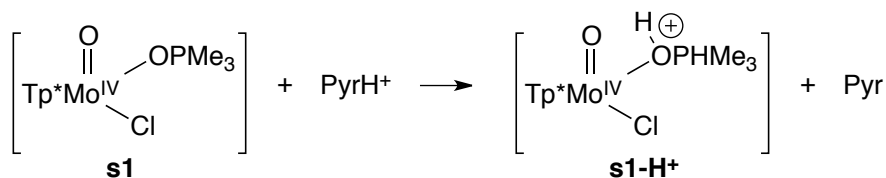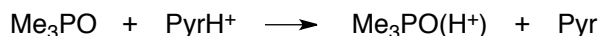
Me₃PO

1\1\GINC-JOKER-C8\Stability\RM06L\Gen\C3H9O1P1\SOFIBALI\24-Feb-2017\0\
\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(read) geom(al
lcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)\\Title\\0,
1\O,0,3.2281644678,4.7284939737,2.2524629079\P,0,1.8696344252,5.296652
5601,1.9184201838\C,0,1.8431028169,7.1044737761,1.8194024896\C,0,0.588
969584,4.8739899119,3.1269956092\C,0,1.2171270217,4.7309474885,0.32677
41574\H,0,0.8393870074,7.4904714887,1.5730319107\H,0,2.1615679053,7.53
02673243,2.78595954\H,0,2.5539690891,7.4405572117,1.0456209036\H,0,-0.
3904637634,5.3066215423,2.8607315632\H,0,0.8849927962,5.2476330194,4.1
21889968\H,0,0.4892914571,3.7770111116,3.1882653254\H,0,0.2241516101,5
.1604913183,0.1107723326\H,0,1.9128186263,5.0194064175,-0.4793147887\H
,0,1.1360069563,3.630742856,0.3325078976\\Version=ES64L-G09RevE.01\HF=
-536.05441\RMSD=2.493e-09\Dipole=-1.849794,0.7735321,-0.4550932\Quadru
pole=-15.8251185,17.0081227,-1.1830042,-13.6135795,-9.5878303,-1.21860
96\PG=C01 [X(C3H9O1P1)]\\@

Me₃PO(H⁺)

1\1\GINC-JOKER-C7\Stability\RM06L\Gen\C3H10O1P1(1+)\SOFIBALI\29-Oct-20
17\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(read) ge
om(allcheck) scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)\\Title\\1,1
\O,0,3.3488761735,4.7353746501,1.9469094854\P,0,1.831495187,5.18621947
38,1.6578140867\C,0,1.9710567312,6.9468570215,1.4679308836\C,0,0.78680
97726,4.7639088587,3.0397469185\C,0,1.2320262484,4.4184992118,0.164263
0118\H,0,0.9800544827,7.3832243838,1.262074741\H,0,2.3773398492,7.3855
100259,2.3930041274\H,0,2.6501616944,7.1738482785,0.6309515799\H,0,-0.
2359243384,5.1377337427,2.8683462437\H,0,1.1898170226,5.2179758268,3.9
589971558\H,0,0.7464897089,3.6696615585,3.1644036454\H,0,0.218791917,4
.7849539384,-0.0684931271\H,0,1.9068222675,4.6617059179,-0.6718670526\
H,0,1.1915439843,3.3243777506,0.2899673292\H,0,3.495962891,3.778739694
3,2.0845963532\\Version=ES64L-G09RevE.01\State=1-A'\HF=-536.486784\RMS
D=1.505e-09\Dipole=-0.6377916,-0.5254014,-0.035638\Quadrupole=-2.45727
88,2.6595492,-0.2022704,-1.6481586,-0.1433505,-0.6050196\PG=CS [SG(C1H
2O1P1),X(C2H8)]\\@

PyrH⁺

1\1\GINC-JOKER-C8\Stability\RM06L\Gen\C5H6N1(1+)\SOFIBALI\07-Feb-2017\
0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(read) geom(
allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)\\Title\\
1,1\H,0,-0.0147942353,-0.5160697853,0.703748899\C,0,-0.6157719212,0.36

5356355,0.9477638567\C,0,-1.9824814189,0.2313630146,1.1967557961\H,0,-
2.4785533712,-0.7409923562,1.154755379\C,0,-2.7224418175,1.3588528417,
1.5040119698\H,0,-3.7934120746,1.3500997921,1.712943446\N,0,-2.1092545
285,2.556312772,1.5555494595\C,0,-0.7942322286,2.7248314793,1.31996692
42\H,0,-0.4120464845,3.7445596879,1.3890857101\C,0,-0.0160571683,1.624
1560195,1.0094434327\H,0,1.0511114847,1.7581724613,0.8184243084\H,0,-2
.6715462363,3.379807718,1.7847908185\\Version=ES64L-G09RevE.01\HF=-248
.5030676\RMSD=2.145e-09\Dipole=-0.5563695,0.8146408,0.225747\Quadrupol
e=3.0906832,7.2461454,-10.3368286,-12.3371314,-10.5510402,11.3699452\P
G=C01 [X(C5H6N1)]\\@

Pyr

1\1\GINC-JOKER-C8\Stability\RM06L\Gen\C5H5N1\SOFIBALI\29-Oct-2017\0\\#
P M06L/chkbasis stable(opt) pop(nbo) scrf(check) guess(read) geom(allc
heck) scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)\\Title\\0,1\N,0,5.
3969326412,4.2959311698,0.1613190131\C,0,6.3755567456,3.3898103365,0.2
220583292\H,0,6.2362185264,2.5692816839,0.9411190573\C,0,5.5430987659,
5.3018549465,-0.70424565\C,0,7.5276166281,3.4421140729,-0.5640226931\H
,0,4.726223387,6.037538506,-0.7391032965\C,0,6.6533084435,5.4502830047
,-1.5368948022\C,0,7.668240764,4.4974649584,-1.4638785579\H,0,8.298265
1948,2.6692938253,-0.470770947\H,0,6.7187244959,6.2972874937,-2.228378
9829\H,0,8.5573783763,4.5763583811,-2.1000865092\\Version=ES64L-G09Rev
E.01\State=1-A1\HF=-248.0609032\RMSD=6.455e-09\Dipole=0.8857475,0.0785
926,-0.6337822\Quadrupole=-0.9480458,1.9874407,-1.0393948,-1.8386013,0
.4946137,-2.1414176\PG=C02V [C2(H1C1N1),SGV(C4H4)]\\@

s1-H+

1\1\GINC-JOKER-C8\Stability\RM06L\Gen\C18H32B1Cl1Mo1N6O2P1(1+)\SOFIBAL
I\29-Oct-2017\0\\#P M06L/chkbasis stable(opt) pop(nbo) scrf(check) gue
ss(read) geom(allcheck) nosym scf(fermi,xqc,maxcyc=200) int(grid=ultra
fine)\\Title\\1,1\Mo,0,4.1920162697,3.9195938949,3.9524251907\O,0,2.87
79224011,2.9990307291,4.5214985671\O,0,3.1081590173,4.4992311667,1.970
9677366\P,0,1.6629124342,5.2787736999,1.7336053322\B,0,7.2996566718,2.
8131815276,4.0452390929\Cl,0,3.7142949012,6.2790119328,4.5505155148\N,
0,6.1933823631,4.808114123,2.9633002543\N,0,7.3454295367,4.1449382168,
3.2718982259\N,0,5.4779889297,3.6019601833,5.6145252396\N,0,6.71710661
55,3.0524364564,5.4566794488\N,0,5.1042871269,2.158154615,3.003081286\
N,0,6.3989401847,1.8325622356,3.2689144737\C,0,1.9526237008,7.01649360
35,1.5053691619\C,0,0.7142927628,4.9481605879,3.1944009114\C,0,0.92462
15358,4.5561369022,0.2861869761\C,0,8.4217455679,4.8105474931,2.794417
3248\C,0,7.9487228109,5.944954439,2.1451373181\C,0,6.5536436734,5.9079
0504,2.2744702778\C,0,5.5825993427,6.9053306839,1.7581267167\C,0,9.816
5468341,4.3362377527,2.9771554181\C,0,7.2883454767,2.8568922015,6.6648
014742\C,0,6.374035281,3.2673979322,7.6333999658\C,0,5.2515418459,3.73
03518232,6.9401144566\C,0,3.9591641422,4.2170267477,7.4792445274\C,0,8
.6554843216,2.3051111908,6.8324634435\C,0,6.7189107332,0.6621819703,2.
6704642185\C,0,5.5800289021,0.2081017343,2.0143261276\C,0,4.5892308305
,1.1732670428,2.2411240811\C,0,3.188304191,1.1738463308,1.7449408846\C
,0,8.0715513368,0.0572190774,2.7525617101\H,0,5.479199872,-0.714668962
9,1.4419051361\H,0,8.0848245753,-0.9122892145,2.2311726007\H,0,8.83950
3002,0.7007279694,2.2878434417\H,0,8.3860067213,-0.113054469,3.7970611
317\H,0,2.8148207016,0.1418941354,1.6454747613\H,0,3.1098396723,1.6272
038636,0.738643258\H,0,2.5067753013,1.715593585,2.4202137081\H,0,6.509
7913369,3.2329830068,8.7148056862\H,0,4.0520816805,4.4553969667,8.5504
356608\H,0,3.60645679,5.1130360118,6.9420919781\H,0,3.1706803163,3.448
9462917,7.3747041129\H,0,8.5431692195,6.704828365,1.6362051039\H,0,10.
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439571736\H,0,9.9848350185,3.3518649492,2.5059281571\H,0,0.9748370121,
7.5185918233,1.4034089374\H,0,2.4825550852,7.4146011203,2.3859443663\H
,0,2.539096607,7.1971841658,0.5907279704\H,0,-0.2732347828,5.427089718
2,3.0785678364\H,0,1.2269269663,5.3724775024,4.0732845695\H,0,0.583105
944,3.8621713535,3.3226477187\H,0,-0.055454394,5.032376351,0.117786955
2\H,0,1.5545611118,4.7334856669,-0.6005436208\H,0,0.7764628494,3.47413
04216,0.4315713644\H,0,8.411890191,2.3539670376,4.1456866112\H,0,8.900
7883115,2.2207294818,7.902248033\H,0,9.4195023537,2.946122135,6.358801
9167\H,0,8.7534423654,1.3026130565,6.3804639744\H,0,6.0141625111,7.457
9754289,0.9080878468\H,0,5.3020614946,7.6438339208,2.5297063293\H,0,4.
6522350928,6.4287047445,1.4176282727\H,0,3.5272929874,4.1476581591,1.1
590741552\\Version=ES64L-G09RevE.01\HF=-2077.5889649\RMSD=3.871e-09\Di
pole=-4.4787535,0.9875036,-5.3359799\Quadrupole=18.5200825,28.1218522,
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1)]\\@