**Supporting Information for:**

# Highly Stereoselective Proton/Hydride-Exchange: Assistance of Hydrogen-Bonding for the Heterolytic Splitting of $H_2$.

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**Experimental Details**

*Materials and Methods.* All experiments were carried out under an atmosphere of argon using Schlenk and glove-box techniques. $d^8$-THF was dried by distillation from Na/K alloy and deoxygenated by three *freeze-pump-thaw* cycles. Water was deoxygenated by three *freeze-pump-thaw* cycles prior to use. [Ru(H)$PMe_3$(PNP)] (**1**) was synthesized as reported earlier.[1] [Ru$(H)_2PMe_3$(*H*PNP)] (**3**) was prepared in situ from reaction of **1** with $H_2$ in a *J-Young* NMR tube. For NMR exchange measurements the tube was subsequently evacuated and backfilled with Argon. NMR spectra were recorded on Jeol Lambda 400, Bruker Avance III 400, and Bruker DPX 500 spectrometers and calibrated to the residual proton resonance. $T_1$ measurements were performed by the inversion-recovery method with relaxation delays set to 5-10 times the expected $T_1$ times. $^1$H 2D EXSY NMR spectra were obtained at 300 K in $d^8$ THF using the BRUKER pulse sequence *noesyph* with d1 set to 2s.

*Synthesis of [Ru$(H)_2PMe_3$(MePNP)] (**5**).* MeOTf (42.3 mg; 0.258 mmol) is added dropwise to a vigorously stirred solution of **1** (104.3 g; 0.216 mmol) in pentane (5 mL) at r.t. and a yellow solid precipitates immediately. After filtration the residue is washed with pentane (2 x 5 mL) an dried *in vacuo* to give [RuH($PMe_3$)OTf(*Me*PNP)]: NMR ($C_6D_6$, r.t., [ppm]) $^1$H NMR (399.8 MHz): δ = -27.20 (q, $^2J_{HP}$ = 25.0 Hz, 1H, RuH), 0.83-0.89 (m, 12H, CHC*H*$_3$), 1.10 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 12.2 Hz, 6H, CHC*H*$_3$), 1.30 + 1.25-1.31 (d + m, $^2J_{HP}$ = 8.6 Hz, 15H, P(C*H*$_3$)$_3$ + CHC*H*$_3$), 1.40-1.48 (m, 2H), 1.76-1.85 (m, 4H), 1.96 (s, 3H, NC*H*$_3$), 1.96-2.03 (m, 2H), 2.24 (sp, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*$CH_3$), 2.35-2.47 (m, 2H, NC*H*$_2$). $^{31}$P{$^1$H} NMR (161.83 MHz): δ = 61.4 (d, $^2J_{PP}$ = 28.7 Hz, P$^i$Pr$_2$), 11.4 (t, $^2J_{PP}$ = 28.7 Hz, P$(CH_3)_3$). $^{19}$F{$^1$H} NMR (376.17 MHz): δ = -77.4 (s, $SO_3CF_3$). [RuH($PMe_3$)OTf(*Me*PNP)] is redissolved in THF (10 mL) and NaH (23.8 g; 0.992 mmol) is added. After 5 h at room temperature the solvent is evaporated *in vacuo* and the residue is extracted with pentanes. Evaporation of the filtrate gives **5** as a bright yellow solid. Yield starting from **1**: 59.0 mg (0.118 mmol; 55 %). Anal. calcd. for $C_{20}H_{50}NP_3Ru$ (498.61): C, 48.18; H, 10.11; N, 2.81. Found: C 48.59; H, 9.83; N, 2.54. IR (cm$^{-1}$) ν = 1911 (w, Ru-$H_{sym}$), 1556 (s, Ru-$H_{as}$). NMR ($C_6D_6$, r.t., [ppm]) $^1$H NMR (399.8 MHz): δ = -8.31 (ddt, $^2J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 17.1 Hz, $^2J_{HP}$ = 29.3 Hz, 1H, Ru*H*), -7.43 (ddt, $^2J_{HH}$ =

7.3 Hz, $^{2}J_{HP}$ = 16.5 Hz, $^{2}J_{HP}$ = 31.1 Hz, 1H, Ru*H*), 1.13-1.18 (m, 12H, CHC*H*$_3$), 1.31 (d , $^{2}J_{HP}$ = 7.3 Hz, 9H, P(C*H*$_3$)$_3$), 1.35 (m, $^{2}J_{HP}$ = 7.3 Hz, 2H, PC*H*$_2$), 1.44 (dd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{HP}$ = 13.4 Hz, 6H, CHC*H*$_3$), 1.65 (m, 2H, PC*H*$_2$), 1.70 (dd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{HP}$ = 14.6 Hz, 6H, CHC*H*$_3$), 1.98 (sp, $^{3}J_{HH}$ = 7.3 Hz, 4H, C*H*CH$_3$ + NC*H*$_2$), 2.07 (sp, $^{3}J_{HH}$ = 7.3 Hz, 2H, C*H*CH$_3$), 2.22 (s + m, 5H, NC*H*$_3$ + NC*H*$_2$). $^{13}$C-{$^{1}$H} NMR (100.6 MHz): δ 16.4 (t, $J_{CP}$ = 2.0 Hz, CH*C*H$_3$), 19.4 (t, $J_{CP}$ = 3.5 Hz, CH*C*H$_3$), 19.7 (t, $J_{CP}$ = 2.5 Hz, CH*C*H$_3$), 20.3 (t, $J_{CP}$ = 4.0 Hz, CH*C*H$_3$), 24.6 (dt, $^{1}J_{CP}$ = 8.0 Hz, $^{3}J_{CP}$ = 2.0 Hz, *C*HCH$_3$), 25.5 (dt, $^{1}J_{CP}$ = 6.5 Hz, $^{3}J_{CP}$ = 3.0 Hz, P*C*H$_2$), 27.9 (t, $J_{CP}$ = 11.1 Hz, $^{3}J_{CP}$ = 2.7 Hz, *C*HCH$_3$), 30.2 (dt, $^{1}J_{CP}$ = 24.1 Hz, $^{3}J_{CP}$ = 3.0 Hz, P(*C*H$_3$)$_3$), 54.05 (s, NCH$_3$), 65.3 (dt, $^{3}J_{CP}$ = 5.0 Hz, $^{3}J_{CP}$ = 1.0 Hz, N*C*H$_2$). $^{31}$P{$^{1}$H} NMR (161.83 MHz): δ = 85.1 (d, $^{2}J_{PP}$ = 34.7 Hz, P$^{i}$Pr$_2$), 14.5 (t, $^{2}J_{PP}$ = 34.7 Hz, P(CH$_3$)$_3$). Assignments were confirmed by $^{1}$H-$^{1}$H COSY and $^{1}$H-$^{13}$C HMQC.

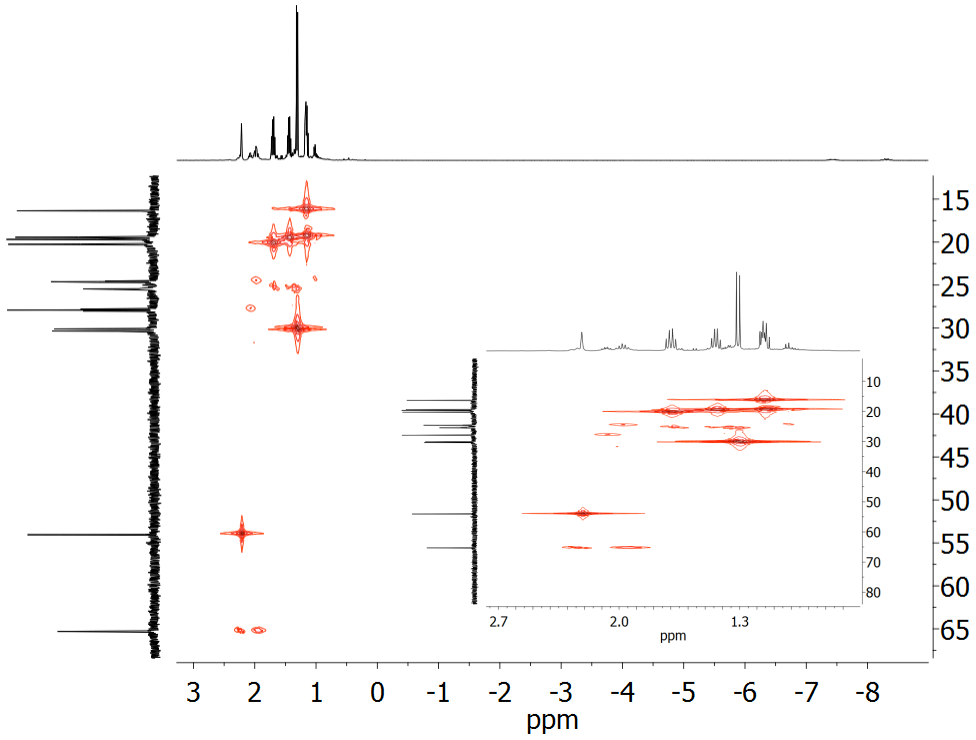


**Figure S1.** $^{1}$H-$^{13}$C HMQC NMR of **5** in benzene.

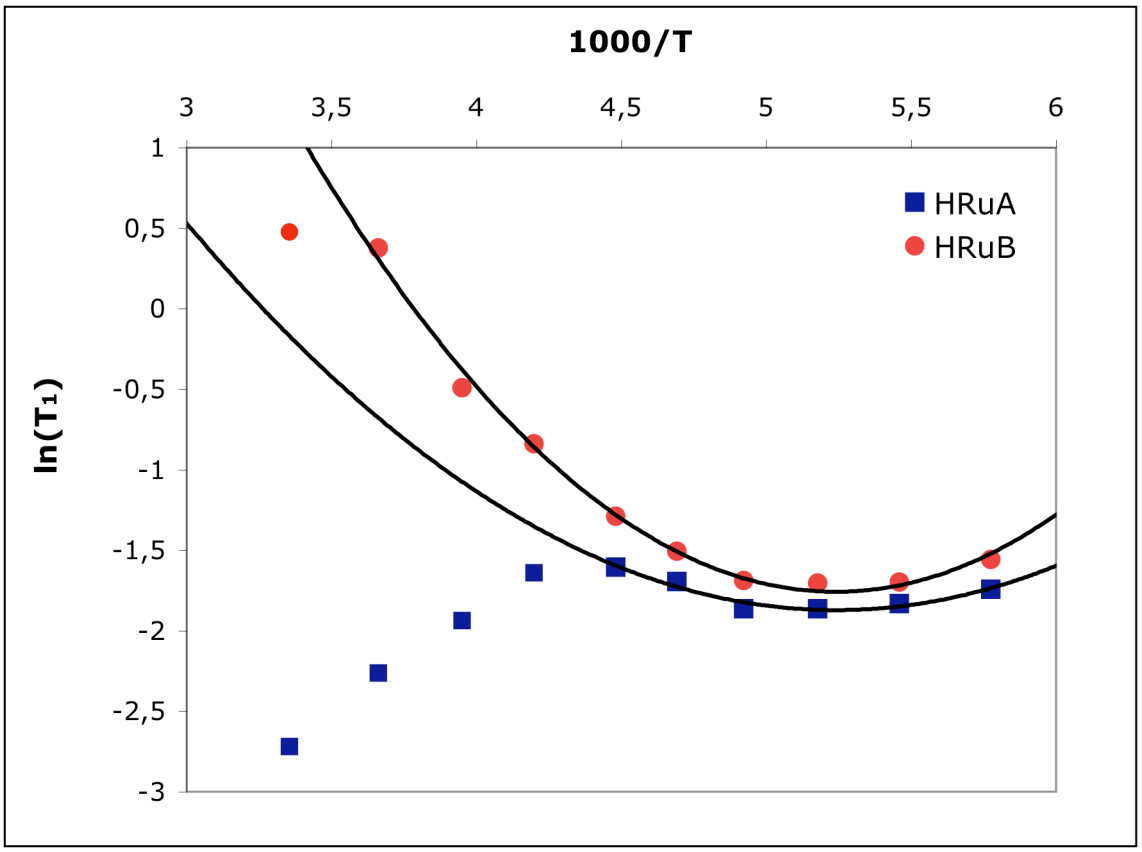


**Figure S2.** Plot of ln($T_1$) *vs* 1/T (recorded at 400 MHz) of the two hydride signals $H^{RuA}$ (■) and $H^{RuB}$ (●) of **3** in the presence of 2 equiv. $H_2O$.

*$^1$H 2D EXSY NMR measurements*. Mixing times ($\tau_m$) of 500 and 1000 ms were used for **3** in dry $d^8$-THF and for **5** in $d^8$-THF with $H_2O$ (2 equiv.). For **3** with 2 - 5 equiv. $H_2O$ in $d^8$-THF, $\tau_m$ was varied over a wide range (0.01, 0.1, 0.5, 1, 10, 100, 500, and 1000 ms) to account for the largely different exchange rates. Typical spectra are shown in Figures S3 – S5. Intensities were determined by integration of the exchange cross-peaks and diagonal peaks. In the next step, magnetization exchange rate constants were determined using two different approaches which are based on the peak intensities not the lineshapes in 2D EXSY spectra. In case of **5** the situation is simplified by the fact that the processes to be investigated have similarly slow rates, so analysis can be done following the eigen-values eigenvectors method[2] implemented in EXSY Calc developed by Mestrelab Research.[3] In case of **3** several processes with rate constants differing several orders of magnitudes take place. In such a situation a simple iterative scheme which considers the intensities of several 2D EXSY spectra at different mixing times is indicated,[4] which was implemented in a home-written Fortran90 program which allows non-linear least square fitting using the MINUIT routines from the CERN library. The program minimizes the sum of the difference between experimental and calculates intensities of all peaks at different mixing times. If all peaks are given the same weight, small deviations in the diagonal peaks (for example the intense water peak) distort the fitted curves tremendously. For this reason, the residuals of each peak intensity were normalized on the square root of maximum intensity occurring in the time series of each peak. Nine times more weight was given to off-diagonal peaks than to diagonal peaks. The best-fit result is displayed in Figure S6 and the magnetization rate matrix in Table S1. The fit is numerically stable with acceptable correlation coefficients. Conversion to reaction rate constants for exchange of $H^{H2O}$ with $H^{RuA}$ ($k_A$) and $H^{NH}$ ($k_B$), respectively, were calculated assuming second order rate laws for the forward and reverse reactions:

$$r_1 = r_{-1} = k_1 \cdot [H^{RuA}] \cdot [H^{H2O}] = k_{-1} \cdot [H^{RuA}] \cdot [H^{H2O}]$$
$$r_2 = r_{-2} = k_2 \cdot [H^{NH}] \cdot [H^{H2O}] = k_{-2} \cdot [H^{NH}] \cdot [H^{H2O}]$$

$$k_A = k_1 \cdot [H^{H2O}] = k_A' = k_{-1} \cdot [H^{RuA}]$$
$$k_B = k_2 \cdot [H^{H2O}] = k_B' = k_{-2} \cdot [H^{NH}]$$

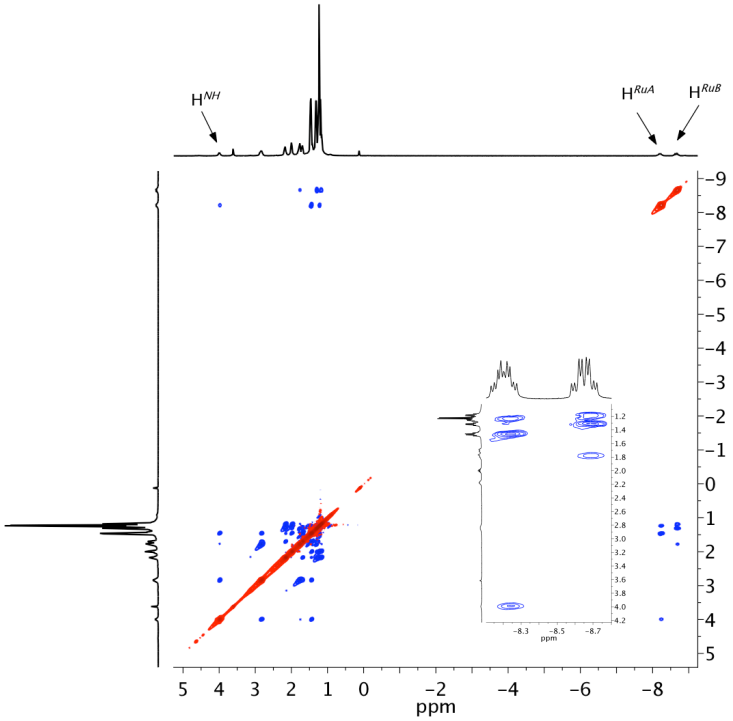


**Figure S3.** $^{1}$H EXSY NMR of **3** in dry THF ($\tau_m$ = 1000 ms).

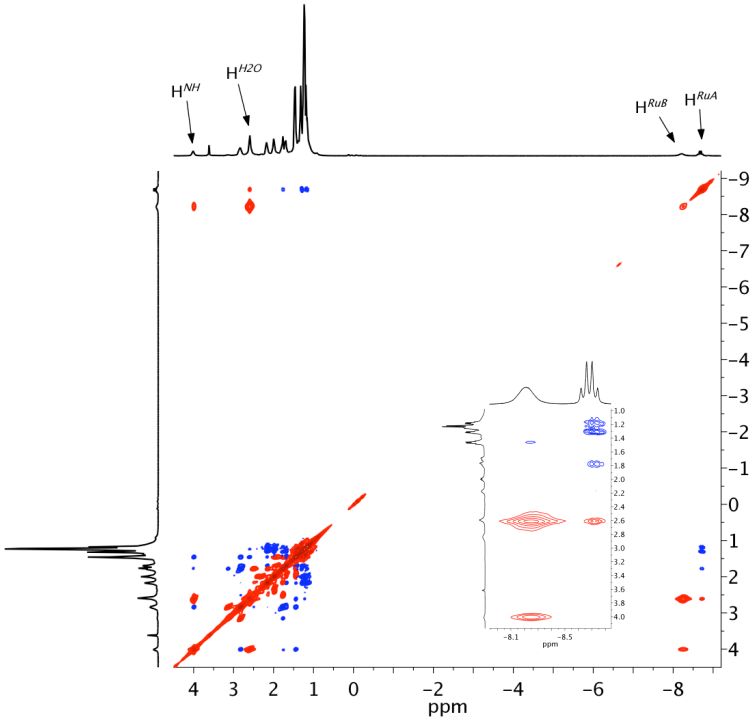


**Figure S4.** Typical $^{1}$H EXSY NMR of **3** in the presence of 2 equiv. $H_2O$ in THF ($\tau_m$ = 500 ms).

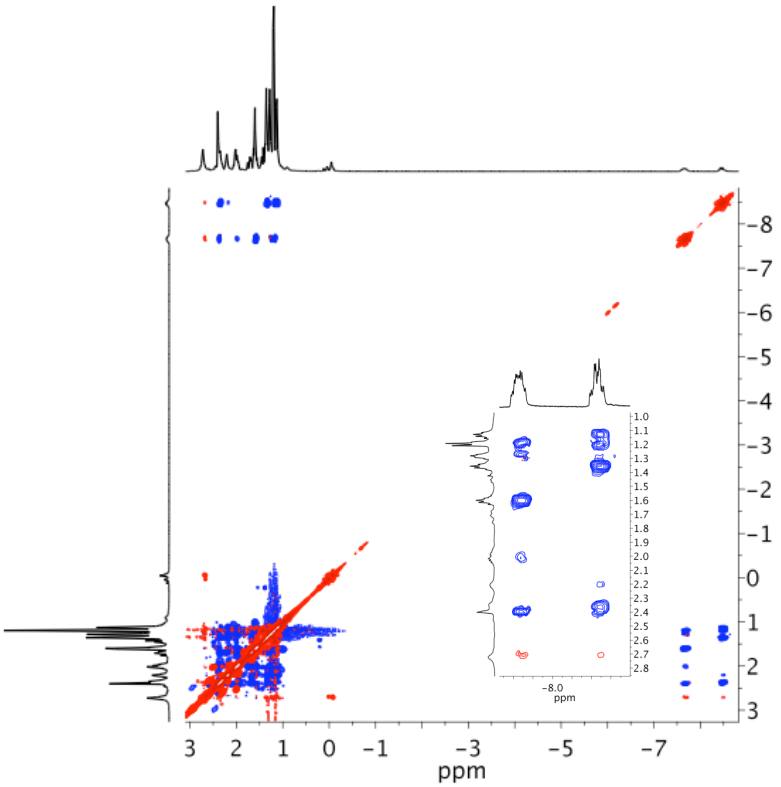


**Figure S5.** Typical $^{1}$H EXSY NMR of **5** with 2 equiv. $H_2O$ in THF ($\tau_m$ = 1000 ms).

**Table S1.** Magnetization exchange rate matrix for **3** with $H_2O$ (4.25 equiv.).

| | $\mathbf{H}^{NH}$ | $\mathbf{H}^{H2O}$ | $\mathbf{H}^{RuHA}$ | $\mathbf{H}^{RuHB}$ |
|---|---|---|---|---|
| $\mathbf{H}^{RuHB}$ | 0 $s^{-1}$ | 0 $s^{-1}$ | 0.131 $s^{-1}$ | -- |
| $\mathbf{H}^{RuHA}$ | 0.042 $s^{-1}$ | 16.5 $s^{-1}$ | -- | 0.155 $s^{-1}$ |
| $\mathbf{H}^{H2O}$ | 3.45 $s^{-1}$ | -- | 154 $s^{-1}$ | 0 $s^{-1}$ |
| $\mathbf{H}^{NH}$ | -- | 0.416 $s^{-1}$ | 0 $s^{-1}$ | 0 $s^{-1}$ |

**Table S2.** Reaction rate constant matrix for **3** with $H_2O$ (4.25 equiv.).

| | $\mathbf{H}^{NH}$ | $\mathbf{H}^{H2O}$ | $\mathbf{H}^{RuHA}$ | $\mathbf{H}^{RuHB}$ |
|---|---|---|---|---|
| $\mathbf{H}^{RuHB}$ | 0 $s^{-1}$ | 0 $s^{-1}$ | 0.131 $s^{-1}$ | -- |
| $\mathbf{H}^{RuHA}$ | 0.042 $s^{-1}$ | 320 $Lmol^{-1}s^{-1}$ | -- | 0.155 $s^{-1}$ |
| $\mathbf{H}^{H2O}$ | 7.91 $Lmol^{-1}s^{-1}$ | -- | 354 $Lmol^{-1}s^{-1}$ | 0 $Lmol^{-1}s^{-1}$ |
| $\mathbf{H}^{NH}$ | -- | 8.11 $Lmol^{-1}s^{-1}$ | 0 $s^{-1}$ | 0 $s^{-1}$ |

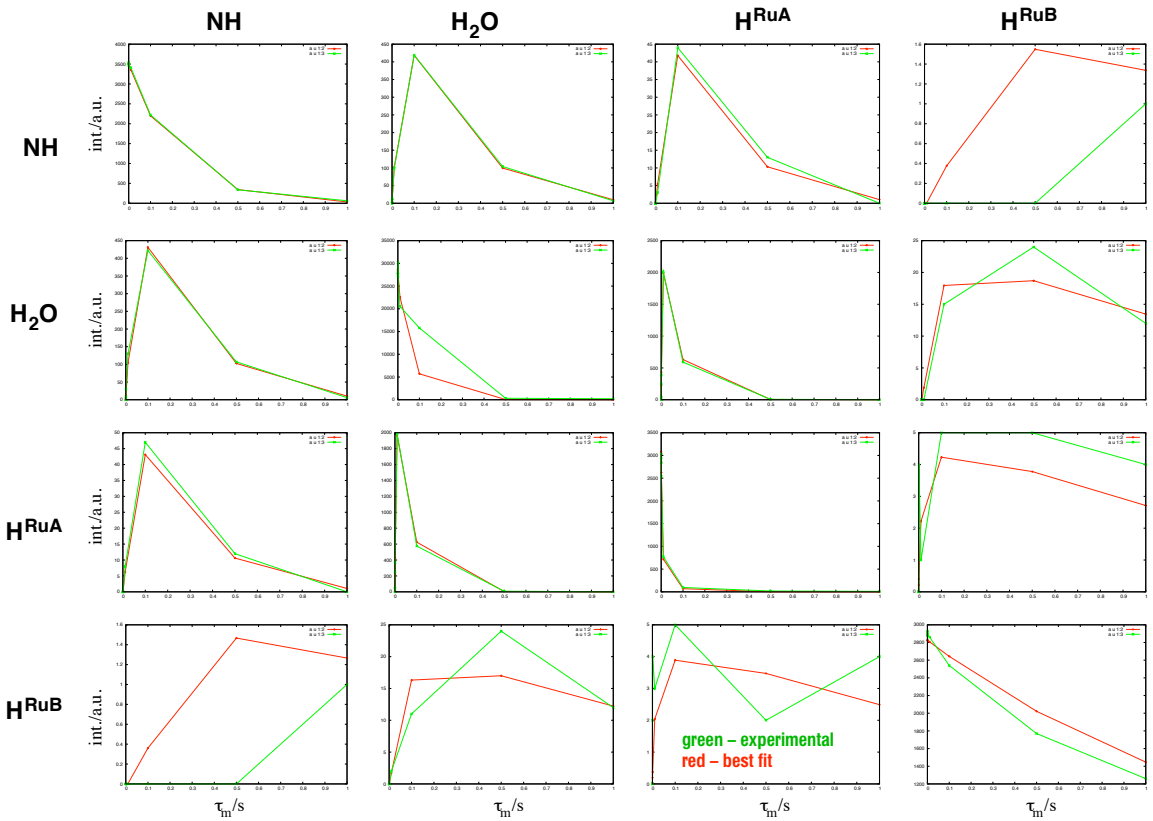


**Figure S6.** Magnetization exchange curves of $H^{H_2O}$, $H^{RuA}$, $H^{RuB}$, and $H^{NH}$ of **3** with $H_2O$ (4.25 equiv.); green: experimental data, red: simulated data; all curves are scaled to the maximum intensity found in the time series of the respective peak.

**Computational results**

The following theoretical studies were performed with the program package Gaussian-03.[5] Reactions of [Ru(H)$_2$PMe$_3$(PNP$^H$)] (**3**) with $H_2O$ were studied by DFT methods using a slightly simplified model bearing $PMe_2$ substituents on the pincer ligand (**3$^{Me}$**: [Ru(H)$_2$PMe$_3${HN(CH$_2$CH$_2$PMe$_2$)$_2$}] instead of P$^i$Pr$_2$, to save computational time. The hybrid functional B3LYP was utilized with Hay's and Wadt's ECP and corresponding basis set for ruthenium and the basis set 6-31+G** for all other atoms.[6,7,8] Minima and transition states were distinguished by the number of imaginary frequencies (ground states: 0, transition states: 1). The transition states were found using the Berny algorithm as implemented in Gaussian03.[9] The solvent influence was introduced applying the PCM model. Free energies are reported for standard conditions (298.15 K, 1 bar atmospheric pressure).

*Optimized structures for water free $H_2$-activation (Bond length in parantheses from PCM calculation)*

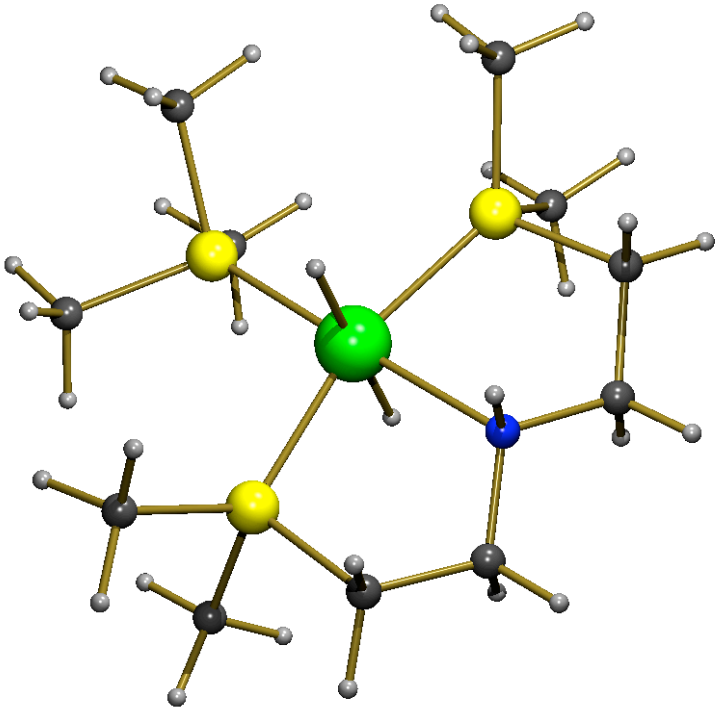

**Figure S7**. Optimized structure of **3$^{Me}$**.

**Table S3.** Coordinates and energy values of $\mathbf{3^{Me}}$.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | 0.016629 | -0.067828 | -0.072159 |
| 2 | 15 | 0 | -2.266126 | -0.494964 | -0.044655 |
| 3 | 15 | 0 | 2.322808 | -0.312934 | -0.044714 |
| 4 | 7 | 0 | 0.108009 | -2.335356 | -0.236220 |
| 5 | 6 | 0 | -2.351303 | -2.351965 | -0.293533 |
| 6 | 6 | 0 | -1.101141 | -2.998926 | 0.297047 |
| 7 | 6 | 0 | 1.356692 | -2.899148 | 0.318694 |
| 8 | 6 | 0 | 2.560836 | -2.161859 | -0.262243 |
| 9 | 6 | 0 | -3.492744 | 0.067625 | -1.324542 |
| 10 | 6 | 0 | -3.294848 | -0.275430 | 1.489599 |
| 11 | 6 | 0 | 3.326292 | 0.014052 | 1.486310 |
| 12 | 6 | 0 | 3.488902 | 0.326364 | -1.343576 |
| 13 | 1 | 0 | -3.258704 | -2.779219 | 0.149403 |
| 14 | 1 | 0 | -2.394756 | -2.536745 | -1.374545 |
| 15 | 1 | 0 | -1.080465 | -2.870944 | 1.384545 |
| 16 | 1 | 0 | -1.080259 | -4.079689 | 0.080798 |
| 17 | 1 | 0 | 1.310107 | -2.761543 | 1.404083 |
| 18 | 1 | 0 | 3.491508 | -2.507979 | 0.202788 |
| 19 | 1 | 0 | -3.727653 | 1.126211 | -1.179075 |
| 20 | 1 | 0 | -2.764511 | -0.716815 | 2.336970 |
| 21 | 1 | 0 | 3.324302 | 1.085892 | 1.705500 |
| 22 | 1 | 0 | 3.052883 | 0.136291 | -2.327804 |
| 23 | 1 | 0 | -0.284737 | 2.616721 | 2.453353 |
| 24 | 1 | 0 | 0.023669 | -0.223549 | 1.632158 |
| 25 | 15 | 0 | -0.116409 | 2.207232 | 0.052760 |
| 26 | 6 | 0 | -0.860550 | 2.952905 | 1.587008 |
| 27 | 1 | 0 | -0.868923 | 4.048754 | 1.549556 |
| 28 | 1 | 0 | -1.885884 | 2.594057 | 1.712684 |
| 29 | 6 | 0 | 1.439212 | 3.227783 | -0.037688 |
| 30 | 1 | 0 | 1.215931 | 4.295253 | 0.070361 |
| 31 | 1 | 0 | 2.129878 | 2.933281 | 0.757425 |
| 32 | 1 | 0 | 1.926903 | 3.067926 | -1.003220 |
| 33 | 6 | 0 | -1.097882 | 3.093054 | -1.255818 |
| 34 | 1 | 0 | -1.068464 | 4.180918 | -1.122953 |
| 35 | 1 | 0 | -0.690389 | 2.828291 | -2.234999 |
| 36 | 1 | 0 | -2.138868 | 2.761555 | -1.227297 |
| 37 | 1 | 0 | 1.422766 | -3.980212 | 0.113242 |
| 38 | 1 | 0 | 2.639291 | -2.361802 | -1.338741 |
| 39 | 1 | 0 | 0.025228 | 0.017262 | -1.788776 |
| 40 | 1 | 0 | 0.120466 | -2.444973 | -1.250174 |
| 41 | 1 | 0 | 2.852814 | -0.495115 | 2.329543 |
| 42 | 1 | 0 | 4.364450 | -0.322713 | 1.380164 |
| 43 | 1 | 0 | 3.617628 | 1.406411 | -1.230918 |
| 44 | 1 | 0 | 4.474011 | -0.150521 | -1.275770 |
| 45 | 1 | 0 | -3.047055 | -0.048505 | -2.315740 |
| 46 | 1 | 0 | -4.427315 | -0.503082 | -1.268129 |
| 47 | 1 | 0 | -3.419694 | 0.791372 | 1.697819 |
| 48 | 1 | 0 | -4.286791 | -0.731600 | 1.387862 |

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**Table S4.** Coordinates and energy values of $\mathbf{3^{Me}}$ (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | 0.016388 | -0.067211 | -0.079286 |
| 2 | 15 | 0 | -2.270514 | -0.496262 | -0.048057 |
| 3 | 15 | 0 | 2.325466 | -0.319003 | -0.047764 |
| 4 | 7 | 0 | 0.104923 | -2.336609 | -0.233340 |
| 5 | 6 | 0 | -2.355330 | -2.353714 | -0.280709 |
| 6 | 6 | 0 | -1.103430 | -2.995765 | 0.311249 |
| 7 | 6 | 0 | 1.353742 | -2.900028 | 0.325612 |
| 8 | 6 | 0 | 2.559233 | -2.167349 | -0.258283 |
| 9 | 6 | 0 | -3.498098 | 0.060454 | -1.329477 |
| 10 | 6 | 0 | -3.298675 | -0.260735 | 1.483890 |
| 11 | 6 | 0 | 3.325770 | 0.014100 | 1.483766 |
| 12 | 6 | 0 | 3.496243 | 0.319625 | -1.342428 |
| 13 | 1 | 0 | -3.261796 | -2.776776 | 0.167775 |
| 14 | 1 | 0 | -2.401128 | -2.548557 | -1.359829 |
| 15 | 1 | 0 | -1.079640 | -2.861190 | 1.397885 |
| 16 | 1 | 0 | -1.083396 | -4.077144 | 0.101854 |
| 17 | 1 | 0 | 1.308025 | -2.760090 | 1.410765 |
| 18 | 1 | 0 | 3.489745 | -2.513355 | 0.206870 |
| 19 | 1 | 0 | -3.730370 | 1.120728 | -1.192164 |
| 20 | 1 | 0 | -2.771906 | -0.699538 | 2.334863 |
| 21 | 1 | 0 | 3.323768 | 1.086556 | 1.700289 |
| 22 | 1 | 0 | 3.067253 | 0.125739 | -2.329037 |
| 23 | 1 | 0 | -0.268660 | 2.612481 | 2.456899 |
| 24 | 1 | 0 | 0.022972 | -0.223356 | 1.626014 |
| 25 | 15 | 0 | -0.112580 | 2.209577 | 0.053895 |
| 26 | 6 | 0 | -0.848578 | 2.951646 | 1.594332 |
| 27 | 1 | 0 | -0.853999 | 4.047558 | 1.560507 |
| 28 | 1 | 0 | -1.874098 | 2.594640 | 1.723436 |
| 29 | 6 | 0 | 1.443277 | 3.229416 | -0.039905 |
| 30 | 1 | 0 | 1.221749 | 4.296604 | 0.074233 |
| 31 | 1 | 0 | 2.137918 | 2.930333 | 0.750011 |
| 32 | 1 | 0 | 1.926798 | 3.073179 | -1.008209 |
| 33 | 6 | 0 | -1.101483 | 3.105591 | -1.242431 |
| 34 | 1 | 0 | -1.071939 | 4.192191 | -1.100195 |
| 35 | 1 | 0 | -0.698115 | 2.851259 | -2.226199 |
| 36 | 1 | 0 | -2.141914 | 2.772794 | -1.211785 |
| 37 | 1 | 0 | 1.417899 | -3.981003 | 0.123166 |
| 38 | 1 | 0 | 2.635831 | -2.371987 | -1.333974 |
| 39 | 1 | 0 | 0.024418 | 0.022631 | -1.798734 |
| 40 | 1 | 0 | 0.115146 | -2.475998 | -1.244669 |
| 41 | 1 | 0 | 2.853714 | -0.495268 | 2.327712 |
| 42 | 1 | 0 | 4.363568 | -0.323384 | 1.378660 |
| 43 | 1 | 0 | 3.623630 | 1.400099 | -1.231824 |
| 44 | 1 | 0 | 4.480767 | -0.157093 | -1.268050 |
| 45 | 1 | 0 | -3.057176 | -0.066031 | -2.321553 |
| 46 | 1 | 0 | -4.433115 | -0.508362 | -1.265233 |
| 47 | 1 | 0 | -3.422187 | 0.807828 | 1.683938 |
| 48 | 1 | 0 | -4.290892 | -0.716094 | 1.383747 |

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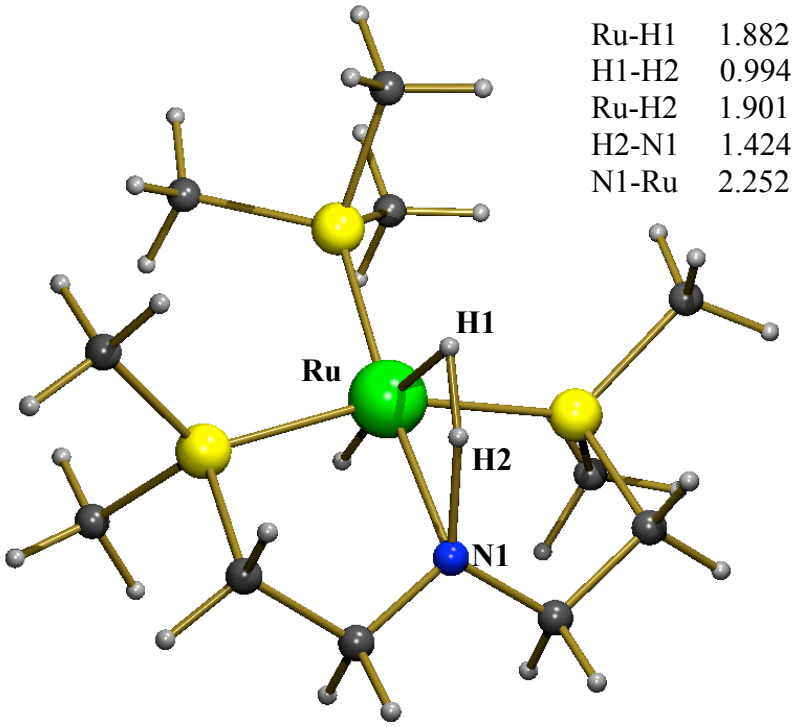



**Figure S8**. Optimized structure of **TS($3^{Me}$⇔$1^{Me}$-$H_2$)**.

**Table S5.** Coordinates and energy values of **TS($3^{Me}$⇔$1^{Me}$-$H_2$)**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | 0.017423 | -0.057529 | -0.055226 |
| 2 | 15 | 0 | -2.256603 | -0.581881 | 0.061487 |
| 3 | 15 | 0 | 2.347058 | -0.289002 | 0.056804 |
| 4 | 7 | 0 | 0.157650 | -2.280333 | -0.388130 |
| 5 | 6 | 0 | -2.299020 | -2.369452 | -0.462898 |
| 6 | 6 | 0 | -1.008500 | -3.049138 | 0.004859 |
| 7 | 6 | 0 | 1.396420 | -2.896070 | 0.046286 |
| 8 | 6 | 0 | 2.605607 | -2.077073 | -0.411559 |
| 9 | 6 | 0 | -3.579156 | 0.155352 | -1.014500 |
| 10 | 6 | 0 | -3.103821 | -0.603252 | 1.709017 |
| 11 | 6 | 0 | 3.192588 | -0.150740 | 1.699350 |
| 12 | 6 | 0 | 3.583733 | 0.546631 | -1.050260 |
| 13 | 1 | 0 | -3.188079 | -2.884708 | -0.079918 |
| 14 | 1 | 0 | -2.347762 | -2.379076 | -1.558493 |
| 15 | 1 | 0 | -1.042020 | -3.173997 | 1.106805 |
| 16 | 1 | 0 | -0.964674 | -4.069987 | -0.418814 |
| 17 | 1 | 0 | 1.417964 | -2.991795 | 1.151358 |
| 18 | 1 | 0 | 3.540724 | -2.472248 | 0.003396 |
| 19 | 1 | 0 | -3.744832 | 1.203754 | -0.748503 |
| 20 | 1 | 0 | -2.498254 | -1.187888 | 2.406025 |
| 21 | 1 | 0 | 3.150468 | 0.885451 | 2.047465 |
| 22 | 1 | 0 | 3.236313 | 0.485880 | -2.085435 |

| | | | | | |
|---|---|---|---|---|---|
| 23 | 1 | 0 | -1.317083 | 2.674883 | 2.086282 |
| 24 | 1 | 0 | 0.015267 | 0.035755 | 1.575678 |
| 25 | 15 | 0 | -0.178017 | 2.237914 | -0.030761 |
| 26 | 6 | 0 | -1.493049 | 2.984494 | 1.052325 |
| 27 | 1 | 0 | -1.491188 | 4.079015 | 0.996403 |
| 28 | 1 | 0 | -2.479547 | 2.620051 | 0.751768 |
| 29 | 6 | 0 | 1.263962 | 3.270644 | 0.530162 |
| 30 | 1 | 0 | 1.020948 | 4.339341 | 0.520916 |
| 31 | 1 | 0 | 1.545281 | 2.978636 | 1.546179 |
| 32 | 1 | 0 | 2.119576 | 3.101281 | -0.128920 |
| 33 | 6 | 0 | -0.561230 | 3.076842 | -1.646740 |
| 34 | 1 | 0 | -0.639250 | 4.165315 | -1.540520 |
| 35 | 1 | 0 | 0.225897 | 2.839037 | -2.368214 |
| 36 | 1 | 0 | -1.502963 | 2.685636 | -2.042663 |
| 37 | 1 | 0 | 1.484578 | -3.923212 | -0.354909 |
| 38 | 1 | 0 | 2.682111 | -2.110017 | -1.505197 |
| 39 | 1 | 0 | 0.042407 | -0.450584 | -1.895420 |
| 40 | 1 | 0 | 0.105217 | -1.340316 | -1.455920 |
| 41 | 1 | 0 | -4.109448 | -1.034207 | 1.642926 |
| 42 | 1 | 0 | -3.173221 | 0.415136 | 2.101668 |
| 43 | 1 | 0 | -4.527651 | -0.384587 | -0.913559 |
| 44 | 1 | 0 | -3.252492 | 0.115857 | -2.057447 |
| 45 | 1 | 0 | 2.655045 | -0.767735 | 2.423594 |
| 46 | 1 | 0 | 4.239786 | -0.469897 | 1.646974 |
| 47 | 1 | 0 | 4.568703 | 0.071787 | -0.972645 |
| 48 | 1 | 0 | 3.686246 | 1.602133 | -0.783207 |

HF= -1611.2317801 / Enthalpies= -1610.797419 / Free Energies= -1610.875631
NImag=1 (Imag. Freq. = -1258.2602 $cm^{-1}$)

**Table S6.** Coordinates and energy values of **TS($3^{Me}$⇔$1^{Me}$-$H_2$)** (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | 0.016912 | -0.060803 | -0.053383 |
| 2 | 15 | 0 | -2.264286 | -0.569817 | 0.057045 |
| 3 | 15 | 0 | 2.348672 | -0.298132 | 0.052524 |
| 4 | 7 | 0 | 0.146497 | -2.286844 | -0.385397 |
| 5 | 6 | 0 | -2.312738 | -2.361108 | -0.455436 |
| 6 | 6 | 0 | -1.025195 | -3.043435 | 0.016899 |
| 7 | 6 | 0 | 1.381951 | -2.901459 | 0.061628 |
| 8 | 6 | 0 | 2.597502 | -2.092729 | -0.397914 |
| 9 | 6 | 0 | -3.573983 | 0.169385 | -1.031699 |
| 10 | 6 | 0 | -3.123249 | -0.576946 | 1.698321 |
| 11 | 6 | 0 | 3.207844 | -0.144731 | 1.686384 |
| 12 | 6 | 0 | 3.578957 | 0.522422 | -1.071418 |
| 13 | 1 | 0 | -3.203883 | -2.869851 | -0.068996 |
| 14 | 1 | 0 | -2.363220 | -2.378686 | -1.550994 |
| 15 | 1 | 0 | -1.058079 | -3.155399 | 1.120482 |
| 16 | 1 | 0 | -0.989097 | -4.069953 | -0.394388 |
| 17 | 1 | 0 | 1.397302 | -2.984249 | 1.168059 |
| 18 | 1 | 0 | 3.528313 | -2.489120 | 0.025095 |
| 19 | 1 | 0 | -3.735265 | 1.219994 | -0.772122 |
| 20 | 1 | 0 | -2.531082 | -1.167537 | 2.401967 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 1 | 0 | 3.172069 | 0.895212 | 2.023712 |
| 22 | 1 | 0 | 3.227023 | 0.449601 | -2.104253 |
| 23 | 1 | 0 | -1.326684 | 2.682168 | 2.078020 |
| 24 | 1 | 0 | 0.014681 | 0.031031 | 1.578287 |
| 25 | 15 | 0 | -0.165951 | 2.239024 | -0.026163 |
| 26 | 6 | 0 | -1.489053 | 2.991107 | 1.041598 |
| 27 | 1 | 0 | -1.479590 | 4.085392 | 0.984854 |
| 28 | 1 | 0 | -2.474313 | 2.632763 | 0.730205 |
| 29 | 6 | 0 | 1.276948 | 3.258833 | 0.552242 |
| 30 | 1 | 0 | 1.043526 | 4.329417 | 0.535336 |
| 31 | 1 | 0 | 1.540942 | 2.968712 | 1.573442 |
| 32 | 1 | 0 | 2.140882 | 3.079441 | -0.093113 |
| 33 | 6 | 0 | -0.525233 | 3.080069 | -1.645904 |
| 34 | 1 | 0 | -0.601280 | 4.168289 | -1.537473 |
| 35 | 1 | 0 | 0.271945 | 2.842989 | -2.356601 |
| 36 | 1 | 0 | -1.463167 | 2.693259 | -2.055093 |
| 37 | 1 | 0 | 1.469076 | -3.934116 | -0.326286 |
| 38 | 1 | 0 | 2.680725 | -2.136863 | -1.490782 |
| 39 | 1 | 0 | 0.039768 | -0.454842 | -1.894991 |
| 40 | 1 | 0 | 0.098405 | -1.341128 | -1.451435 |
| 41 | 1 | 0 | -4.132688 | -0.997077 | 1.624475 |
| 42 | 1 | 0 | -3.185455 | 0.443240 | 2.087360 |
| 43 | 1 | 0 | -4.525940 | -0.364589 | -0.933371 |
| 44 | 1 | 0 | -3.241830 | 0.122550 | -2.072629 |
| 45 | 1 | 0 | 2.677406 | -0.754057 | 2.422346 |
| 46 | 1 | 0 | 4.253580 | -0.466724 | 1.626593 |
| 47 | 1 | 0 | 4.563750 | 0.047764 | -0.992397 |
| 48 | 1 | 0 | 3.683557 | 1.581036 | -0.818000 |

HF= -1611.2339386 / Enthalpies= -1610.799904 / Free Energies= -1610.878141
NImag=1 (Imag. Freq. = -1282.0310 $cm^{-1}$)

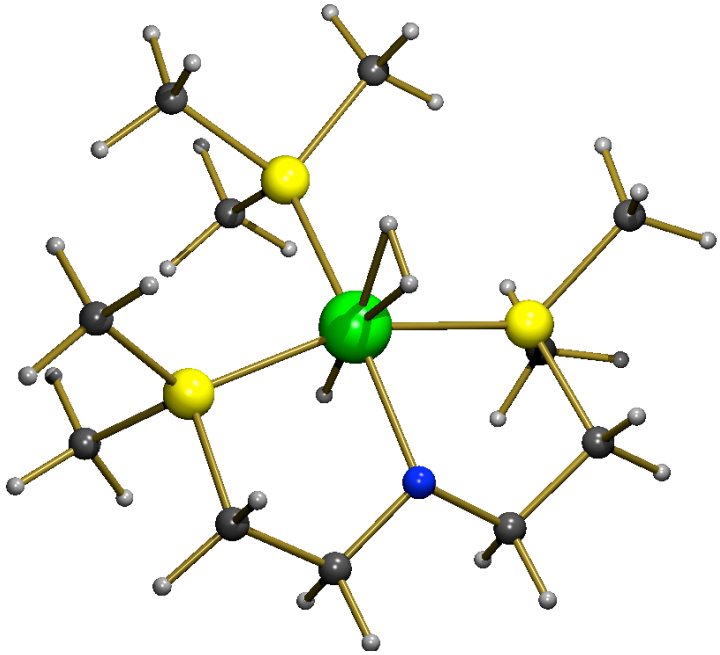


**Figure S9**. Optimized structure of $\mathbf{1^{Me}\text{-}H_2}$.

**Table S7.** Coordinates and energy values of $\mathbf{1^{Me}\text{-}H_2}$.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.006247 | -0.092855 | -0.196118 |
| 2 | 15 | 0 | -2.322468 | -0.429841 | -0.054007 |
| 3 | 15 | 0 | 2.302966 | -0.496736 | -0.054885 |
| 4 | 7 | 0 | -0.036641 | -2.300097 | -0.211751 |
| 5 | 6 | 0 | -2.486734 | -2.269450 | -0.232659 |
| 6 | 6 | 0 | -1.225644 | -2.894895 | 0.366182 |
| 7 | 6 | 0 | 1.132564 | -2.927109 | 0.372673 |
| 8 | 6 | 0 | 2.413471 | -2.341198 | -0.223648 |
| 9 | 6 | 0 | -3.561485 | 0.210618 | -1.281232 |
| 10 | 6 | 0 | -3.189697 | -0.070742 | 1.543780 |
| 11 | 6 | 0 | 3.180565 | -0.149485 | 1.539689 |
| 12 | 6 | 0 | 3.562265 | 0.097932 | -1.285200 |
| 13 | 1 | 0 | -3.406364 | -2.643559 | 0.234119 |
| 14 | 1 | 0 | -2.528269 | -2.489635 | -1.306277 |
| 15 | 1 | 0 | -1.265165 | -2.790100 | 1.476269 |
| 16 | 1 | 0 | -1.242360 | -3.984781 | 0.171805 |
| 17 | 1 | 0 | 1.171324 | -2.820199 | 1.482550 |
| 18 | 1 | 0 | 3.320231 | -2.739721 | 0.248100 |
| 19 | 1 | 0 | -3.664138 | 1.295838 | -1.192823 |
| 20 | 1 | 0 | -2.643708 | -0.558217 | 2.355409 |
| 21 | 1 | 0 | 3.212072 | 0.929428 | 1.721035 |
| 22 | 1 | 0 | 3.207883 | -0.118359 | -2.297360 |
| 23 | 1 | 0 | 1.041529 | 2.437772 | 2.284892 |
| 24 | 1 | 0 | -0.010214 | -0.177415 | 1.405016 |
| 25 | 15 | 0 | 0.039916 | 2.239056 | 0.059837 |

| | | | | | |
|---|---|---|---|---|---|
| 26 | 6 | 0 | 0.140722 | 2.841595 | 1.814549 |
| 27 | 1 | 0 | 0.160870 | 3.936041 | 1.870271 |
| 28 | 1 | 0 | -0.719311 | 2.465102 | 2.374897 |
| 29 | 6 | 0 | 1.431211 | 3.229279 | -0.686582 |
| 30 | 1 | 0 | 1.301564 | 4.303648 | -0.512264 |
| 31 | 1 | 0 | 2.382714 | 2.918682 | -0.245913 |
| 32 | 1 | 0 | 1.479605 | 3.045314 | -1.764077 |
| 33 | 6 | 0 | -1.389402 | 3.274268 | -0.538170 |
| 34 | 1 | 0 | -1.224021 | 4.340303 | -0.343334 |
| 35 | 1 | 0 | -1.528920 | 3.126162 | -1.613312 |
| 36 | 1 | 0 | -2.307476 | 2.966289 | -0.029839 |
| 37 | 1 | 0 | 1.118305 | -4.017600 | 0.181615 |
| 38 | 1 | 0 | 2.452528 | -2.566972 | -1.296172 |
| 39 | 1 | 0 | -0.011593 | 0.249289 | -2.073387 |
| 40 | 1 | 0 | -0.002837 | -0.547841 | -2.020059 |
| 41 | 1 | 0 | -3.215917 | -0.017923 | -2.293770 |
| 42 | 1 | 0 | -4.544501 | -0.249975 | -1.129123 |
| 43 | 1 | 0 | -4.224222 | -0.431895 | 1.531008 |
| 44 | 1 | 0 | -3.192160 | 1.006609 | 1.736569 |
| 45 | 1 | 0 | 2.621677 | -0.613575 | 2.356210 |
| 46 | 1 | 0 | 4.205019 | -0.538360 | 1.530625 |
| 47 | 1 | 0 | 3.706363 | 1.178562 | -1.198285 |
| 48 | 1 | 0 | 4.527602 | -0.398688 | -1.133410 |

HF= -1611.2484485 / Enthalpies= -1610.810919 / Free Energies= -1610.889892
NImag=0

**Table S8.** Coordinates and energy values of $\mathbf{1^{Me}\text{-}H_2}$ (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.006249 | -0.098414 | -0.200778 |
| 2 | 15 | 0 | -2.324790 | -0.422785 | -0.054816 |
| 3 | 15 | 0 | 2.304740 | -0.492429 | -0.056451 |
| 4 | 7 | 0 | -0.037832 | -2.315395 | -0.223339 |
| 5 | 6 | 0 | -2.493223 | -2.265247 | -0.215872 |
| 6 | 6 | 0 | -1.227965 | -2.892423 | 0.372713 |
| 7 | 6 | 0 | 1.130147 | -2.924848 | 0.384470 |
| 8 | 6 | 0 | 2.418058 | -2.340132 | -0.198414 |
| 9 | 6 | 0 | -3.558968 | 0.206744 | -1.290740 |
| 10 | 6 | 0 | -3.194225 | -0.047611 | 1.537503 |
| 11 | 6 | 0 | 3.186073 | -0.122541 | 1.530485 |
| 12 | 6 | 0 | 3.558463 | 0.085467 | -1.298513 |
| 13 | 1 | 0 | -3.408069 | -2.633553 | 0.264598 |
| 14 | 1 | 0 | -2.551490 | -2.493467 | -1.287236 |
| 15 | 1 | 0 | -1.252771 | -2.769867 | 1.481882 |
| 16 | 1 | 0 | -1.257696 | -3.986414 | 0.197243 |
| 17 | 1 | 0 | 1.150699 | -2.797705 | 1.493123 |
| 18 | 1 | 0 | 3.317886 | -2.731227 | 0.292274 |
| 19 | 1 | 0 | -3.657964 | 1.293043 | -1.213667 |
| 20 | 1 | 0 | -2.652583 | -0.528969 | 2.355736 |
| 21 | 1 | 0 | 3.215158 | 0.958456 | 1.698605 |
| 22 | 1 | 0 | 3.201937 | -0.145635 | -2.306619 |
| 23 | 1 | 0 | 1.038125 | 2.429200 | 2.290873 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 1 | 0 | -0.009376 | -0.190244 | 1.402388 |
| 25 | 15 | 0 | 0.041441 | 2.236417 | 0.063781 |
| 26 | 6 | 0 | 0.138577 | 2.834004 | 1.819042 |
| 27 | 1 | 0 | 0.160285 | 3.928177 | 1.874966 |
| 28 | 1 | 0 | -0.724406 | 2.459435 | 2.376159 |
| 29 | 6 | 0 | 1.436004 | 3.218696 | -0.682146 |
| 30 | 1 | 0 | 1.307483 | 4.293066 | -0.508719 |
| 31 | 1 | 0 | 2.386675 | 2.907760 | -0.240125 |
| 32 | 1 | 0 | 1.484111 | 3.034174 | -1.759502 |
| 33 | 6 | 0 | -1.386496 | 3.266798 | -0.539937 |
| 34 | 1 | 0 | -1.219143 | 4.332955 | -0.348894 |
| 35 | 1 | 0 | -1.524386 | 3.115095 | -1.614755 |
| 36 | 1 | 0 | -2.305546 | 2.963056 | -0.030976 |
| 37 | 1 | 0 | 1.128096 | -4.020061 | 0.214291 |
| 38 | 1 | 0 | 2.477839 | -2.579374 | -1.267310 |
| 39 | 1 | 0 | -0.009006 | 0.275566 | -2.061637 |
| 40 | 1 | 0 | -0.004496 | -0.524649 | -2.022729 |
| 41 | 1 | 0 | -3.212757 | -0.033398 | -2.300341 |
| 42 | 1 | 0 | -4.543591 | -0.248589 | -1.134240 |
| 43 | 1 | 0 | -4.229452 | -0.406256 | 1.523883 |
| 44 | 1 | 0 | -3.195287 | 1.031303 | 1.720662 |
| 45 | 1 | 0 | 2.632871 | -0.578410 | 2.355545 |
| 46 | 1 | 0 | 4.211717 | -0.507841 | 1.521028 |
| 47 | 1 | 0 | 3.700253 | 1.167389 | -1.226876 |
| 48 | 1 | 0 | 4.525130 | -0.406547 | -1.141296 |

HF= -1611.2516627 / Enthalpies= -1610.814499 / Free Energies= -1610.893776
NImag=0

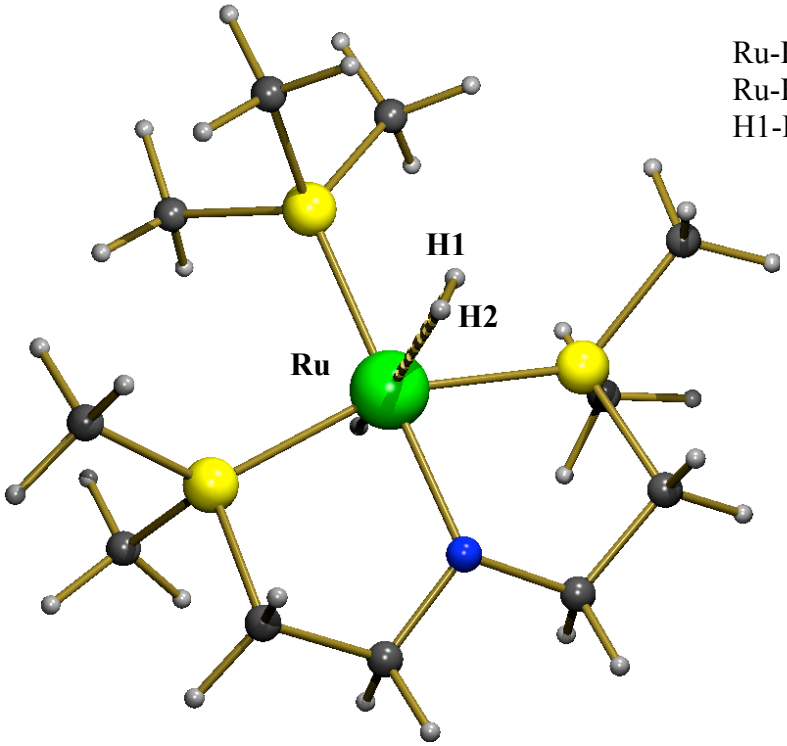



**Figure S10**. Optimized structure of **TS($1^{Me}$-$H_2$⇔$1^{Me}$)**.

**Table S9.** Coordinates and energy values of **TS($1^{Me}$-$H_2$⇔$1^{Me}$)**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.026142 | -0.077475 | -0.080148 |
| 2 | 15 | 0 | -2.361853 | -0.242237 | 0.066281 |
| 3 | 15 | 0 | 2.226501 | -0.687110 | 0.060302 |
| 4 | 7 | 0 | -0.231834 | -2.181551 | -0.365686 |
| 5 | 6 | 0 | -2.676358 | -1.988733 | -0.478140 |
| 6 | 6 | 0 | -1.485594 | -2.832829 | -0.021542 |
| 7 | 6 | 0 | 0.872832 | -3.058946 | -0.011936 |
| 8 | 6 | 0 | 2.205546 | -2.464906 | -0.472196 |
| 9 | 6 | 0 | -3.623936 | 0.707661 | -0.915481 |
| 10 | 6 | 0 | -3.117598 | -0.171830 | 1.757187 |
| 11 | 6 | 0 | 3.002836 | -0.758471 | 1.742556 |
| 12 | 6 | 0 | 3.624204 | 0.020271 | -0.939871 |
| 13 | 1 | 0 | -3.632168 | -2.371785 | -0.098744 |
| 14 | 1 | 0 | -2.718712 | -1.977174 | -1.573870 |
| 15 | 1 | 0 | -1.577691 | -3.029745 | 1.070656 |
| 16 | 1 | 0 | -1.546108 | -3.827150 | -0.503163 |
| 17 | 1 | 0 | 0.923162 | -3.259297 | 1.082226 |
| 18 | 1 | 0 | 3.068554 | -3.019218 | -0.082395 |
| 19 | 1 | 0 | -3.671253 | 1.745450 | -0.573364 |
| 20 | 1 | 0 | -2.579230 | -0.859607 | 2.414342 |
| 21 | 1 | 0 | 3.101946 | 0.251052 | 2.151040 |
| 22 | 1 | 0 | 3.342341 | 0.032015 | -1.996769 |
| 23 | 1 | 0 | 2.538294 | 2.505909 | 0.896785 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 1 | 0 | -0.019838 | 0.013147 | 1.492201 |
| 25 | 15 | 0 | 0.267233 | 2.234479 | -0.015448 |
| 26 | 6 | 0 | 1.551007 | 2.894954 | 1.162966 |
| 27 | 1 | 0 | 1.591366 | 3.990175 | 1.148940 |
| 28 | 1 | 0 | 1.315287 | 2.556734 | 2.176113 |
| 29 | 6 | 0 | 0.803222 | 3.117645 | -1.570473 |
| 30 | 1 | 0 | 0.941908 | 4.192661 | -1.405488 |
| 31 | 1 | 0 | 1.744222 | 2.688294 | -1.927147 |
| 32 | 1 | 0 | 0.051551 | 2.973311 | -2.352618 |
| 33 | 6 | 0 | -1.148946 | 3.342223 | 0.473110 |
| 34 | 1 | 0 | -0.836604 | 4.390987 | 0.535626 |
| 35 | 1 | 0 | -1.952580 | 3.261682 | -0.264127 |
| 36 | 1 | 0 | -1.539425 | 3.031043 | 1.446567 |
| 37 | 1 | 0 | 0.741320 | -4.050684 | -0.484591 |
| 38 | 1 | 0 | 2.254078 | -2.474446 | -1.567658 |
| 39 | 1 | 0 | -0.374834 | 0.333766 | -2.429334 |
| 40 | 1 | 0 | 0.026844 | -0.116296 | -2.875814 |
| 41 | 1 | 0 | 4.538939 | -0.572137 | -0.821777 |
| 42 | 1 | 0 | 3.832775 | 1.049131 | -0.630657 |
| 43 | 1 | 0 | 3.990759 | -1.231611 | 1.709893 |
| 44 | 1 | 0 | 2.349659 | -1.328201 | 2.408328 |
| 45 | 1 | 0 | -4.179456 | -0.441818 | 1.737712 |
| 46 | 1 | 0 | -3.011389 | 0.837368 | 2.165834 |
| 47 | 1 | 0 | -4.619771 | 0.260793 | -0.813774 |
| 48 | 1 | 0 | -3.342362 | 0.706222 | -1.972737 |

HF= -1611.2426722 / Enthalpies= -1610.807918 / Free Energies= -1610.888490
NImag=1 (Imag. Freq. = -238.2838 $cm^{-1}$)

**Table S10.** Coordinates and energy values of **TS($1^{Me}$-$H_2$⇔$1^{Me}$)** (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.025935 | -0.081305 | -0.079152 |
| 2 | 15 | 0 | -2.362750 | -0.247326 | 0.065525 |
| 3 | 15 | 0 | 2.232102 | -0.677059 | 0.060276 |
| 4 | 7 | 0 | -0.224462 | -2.187860 | -0.373796 |
| 5 | 6 | 0 | -2.672596 | -2.000526 | -0.463918 |
| 6 | 6 | 0 | -1.474666 | -2.837662 | -0.013061 |
| 7 | 6 | 0 | 0.884964 | -3.056240 | -0.011078 |
| 8 | 6 | 0 | 2.217765 | -2.457952 | -0.465737 |
| 9 | 6 | 0 | -3.624831 | 0.689239 | -0.927285 |
| 10 | 6 | 0 | -3.122880 | -0.164865 | 1.753794 |
| 11 | 6 | 0 | 3.014855 | -0.739039 | 1.739704 |
| 12 | 6 | 0 | 3.621250 | 0.032788 | -0.948205 |
| 13 | 1 | 0 | -3.623467 | -2.384988 | -0.073943 |
| 14 | 1 | 0 | -2.726391 | -1.996040 | -1.559339 |
| 15 | 1 | 0 | -1.555032 | -3.023016 | 1.082685 |
| 16 | 1 | 0 | -1.539557 | -3.838375 | -0.482859 |
| 17 | 1 | 0 | 0.930487 | -3.248358 | 1.085382 |
| 18 | 1 | 0 | 3.080557 | -3.008244 | -0.070053 |
| 19 | 1 | 0 | -3.677376 | 1.729147 | -0.592776 |
| 20 | 1 | 0 | -2.586410 | -0.846912 | 2.418586 |
| 21 | 1 | 0 | 3.111206 | 0.272533 | 2.143666 |

| | | | | | |
|---|---|---|---|---|---|
| 22 | 1 | 0 | 3.336766 | 0.036002 | -2.004449 |
| 23 | 1 | 0 | 2.528363 | 2.511908 | 0.901360 |
| 24 | 1 | 0 | -0.022520 | 0.014675 | 1.492972 |
| 25 | 15 | 0 | 0.258954 | 2.234647 | -0.012934 |
| 26 | 6 | 0 | 1.539579 | 2.898307 | 1.165656 |
| 27 | 1 | 0 | 1.576482 | 3.993454 | 1.149224 |
| 28 | 1 | 0 | 1.303546 | 2.562067 | 2.179416 |
| 29 | 6 | 0 | 0.791671 | 3.114298 | -1.569456 |
| 30 | 1 | 0 | 0.927444 | 4.189505 | -1.404606 |
| 31 | 1 | 0 | 1.733703 | 2.687249 | -1.926023 |
| 32 | 1 | 0 | 0.039330 | 2.967558 | -2.350405 |
| 33 | 6 | 0 | -1.162787 | 3.334448 | 0.473396 |
| 34 | 1 | 0 | -0.854581 | 4.384350 | 0.534892 |
| 35 | 1 | 0 | -1.965103 | 3.250046 | -0.264778 |
| 36 | 1 | 0 | -1.552979 | 3.023116 | 1.446912 |
| 37 | 1 | 0 | 0.762785 | -4.053531 | -0.476612 |
| 38 | 1 | 0 | 2.273718 | -2.470911 | -1.560951 |
| 39 | 1 | 0 | -0.389113 | 0.328322 | -2.442918 |
| 40 | 1 | 0 | 0.028758 | -0.045448 | -2.941443 |
| 41 | 1 | 0 | 4.540130 | -0.552546 | -0.828188 |
| 42 | 1 | 0 | 3.823351 | 1.064889 | -0.645837 |
| 43 | 1 | 0 | 4.004980 | -1.207000 | 1.703672 |
| 44 | 1 | 0 | 2.368180 | -1.309871 | 2.410994 |
| 45 | 1 | 0 | -4.184236 | -0.436234 | 1.732483 |
| 46 | 1 | 0 | -3.019784 | 0.847872 | 2.154368 |
| 47 | 1 | 0 | -4.618852 | 0.238910 | -0.824247 |
| 48 | 1 | 0 | -3.340534 | 0.681583 | -1.983766 |

HF= -1611.2445368 / Enthalpies= -1610.810145 / Free Energies= -1610.890836

NImag=1 (Imag. Freq. = -236.7815 $cm^{-1}$)

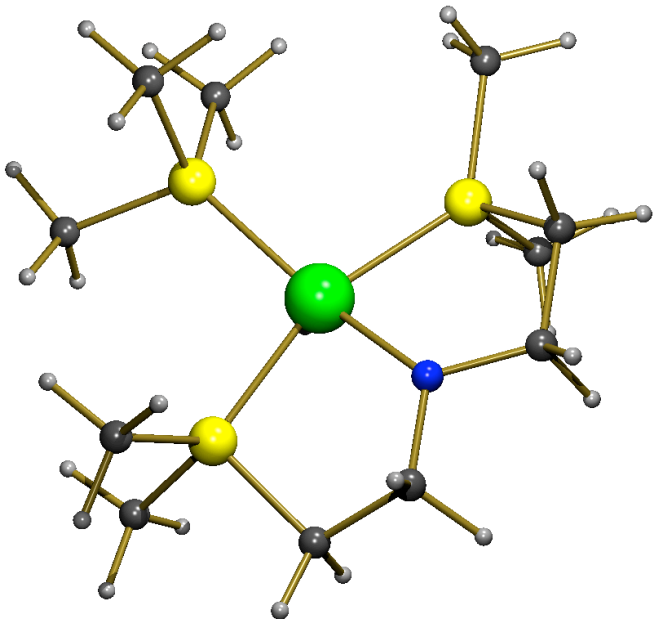


**Figure S11**. Optimized structure of $\mathbf{1}^{\mathbf{Me}}$.

**Table S11.** Coordinates and energy values of $\mathbf{1}^{\mathbf{Me}}$.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.012327 | -0.066652 | 0.114086 |
| 2 | 15 | 0 | -2.330097 | -0.336542 | 0.190405 |
| 3 | 15 | 0 | 2.252161 | -0.595733 | 0.189041 |
| 4 | 7 | 0 | -0.132848 | -2.035804 | -0.474527 |
| 5 | 6 | 0 | -2.567627 | -1.829583 | -0.888166 |
| 6 | 6 | 0 | -1.378556 | -2.771303 | -0.681130 |
| 7 | 6 | 0 | 0.999805 | -2.966430 | -0.493581 |
| 8 | 6 | 0 | 2.183139 | -2.444851 | 0.331266 |
| 9 | 6 | 0 | -3.691910 | 0.781138 | -0.403783 |
| 10 | 6 | 0 | -3.022916 | -0.862746 | 1.827667 |
| 11 | 6 | 0 | 3.398036 | -0.125810 | 1.567884 |
| 12 | 6 | 0 | 3.353187 | -0.335952 | -1.288953 |
| 13 | 1 | 0 | -3.524798 | -2.332968 | -0.699370 |
| 14 | 1 | 0 | -2.574939 | -1.458486 | -1.920225 |
| 15 | 1 | 0 | -1.586684 | -3.442204 | 0.177761 |
| 16 | 1 | 0 | -1.290820 | -3.436988 | -1.558717 |
| 17 | 1 | 0 | 0.702219 | -3.949260 | -0.085057 |
| 18 | 1 | 0 | 3.130258 | -2.920371 | 0.044036 |
| 19 | 1 | 0 | -3.809275 | 1.628837 | 0.277464 |
| 20 | 1 | 0 | -2.420335 | -1.687316 | 2.216957 |
| 21 | 1 | 0 | 3.635602 | 0.940358 | 1.513403 |
| 22 | 1 | 0 | 2.856943 | -0.736889 | -2.177459 |
| 23 | 1 | 0 | 2.573459 | 2.670243 | -0.100423 |
| 24 | 1 | 0 | 0.016557 | 0.386225 | 1.644931 |
| 25 | 15 | 0 | 0.155299 | 2.217942 | -0.153018 |
| 26 | 6 | 0 | 1.701709 | 3.088854 | 0.411286 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | 1 | 0 | 1.658746 | 4.164572 | 0.205827 |
| 28 | 1 | 0 | 1.828185 | 2.934523 | 1.486755 |
| 29 | 6 | 0 | 0.077169 | 2.834858 | -1.910914 |
| 30 | 1 | 0 | 0.175562 | 3.925563 | -1.971360 |
| 31 | 1 | 0 | 0.876974 | 2.369048 | -2.494143 |
| 32 | 1 | 0 | -0.876568 | 2.536899 | -2.356593 |
| 33 | 6 | 0 | -1.098571 | 3.351617 | 0.628886 |
| 34 | 1 | 0 | -0.861170 | 4.405451 | 0.442973 |
| 35 | 1 | 0 | -2.092700 | 3.142221 | 0.226295 |
| 36 | 1 | 0 | -1.120776 | 3.172615 | 1.707713 |
| 37 | 1 | 0 | 1.325048 | -3.163799 | -1.532777 |
| 38 | 1 | 0 | 2.006198 | -2.652911 | 1.393034 |
| 39 | 1 | 0 | 2.900153 | -0.314446 | 2.522678 |
| 40 | 1 | 0 | 4.331507 | -0.698430 | 1.524032 |
| 41 | 1 | 0 | 4.322336 | -0.832634 | -1.163741 |
| 42 | 1 | 0 | 3.523922 | 0.732733 | -1.451362 |
| 43 | 1 | 0 | -4.068954 | -1.179904 | 1.746790 |
| 44 | 1 | 0 | -2.948948 | -0.031632 | 2.534778 |
| 45 | 1 | 0 | -4.645087 | 0.242148 | -0.452572 |
| 46 | 1 | 0 | -3.451542 | 1.166363 | -1.398914 |

HF= -1610.0651913 / Enthalpies= -1609.645828 / Free Energies= -1609.722081
NImag=0

**Table S12.** Coordinates and energy values of $\mathbf{1}^{\mathbf{Me}}$ (PCM).

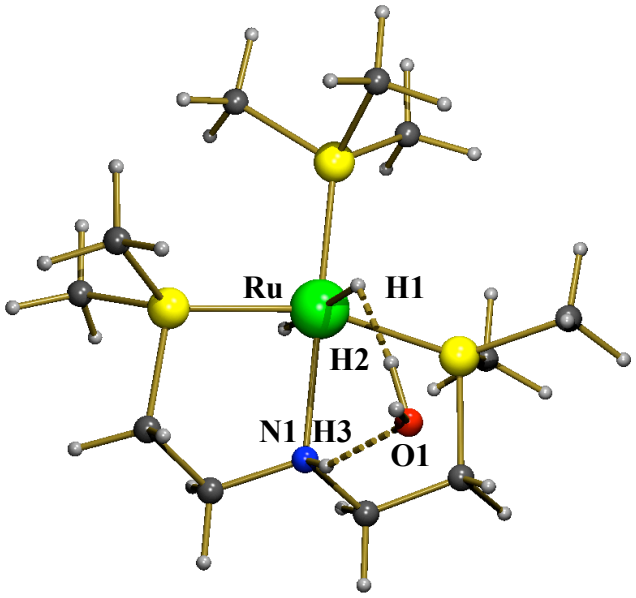
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.006448 | -0.069441 | 0.120373 |
| 2 | 15 | 0 | -2.322089 | -0.375446 | 0.191485 |
| 3 | 15 | 0 | 2.269908 | -0.554969 | 0.188342 |
| 4 | 7 | 0 | -0.091401 | -2.038415 | -0.475364 |
| 5 | 6 | 0 | -2.530392 | -1.874907 | -0.885189 |
| 6 | 6 | 0 | -1.325507 | -2.795670 | -0.676444 |
| 7 | 6 | 0 | 1.059234 | -2.947822 | -0.498714 |
| 8 | 6 | 0 | 2.235574 | -2.406254 | 0.323678 |
| 9 | 6 | 0 | -3.694319 | 0.721045 | -0.414788 |
| 10 | 6 | 0 | -3.020110 | -0.908968 | 1.824202 |
| 11 | 6 | 0 | 3.405662 | -0.066131 | 1.568035 |
| 12 | 6 | 0 | 3.366395 | -0.270853 | -1.287276 |
| 13 | 1 | 0 | -3.479264 | -2.393911 | -0.697310 |
| 14 | 1 | 0 | -2.543749 | -1.504965 | -1.917707 |
| 15 | 1 | 0 | -1.520664 | -3.466485 | 0.185736 |
| 16 | 1 | 0 | -1.228804 | -3.463909 | -1.551755 |
| 17 | 1 | 0 | 0.780658 | -3.937008 | -0.091503 |
| 18 | 1 | 0 | 3.190480 | -2.862143 | 0.030864 |
| 19 | 1 | 0 | -3.832148 | 1.567117 | 0.264595 |
| 20 | 1 | 0 | -2.405058 | -1.718669 | 2.225049 |
| 21 | 1 | 0 | 3.621223 | 1.004817 | 1.515576 |
| 22 | 1 | 0 | 2.878432 | -0.674027 | -2.179287 |
| 23 | 1 | 0 | 2.516398 | 2.723573 | -0.223230 |
| 24 | 1 | 0 | 0.019842 | 0.391109 | 1.650656 |
| 25 | 15 | 0 | 0.107186 | 2.219434 | -0.153648 |

| | | | | | |
|---|---|---|---|---|---|
| 26 | 6 | 0 | 1.661022 | 3.125375 | 0.327903 |
| 27 | 1 | 0 | 1.582419 | 4.198085 | 0.117664 |
| 28 | 1 | 0 | 1.844045 | 2.984466 | 1.397238 |
| 29 | 6 | 0 | -0.077183 | 2.827180 | -1.906228 |
| 30 | 1 | 0 | -0.005224 | 3.919473 | -1.972985 |
| 31 | 1 | 0 | 0.702065 | 2.377729 | -2.529248 |
| 32 | 1 | 0 | -1.047066 | 2.508012 | -2.299974 |
| 33 | 6 | 0 | -1.128099 | 3.323878 | 0.695600 |
| 34 | 1 | 0 | -0.937039 | 4.381987 | 0.483048 |
| 35 | 1 | 0 | -2.139798 | 3.077189 | 0.364009 |
| 36 | 1 | 0 | -1.073041 | 3.158154 | 1.775396 |
| 37 | 1 | 0 | 1.386687 | -3.137263 | -1.538989 |
| 38 | 1 | 0 | 2.068079 | -2.622588 | 1.385403 |
| 39 | 1 | 0 | 2.912201 | -0.267929 | 2.522495 |
| 40 | 1 | 0 | 4.351054 | -0.618778 | 1.523202 |
| 41 | 1 | 0 | 4.342123 | -0.754396 | -1.162267 |
| 42 | 1 | 0 | 3.522499 | 0.801009 | -1.442675 |
| 43 | 1 | 0 | -4.058185 | -1.248560 | 1.733030 |
| 44 | 1 | 0 | -2.974357 | -0.071882 | 2.526958 |
| 45 | 1 | 0 | -4.638665 | 0.167653 | -0.472583 |
| 46 | 1 | 0 | -3.450341 | 1.109906 | -1.407629 |

HF= -1610.0668654 / Enthalpies= -1609.646864 / Free Energies= -1609.726165
NImag=0

*Optimized structures for water assisted $H_2$-activation (Bond length in parantheses from PCM calculation)*

**Figure S12**. Optimized structure of **$3^{Me}$-$H_2O$.**




| | |
|---|---|
| Ru-H1 | 1.738 (1.737) |
| H1-H2 | 1.512 (1.511) |
| O1-H2 | 1.001 (1.001) |
| O1-H3 | 2.062 (2.081) |
| N1-H3 | 1.025 (1.024) |
| N1-Ru | 2.289 (2.288) |

**Table S13.** Coordinates and energy values of **$3^{Me}$-$H_2O$.**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.034334 | 0.032477 | -0.051915 |
| 2 | 15 | 0 | 2.290892 | -0.047813 | -0.215776 |
| 3 | 15 | 0 | -2.277987 | -0.563878 | -0.095904 |
| 4 | 7 | 0 | 0.224485 | -2.236629 | -0.205414 |
| 5 | 6 | 0 | 2.656625 | -1.882545 | -0.233945 |
| 6 | 6 | 0 | 1.484561 | -2.618664 | -0.880662 |
| 7 | 6 | 0 | -0.955742 | -2.904795 | -0.792250 |
| 8 | 6 | 0 | -2.221508 | -2.436006 | -0.076674 |
| 9 | 6 | 0 | 3.458989 | 0.542363 | 1.101623 |
| 10 | 6 | 0 | 3.180340 | 0.529836 | -1.742133 |
| 11 | 6 | 0 | -3.344524 | -0.239542 | -1.583568 |
| 12 | 6 | 0 | -3.497821 | -0.227701 | 1.265266 |
| 13 | 1 | 0 | 3.594513 | -2.100980 | -0.757962 |
| 14 | 1 | 0 | 2.765929 | -2.205682 | 0.807485 |
| 15 | 1 | 0 | 1.386709 | -2.342926 | -1.936303 |
| 16 | 1 | 0 | 1.636718 | -3.708739 | -0.825725 |
| 17 | 1 | 0 | -0.991430 | -2.635301 | -1.853308 |
| 18 | 1 | 0 | -3.116825 | -2.874193 | -0.533692 |
| 19 | 1 | 0 | 3.441476 | 1.635616 | 1.152045 |
| 20 | 1 | 0 | 2.686781 | 0.102154 | -2.618617 |
| 21 | 1 | 0 | -3.523719 | 0.834323 | -1.684225 |

| | | | | | |
|---|---|---|---|---|---|
| 22 | 1 | 0 | -3.038547 | -0.487198 | 2.222721 |
| 23 | 1 | 0 | 1.041046 | 3.147597 | -1.784269 |
| 24 | 1 | 0 | -0.085700 | 0.131942 | -1.740656 |
| 25 | 15 | 0 | -0.280283 | 2.298627 | 0.092737 |
| 26 | 6 | 0 | 0.991545 | 3.388056 | -0.718618 |
| 27 | 1 | 0 | 0.744366 | 4.449052 | -0.598986 |
| 28 | 1 | 0 | 1.976009 | 3.207872 | -0.277002 |
| 29 | 6 | 0 | -1.806622 | 3.079248 | -0.630836 |
| 30 | 1 | 0 | -1.792790 | 4.168999 | -0.514982 |
| 31 | 1 | 0 | -1.865223 | 2.831528 | -1.694247 |
| 32 | 1 | 0 | -2.699196 | 2.687921 | -0.134033 |
| 33 | 6 | 0 | -0.308167 | 3.048758 | 1.792531 |
| 34 | 1 | 0 | -0.415375 | 4.139750 | 1.764986 |
| 35 | 1 | 0 | -1.135661 | 2.613697 | 2.359570 |
| 36 | 1 | 0 | 0.617392 | 2.783266 | 2.310372 |
| 37 | 1 | 0 | -0.855668 | -4.000316 | -0.724435 |
| 38 | 1 | 0 | -2.194688 | -2.755887 | 0.972439 |
| 39 | 1 | 0 | 0.004105 | -0.041436 | 1.683850 |
| 40 | 1 | 0 | 0.300656 | -2.524419 | 0.774977 |
| 41 | 1 | 0 | -2.808239 | -0.570046 | -2.476843 |
| 42 | 1 | 0 | -4.309191 | -0.756203 | -1.516116 |
| 43 | 1 | 0 | -3.744396 | 0.838516 | 1.287211 |
| 44 | 1 | 0 | -4.425399 | -0.797443 | 1.134852 |
| 45 | 1 | 0 | 3.124555 | 0.150377 | 2.065588 |
| 46 | 1 | 0 | 4.488550 | 0.217458 | 0.910720 |
| 47 | 1 | 0 | 3.115471 | 1.618076 | -1.823354 |
| 48 | 1 | 0 | 4.236775 | 0.236888 | -1.729763 |
| 49 | 1 | 0 | 0.542393 | -1.265824 | 2.389273 |
| 50 | 8 | 0 | 0.866174 | -2.152054 | 2.723091 |
| 51 | 1 | 0 | 0.493105 | -2.262672 | 3.605596 |

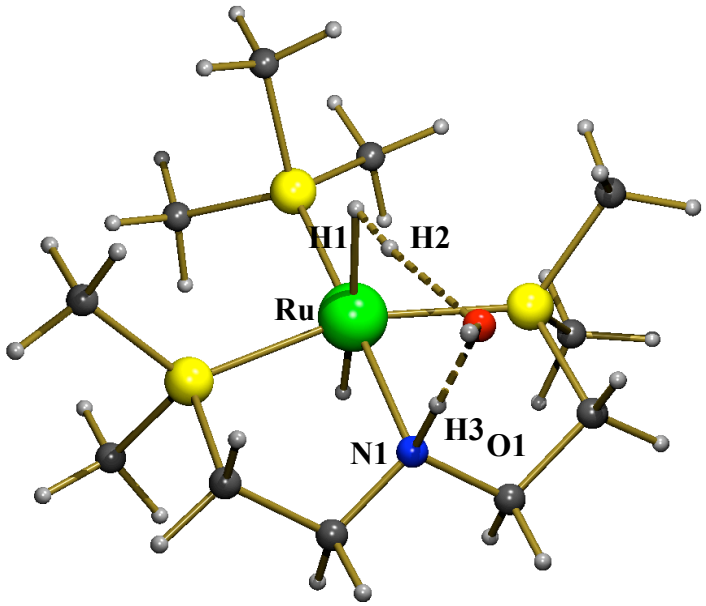
HF= -1687.7216048 / Enthalpies= -1687.252743/ Free Energies= -1687.336924
NImag=0

**Table S14.** Coordinates and energy values of **$3^{Me}$-$H_2O$** (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.029523 | 0.034301 | -0.058936 |
| 2 | 15 | 0 | 2.294948 | -0.068883 | -0.209981 |
| 3 | 15 | 0 | -2.281058 | -0.542901 | -0.101996 |
| 4 | 7 | 0 | 0.206012 | -2.236293 | -0.214967 |
| 5 | 6 | 0 | 2.641397 | -1.907628 | -0.227977 |
| 6 | 6 | 0 | 1.466296 | -2.632220 | -0.882234 |
| 7 | 6 | 0 | -0.978799 | -2.893346 | -0.806632 |
| 8 | 6 | 0 | -2.241435 | -2.415281 | -0.091665 |
| 9 | 6 | 0 | 3.456559 | 0.507697 | 1.119144 |
| 10 | 6 | 0 | 3.205842 | 0.502431 | -1.725933 |
| 11 | 6 | 0 | -3.349691 | -0.202345 | -1.584306 |
| 12 | 6 | 0 | -3.493002 | -0.199989 | 1.264336 |
| 13 | 1 | 0 | 3.580690 | -2.135616 | -0.745237 |
| 14 | 1 | 0 | 2.741573 | -2.232547 | 0.813976 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | 1 | 0 | 1.378632 | -2.356560 | -1.938749 |
| 16 | 1 | 0 | 1.606596 | -3.723646 | -0.825883 |
| 17 | 1 | 0 | -1.009879 | -2.621522 | -1.867201 |
| 18 | 1 | 0 | -3.139961 | -2.842612 | -0.552419 |
| 19 | 1 | 0 | 3.454967 | 1.601261 | 1.166177 |
| 20 | 1 | 0 | 2.721898 | 0.075456 | -2.608134 |
| 21 | 1 | 0 | -3.516563 | 0.873670 | -1.682529 |
| 22 | 1 | 0 | -3.033800 | -0.468120 | 2.219465 |
| 23 | 1 | 0 | 1.076538 | 3.147931 | -1.777100 |
| 24 | 1 | 0 | -0.077630 | 0.140375 | -1.749551 |
| 25 | 15 | 0 | -0.257861 | 2.302331 | 0.092614 |
| 26 | 6 | 0 | 1.024972 | 3.384746 | -0.710696 |
| 27 | 1 | 0 | 0.785528 | 4.447149 | -0.588102 |
| 28 | 1 | 0 | 2.006564 | 3.195219 | -0.266642 |
| 29 | 6 | 0 | -1.776649 | 3.097099 | -0.631228 |
| 30 | 1 | 0 | -1.754276 | 4.186253 | -0.511556 |
| 31 | 1 | 0 | -1.835342 | 2.853745 | -1.695656 |
| 32 | 1 | 0 | -2.673401 | 2.710909 | -0.137834 |
| 33 | 6 | 0 | -0.284720 | 3.047646 | 1.794810 |
| 34 | 1 | 0 | -0.383185 | 4.139488 | 1.769781 |
| 35 | 1 | 0 | -1.117820 | 2.617920 | 2.357761 |
| 36 | 1 | 0 | 0.637412 | 2.773707 | 2.314436 |
| 37 | 1 | 0 | -0.888099 | -3.989571 | -0.740724 |
| 38 | 1 | 0 | -2.220442 | -2.740621 | 0.955957 |
| 39 | 1 | 0 | 0.013054 | -0.048421 | 1.675418 |
| 40 | 1 | 0 | 0.272877 | -2.525466 | 0.765552 |
| 41 | 1 | 0 | -2.822201 | -0.539113 | -2.480537 |
| 42 | 1 | 0 | -4.319865 | -0.707807 | -1.512879 |
| 43 | 1 | 0 | -3.729359 | 0.868431 | 1.291195 |
| 44 | 1 | 0 | -4.426147 | -0.760442 | 1.134149 |
| 45 | 1 | 0 | 3.104762 | 0.124163 | 2.080366 |
| 46 | 1 | 0 | 4.483183 | 0.166923 | 0.940862 |
| 47 | 1 | 0 | 3.147090 | 1.590936 | -1.808981 |
| 48 | 1 | 0 | 4.260422 | 0.203989 | -1.700197 |
| 49 | 1 | 0 | 0.496104 | -1.286583 | 2.395008 |
| 50 | 8 | 0 | 0.792196 | -2.174216 | 2.750053 |
| 51 | 1 | 0 | 0.334383 | -2.291392 | 3.592065 |

HF= -1687.7235358 / Enthalpies= -1687.255012/ Free Energies= -1687.339684
NImag=0




| | |
|---|---|
| Ru-H1 | 1.894 (1.891) |
| H1-H2 | 0.806 (0.796) |
| Ru-H2 | 2.042 (1.945) |
| H2-O1 | 1.898 (2.260) |
| O1-H3 | 1.384 (1.339) |
| H3-N1 | 1.155 (1.187) |
| N1-Ru | 2.235 (2.238) |

**Figure S13**. Optimized structure of **TS($3^{Me}$⇔$1^{Me}$-$H_2$-$H_2O$)**.

**Table S15.** Coordinates and energy values of **TS($3^{Me}$⇔$1^{Me}$-$H_2$-$H_2O$)**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.022728 | 0.035774 | -0.003145 |
| 2 | 15 | 0 | 2.325261 | 0.183846 | -0.166725 |
| 3 | 15 | 0 | -2.204952 | -0.821628 | -0.085812 |
| 4 | 7 | 0 | 0.474175 | -2.136134 | -0.185656 |
| 5 | 6 | 0 | 2.859180 | -1.593289 | -0.302069 |
| 6 | 6 | 0 | 1.720642 | -2.404415 | -0.922665 |
| 7 | 6 | 0 | -0.617392 | -2.996142 | -0.662239 |
| 8 | 6 | 0 | -1.916945 | -2.653112 | 0.067663 |
| 9 | 6 | 0 | 3.354690 | 0.801190 | 1.241725 |
| 10 | 6 | 0 | 3.140529 | 0.975281 | -1.631297 |
| 11 | 6 | 0 | -3.208836 | -0.694760 | -1.639667 |
| 12 | 6 | 0 | -3.501678 | -0.513177 | 1.205048 |
| 13 | 1 | 0 | 3.789111 | -1.692342 | -0.874041 |
| 14 | 1 | 0 | 3.018940 | -1.950785 | 0.721334 |
| 15 | 1 | 0 | 1.585213 | -2.152298 | -1.984596 |
| 16 | 1 | 0 | 1.967296 | -3.477754 | -0.866736 |
| 17 | 1 | 0 | -0.744595 | -2.867294 | -1.747904 |
| 18 | 1 | 0 | -2.764352 | -3.234591 | -0.315522 |
| 19 | 1 | 0 | 3.197629 | 1.874192 | 1.390326 |
| 20 | 1 | 0 | 2.701833 | 0.564465 | -2.544811 |
| 21 | 1 | 0 | -3.490611 | 0.345772 | -1.821623 |
| 22 | 1 | 0 | -3.066080 | -0.671691 | 2.195603 |
| 23 | 1 | 0 | 0.873711 | 3.313483 | -1.619073 |
| 24 | 1 | 0 | -0.072873 | 0.160580 | -1.609346 |
| 25 | 15 | 0 | -0.559395 | 2.292581 | 0.081520 |
| 26 | 6 | 0 | 0.661277 | 3.532790 | -0.569176 |
| 27 | 1 | 0 | 0.274115 | 4.554616 | -0.488359 |

| | | | | | |
|---|---|---|---|---|---|
| 28 | 1 | 0 | 1.596103 | 3.466500 | -0.005443 |
| 29 | 6 | 0 | -2.065426 | 2.855707 | -0.850272 |
| 30 | 1 | 0 | -2.184558 | 3.943581 | -0.798885 |
| 31 | 1 | 0 | -1.975366 | 2.552450 | -1.896900 |
| 32 | 1 | 0 | -2.961465 | 2.388118 | -0.432240 |
| 33 | 6 | 0 | -0.911100 | 3.031505 | 1.750771 |
| 34 | 1 | 0 | -1.165816 | 4.095434 | 1.683854 |
| 35 | 1 | 0 | -1.740877 | 2.493443 | 2.218419 |
| 36 | 1 | 0 | -0.032902 | 2.912462 | 2.392179 |
| 37 | 1 | 0 | -0.365646 | -4.056512 | -0.492626 |
| 38 | 1 | 0 | -1.803479 | -2.873155 | 1.135685 |
| 39 | 1 | 0 | -0.051487 | 0.131575 | 1.887898 |
| 40 | 1 | 0 | 0.697095 | -2.350003 | 0.926998 |
| 41 | 1 | 0 | -2.599561 | -1.028505 | -2.483548 |
| 42 | 1 | 0 | -4.116483 | -1.305693 | -1.579315 |
| 43 | 1 | 0 | -3.852744 | 0.522000 | 1.147229 |
| 44 | 1 | 0 | -4.361376 | -1.181299 | 1.079742 |
| 45 | 1 | 0 | 3.038923 | 0.268834 | 2.143512 |
| 46 | 1 | 0 | 4.421643 | 0.620170 | 1.069239 |
| 47 | 1 | 0 | 2.971217 | 2.054897 | -1.629117 |
| 48 | 1 | 0 | 4.219881 | 0.786096 | -1.630246 |
| 49 | 1 | 0 | 0.279338 | -0.603311 | 1.912950 |
| 50 | 8 | 0 | 1.128442 | -2.268594 | 2.239785 |
| 51 | 1 | 0 | 0.868144 | -2.947255 | 2.873369 |

HF= -1687.6956091/ Enthalpies= -1687.232987 / Free Energies= -1687.315565
NImag=1 (Imag. Freq. = -177.0635 $cm^{-1}$)

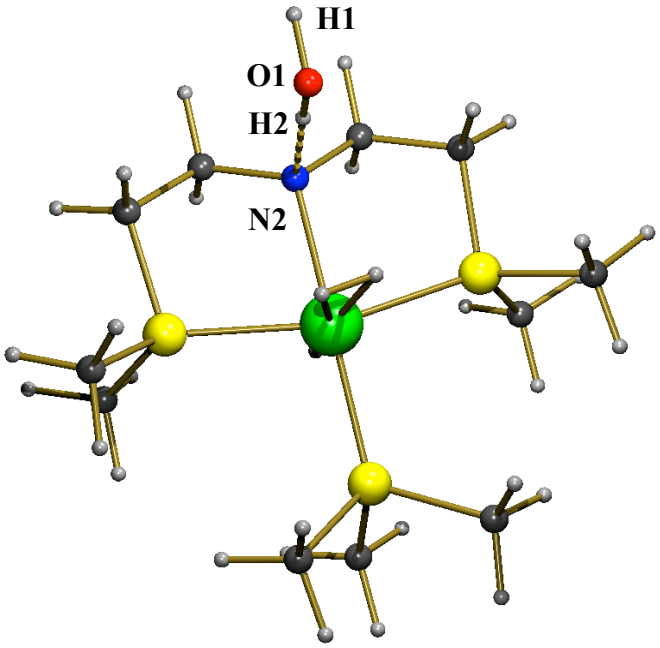
**Table S16.** Coordinates and energy values of **TS($3^{Me}$⇔$1^{Me}$-$H_2$-$H_2O$)** (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.005702 | 0.056731 | -0.073537 |
| 2 | 15 | 0 | 2.320092 | 0.325555 | -0.258740 |
| 3 | 15 | 0 | -2.146683 | -0.881613 | -0.248048 |
| 4 | 7 | 0 | 0.560161 | -2.023019 | -0.110623 |
| 5 | 6 | 0 | 2.946936 | -1.420667 | -0.144973 |
| 6 | 6 | 0 | 1.864096 | -2.350656 | -0.692858 |
| 7 | 6 | 0 | -0.429477 | -2.984666 | -0.601222 |
| 8 | 6 | 0 | -1.809889 | -2.693655 | -0.010073 |
| 9 | 6 | 0 | 3.430167 | 1.208177 | 0.941402 |
| 10 | 6 | 0 | 2.998982 | 0.926158 | -1.875638 |
| 11 | 6 | 0 | -2.992470 | -0.823936 | -1.896164 |
| 12 | 6 | 0 | -3.575244 | -0.580764 | 0.899227 |
| 13 | 1 | 0 | 3.903175 | -1.543972 | -0.667792 |
| 14 | 1 | 0 | 3.107110 | -1.635191 | 0.918096 |
| 15 | 1 | 0 | 1.839895 | -2.284766 | -1.798917 |
| 16 | 1 | 0 | 2.137843 | -3.396627 | -0.458405 |
| 17 | 1 | 0 | -0.493765 | -2.971805 | -1.708078 |
| 18 | 1 | 0 | -2.592502 | -3.319117 | -0.456816 |
| 19 | 1 | 0 | 3.287486 | 2.290222 | 0.872560 |
| 20 | 1 | 0 | 2.561595 | 0.338321 | -2.686898 |
| 21 | 1 | 0 | -3.273727 | 0.205302 | -2.135131 |
| 22 | 1 | 0 | -3.243474 | -0.707874 | 1.933668 |

| | | | | | |
|---|---|---|---|---|---|
| 23 | 1 | 0 | 0.914859 | 3.568715 | -1.139534 |
| 24 | 1 | 0 | -0.092837 | 0.383829 | -1.606953 |
| 25 | 15 | 0 | -0.658728 | 2.272951 | 0.227191 |
| 26 | 6 | 0 | 0.549370 | 3.647185 | -0.111371 |
| 27 | 1 | 0 | 0.087761 | 4.631475 | 0.026037 |
| 28 | 1 | 0 | 1.403498 | 3.564655 | 0.566042 |
| 29 | 6 | 0 | -2.082290 | 2.892892 | -0.798421 |
| 30 | 1 | 0 | -2.285728 | 3.952969 | -0.609798 |
| 31 | 1 | 0 | -1.847209 | 2.755892 | -1.857882 |
| 32 | 1 | 0 | -2.985561 | 2.318740 | -0.573546 |
| 33 | 6 | 0 | -1.236333 | 2.787532 | 1.922279 |
| 34 | 1 | 0 | -1.551810 | 3.837124 | 1.943087 |
| 35 | 1 | 0 | -2.075194 | 2.157619 | 2.233023 |
| 36 | 1 | 0 | -0.424117 | 2.647732 | 2.642160 |
| 37 | 1 | 0 | -0.130293 | -4.016233 | -0.333582 |
| 38 | 1 | 0 | -1.798811 | -2.879810 | 1.070724 |
| 39 | 1 | 0 | -0.170942 | 0.098215 | 3.112591 |
| 40 | 1 | 0 | 0.793186 | -2.470314 | 1.578130 |
| 41 | 1 | 0 | -2.296783 | -1.170046 | -2.665038 |
| 42 | 1 | 0 | -3.889259 | -1.453157 | -1.907606 |
| 43 | 1 | 0 | -3.947650 | 0.441503 | 0.782035 |
| 44 | 1 | 0 | -4.398136 | -1.277092 | 0.701673 |
| 45 | 1 | 0 | 3.187877 | 0.891775 | 1.960065 |
| 46 | 1 | 0 | 4.483561 | 0.981785 | 0.740018 |
| 47 | 1 | 0 | 2.720707 | 1.972780 | -2.028918 |
| 48 | 1 | 0 | 4.090473 | 0.836826 | -1.909613 |
| 49 | 1 | 0 | 0.070260 | -0.608721 | 3.103323 |
| 50 | 8 | 0 | 0.978503 | -2.772107 | 2.525707 |
| 51 | 1 | 0 | 0.706969 | -3.697928 | 2.566429 |

HF= -1687.6977173 / Enthalpies= -1687.235657 / Free Energies= -1687.325190

NImag=1 (Imag. Freq. = -117.4253 $cm^{-1}$)




H1-O1 0.964 (0.966)
O1-H2 1.018 (1.027)
H2-N1 1.703 (1.676)

**Figure S14**. Optimized structure of $\mathbf{1^{Me}\text{-}H_2\text{-}H_2O}$.

**Table S17.** Coordinates and energy values of $\mathbf{1^{Me}\text{-}H_2\text{-}H_2O}$.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.000541 | 0.043684 | 0.061967 |
| 2 | 15 | 0 | 2.329832 | -0.150540 | -0.170857 |
| 3 | 15 | 0 | -2.292422 | -0.450042 | -0.164158 |
| 4 | 7 | 0 | 0.144867 | -2.157417 | -0.191276 |
| 5 | 6 | 0 | 2.593060 | -1.985450 | -0.239703 |
| 6 | 6 | 0 | 1.351357 | -2.608034 | -0.875933 |
| 7 | 6 | 0 | -1.009099 | -2.767576 | -0.843638 |
| 8 | 6 | 0 | -2.308218 | -2.303716 | -0.184696 |
| 9 | 6 | 0 | 3.568692 | 0.371499 | 1.108570 |
| 10 | 6 | 0 | 3.133253 | 0.472681 | -1.719146 |
| 11 | 6 | 0 | -3.159642 | 0.014096 | -1.734144 |
| 12 | 6 | 0 | -3.597522 | -0.059582 | 1.096058 |
| 13 | 1 | 0 | 3.512338 | -2.243048 | -0.779813 |
| 14 | 1 | 0 | 2.689050 | -2.333034 | 0.795456 |
| 15 | 1 | 0 | 1.328995 | -2.360635 | -1.957841 |
| 16 | 1 | 0 | 1.435347 | -3.710492 | -0.821310 |
| 17 | 1 | 0 | -1.041830 | -2.532726 | -1.928338 |
| 18 | 1 | 0 | -3.198368 | -2.697307 | -0.690684 |
| 19 | 1 | 0 | 3.613649 | 1.461055 | 1.185320 |
| 20 | 1 | 0 | 2.591790 | 0.078113 | -2.582530 |
| 21 | 1 | 0 | -3.262664 | 1.101676 | -1.800006 |
| 22 | 1 | 0 | -3.251311 | -0.384829 | 2.081315 |
| 23 | 1 | 0 | 2.118380 | 3.164417 | 0.628499 |
| 24 | 1 | 0 | -0.009526 | 0.190643 | -1.537788 |
| 25 | 15 | 0 | -0.164765 | 2.371116 | 0.181494 |
| 26 | 6 | 0 | 1.143012 | 3.335719 | 1.091693 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | 1 | 0 | 0.933541 | 4.411459 | 1.078755 |
| 28 | 1 | 0 | 1.196513 | 2.995069 | 2.130176 |
| 29 | 6 | 0 | -0.144714 | 3.266688 | -1.444987 |
| 30 | 1 | 0 | -0.238325 | 4.351110 | -1.317063 |
| 31 | 1 | 0 | 0.788840 | 3.042597 | -1.968213 |
| 32 | 1 | 0 | -0.966322 | 2.901404 | -2.067162 |
| 33 | 6 | 0 | -1.670873 | 3.152422 | 0.949192 |
| 34 | 1 | 0 | -1.588996 | 4.245209 | 0.967697 |
| 35 | 1 | 0 | -2.563445 | 2.881304 | 0.378164 |
| 36 | 1 | 0 | -1.794979 | 2.786862 | 1.972642 |
| 37 | 1 | 0 | -0.948280 | -3.870935 | -0.777968 |
| 38 | 1 | 0 | -2.326469 | -2.635101 | 0.860365 |
| 39 | 1 | 0 | -0.370264 | -0.321266 | 1.881729 |
| 40 | 1 | 0 | 0.201753 | -2.699364 | 1.422375 |
| 41 | 1 | 0 | -2.557376 | -0.319555 | -2.582773 |
| 42 | 1 | 0 | -4.154936 | -0.440685 | -1.789932 |
| 43 | 1 | 0 | -3.789494 | 1.015627 | 1.136915 |
| 44 | 1 | 0 | -4.535021 | -0.575866 | 0.860049 |
| 45 | 1 | 0 | 3.268798 | -0.029589 | 2.080935 |
| 46 | 1 | 0 | 4.568209 | -0.004406 | 0.861777 |
| 47 | 1 | 0 | 3.078189 | 1.565140 | -1.755944 |
| 48 | 1 | 0 | 4.184356 | 0.168517 | -1.775600 |
| 49 | 1 | 0 | 0.409101 | -0.143435 | 1.897205 |
| 50 | 8 | 0 | 0.239368 | -2.978413 | 2.400585 |
| 51 | 1 | 0 | 0.288022 | -3.941298 | 2.404489 |

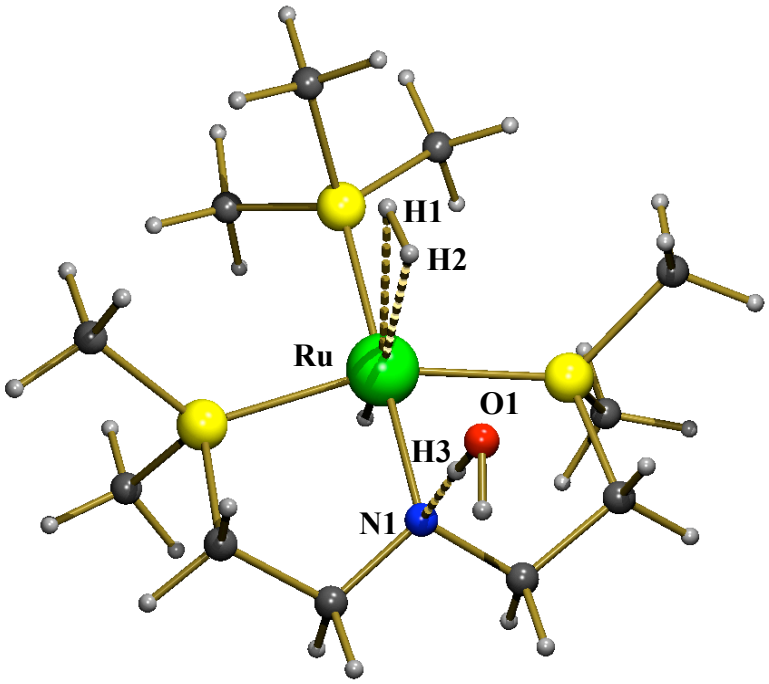
HF= -1687.7033809 / Enthalpies= -1687.238350 / Free Energies= -1687.325470
NImag=0

**Table S18.** Coordinates and energy values of $\mathbf{1^{Me}\text{-}H_2\text{-}H_2O}$ (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | 0.000661 | 0.054977 | 0.039880 |
| 2 | 15 | 0 | 2.305038 | -0.351398 | -0.211645 |
| 3 | 15 | 0 | -2.319164 | -0.229779 | -0.214107 |
| 4 | 7 | 0 | -0.056368 | -2.159615 | -0.115872 |
| 5 | 6 | 0 | 2.403071 | -2.201569 | -0.129256 |
| 6 | 6 | 0 | 1.117536 | -2.757418 | -0.745149 |
| 7 | 6 | 0 | -1.254361 | -2.692698 | -0.757594 |
| 8 | 6 | 0 | -2.514141 | -2.073483 | -0.148802 |
| 9 | 6 | 0 | 3.615643 | 0.185913 | 0.986415 |
| 10 | 6 | 0 | 3.114269 | 0.045197 | -1.829283 |
| 11 | 6 | 0 | -3.108288 | 0.222084 | -1.827165 |
| 12 | 6 | 0 | -3.598530 | 0.364581 | 0.990142 |
| 13 | 1 | 0 | 3.302749 | -2.582915 | -0.627432 |
| 14 | 1 | 0 | 2.449549 | -2.478203 | 0.930724 |
| 15 | 1 | 0 | 1.130912 | -2.585066 | -1.841657 |
| 16 | 1 | 0 | 1.105577 | -3.857227 | -0.615694 |
| 17 | 1 | 0 | -1.249665 | -2.513609 | -1.853029 |
| 18 | 1 | 0 | -3.427604 | -2.402636 | -0.659013 |
| 19 | 1 | 0 | 3.741859 | 1.272175 | 0.955395 |
| 20 | 1 | 0 | 2.516015 | -0.380947 | -2.638433 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 1 | 0 | -3.096704 | 1.306848 | -1.962472 |
| 22 | 1 | 0 | -3.318675 | 0.050770 | 1.999905 |
| 23 | 1 | 0 | 1.589144 | 3.050715 | -1.589812 |
| 24 | 1 | 0 | 0.005643 | 0.203269 | -1.563274 |
| 25 | 15 | 0 | 0.065763 | 2.385569 | 0.208320 |
| 26 | 6 | 0 | 1.509103 | 3.296665 | -0.527323 |
| 27 | 1 | 0 | 1.391861 | 4.380578 | -0.420746 |
| 28 | 1 | 0 | 2.436686 | 2.997606 | -0.031778 |
| 29 | 6 | 0 | -1.308251 | 3.373362 | -0.560404 |
| 30 | 1 | 0 | -1.138826 | 4.449483 | -0.444474 |
| 31 | 1 | 0 | -1.373189 | 3.136117 | -1.626067 |
| 32 | 1 | 0 | -2.262425 | 3.119061 | -0.091014 |
| 33 | 6 | 0 | 0.063124 | 3.108149 | 1.922618 |
| 34 | 1 | 0 | 0.091174 | 4.203684 | 1.907509 |
| 35 | 1 | 0 | -0.836767 | 2.781836 | 2.452662 |
| 36 | 1 | 0 | 0.931225 | 2.737128 | 2.475982 |
| 37 | 1 | 0 | -1.300782 | -3.792361 | -0.634258 |
| 38 | 1 | 0 | -2.586244 | -2.356178 | 0.908081 |
| 39 | 1 | 0 | -0.407337 | -0.190043 | 1.861987 |
| 40 | 1 | 0 | -0.080867 | -2.713090 | 1.465235 |
| 41 | 1 | 0 | -2.532790 | -0.226864 | -2.640557 |
| 42 | 1 | 0 | -4.143706 | -0.132840 | -1.873194 |
| 43 | 1 | 0 | -3.659569 | 1.456784 | 0.975105 |
| 44 | 1 | 0 | -4.587081 | -0.043536 | 0.751271 |
| 45 | 1 | 0 | 3.316553 | -0.095357 | 2.000257 |
| 46 | 1 | 0 | 4.578579 | -0.283432 | 0.755687 |
| 47 | 1 | 0 | 3.157015 | 1.127960 | -1.973757 |
| 48 | 1 | 0 | 4.130514 | -0.361760 | -1.873976 |
| 49 | 1 | 0 | 0.396057 | -0.200496 | 1.862971 |
| 50 | 8 | 0 | -0.097742 | -3.078777 | 2.424679 |
| 51 | 1 | 0 | -0.131051 | -4.039502 | 2.333064 |

HF= -1687.7092559 / Enthalpies= -1687.244731 / Free Energies= -1687.330684
NImag=0




Ru-H1 3.126 (3.191)
Ru-H2 3.255 (3.247)
H1-H2 0.747 (0.747)
N1-H3 1.772 (1.762)
H3-O1 1.008 (1.012)
O1-Ru 3.885 (3.966)

**Figure S15**. Optimized structure of **TS($1^{Me}$-$H_2$-$H_2O$⇔$1^{Me}$-$H_2O$)**.

**Table S19.** Coordinates and energy values of **TS($1^{Me}$-$H_2$-$H_2O$⇔$1^{Me}$-$H_2O$)**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.006406 | 0.050621 | -0.077038 |
| 2 | 15 | 0 | 2.319842 | 0.315627 | -0.253933 |
| 3 | 15 | 0 | -2.145728 | -0.892795 | -0.232135 |
| 4 | 7 | 0 | 0.559787 | -2.026879 | -0.125852 |
| 5 | 6 | 0 | 2.946481 | -1.431182 | -0.162039 |
| 6 | 6 | 0 | 1.859953 | -2.354656 | -0.714513 |
| 7 | 6 | 0 | -0.431941 | -2.992463 | -0.600415 |
| 8 | 6 | 0 | -1.803544 | -2.702153 | 0.011341 |
| 9 | 6 | 0 | 3.415786 | 1.179590 | 0.972199 |
| 10 | 6 | 0 | 3.010428 | 0.943060 | -1.856204 |
| 11 | 6 | 0 | -3.010578 | -0.844470 | -1.871320 |
| 12 | 6 | 0 | -3.561107 | -0.586769 | 0.930628 |
| 13 | 1 | 0 | 3.899699 | -1.549133 | -0.691640 |
| 14 | 1 | 0 | 3.110411 | -1.655863 | 0.898170 |
| 15 | 1 | 0 | 1.833540 | -2.284542 | -1.820146 |
| 16 | 1 | 0 | 2.131642 | -3.402464 | -0.486340 |
| 17 | 1 | 0 | -0.511599 | -2.986219 | -1.706493 |
| 18 | 1 | 0 | -2.592054 | -3.331678 | -0.419344 |
| 19 | 1 | 0 | 3.268264 | 2.262249 | 0.924247 |
| 20 | 1 | 0 | 2.571947 | 0.373865 | -2.680027 |
| 21 | 1 | 0 | -3.298276 | 0.182662 | -2.111919 |
| 22 | 1 | 0 | -3.215114 | -0.709829 | 1.960867 |
| 23 | 1 | 0 | 0.912645 | 3.552665 | -1.169186 |
| 24 | 1 | 0 | -0.093057 | 0.363848 | -1.613191 |

| | | | | | |
|---|---|---|---|---|---|
| 25 | 15 | 0 | -0.659917 | 2.266556 | 0.208115 |
| 26 | 6 | 0 | 0.547557 | 3.640044 | -0.141634 |
| 27 | 1 | 0 | 0.086349 | 4.625789 | -0.012425 |
| 28 | 1 | 0 | 1.402210 | 3.562942 | 0.535858 |
| 29 | 6 | 0 | -2.079151 | 2.875746 | -0.831690 |
| 30 | 1 | 0 | -2.282638 | 3.938711 | -0.659180 |
| 31 | 1 | 0 | -1.840700 | 2.722585 | -1.888125 |
| 32 | 1 | 0 | -2.983627 | 2.305400 | -0.601634 |
| 33 | 6 | 0 | -1.248086 | 2.806120 | 1.892560 |
| 34 | 1 | 0 | -1.564971 | 3.855651 | 1.897151 |
| 35 | 1 | 0 | -2.087695 | 2.179255 | 2.207379 |
| 36 | 1 | 0 | -0.441338 | 2.676002 | 2.620138 |
| 37 | 1 | 0 | -0.126557 | -4.021616 | -0.331706 |
| 38 | 1 | 0 | -1.770978 | -2.881401 | 1.092705 |
| 39 | 1 | 0 | -0.255946 | 0.134994 | 3.037820 |
| 40 | 1 | 0 | 0.800268 | -2.417668 | 1.586118 |
| 41 | 1 | 0 | -2.321438 | -1.190602 | -2.646022 |
| 42 | 1 | 0 | -3.904963 | -1.477446 | -1.871099 |
| 43 | 1 | 0 | -3.934247 | 0.435413 | 0.813769 |
| 44 | 1 | 0 | -4.386893 | -1.283738 | 0.747228 |
| 45 | 1 | 0 | 3.164432 | 0.839478 | 1.980900 |
| 46 | 1 | 0 | 4.472248 | 0.961924 | 0.776905 |
| 47 | 1 | 0 | 2.740142 | 1.994292 | -1.991101 |
| 48 | 1 | 0 | 4.101534 | 0.847010 | -1.887979 |
| 49 | 1 | 0 | 0.020299 | -0.554320 | 3.121569 |
| 50 | 8 | 0 | 0.982750 | -2.631592 | 2.553674 |
| 51 | 1 | 0 | 1.010078 | -3.592673 | 2.623816 |

HF= -1687.6937664 / Enthalpies= -1687.231225 / Free Energies= -1687.320225
NImag=1 (Imag. Freq. = -109.5779 $cm^{-1}$)

**Table S20.** Coordinates and energy values of **TS($1^{Me}$-$H_2$-$H_2O$⇔$1^{Me}$-$H_2O$)** (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 44 | 0 | -0.005702 | 0.056731 | -0.073537 |
| 2 | 15 | 0 | 2.320092 | 0.325555 | -0.258740 |
| 3 | 15 | 0 | -2.146683 | -0.881613 | -0.248048 |
| 4 | 7 | 0 | 0.560161 | -2.023019 | -0.110623 |
| 5 | 6 | 0 | 2.946936 | -1.420667 | -0.144973 |
| 6 | 6 | 0 | 1.864096 | -2.350656 | -0.692858 |
| 7 | 6 | 0 | -0.429477 | -2.984666 | -0.601222 |
| 8 | 6 | 0 | -1.809889 | -2.693655 | -0.010073 |
| 9 | 6 | 0 | 3.430167 | 1.208177 | 0.941402 |
| 10 | 6 | 0 | 2.998982 | 0.926158 | -1.875638 |
| 11 | 6 | 0 | -2.992470 | -0.823936 | -1.896164 |
| 12 | 6 | 0 | -3.575244 | -0.580764 | 0.899227 |
| 13 | 1 | 0 | 3.903175 | -1.543972 | -0.667792 |
| 14 | 1 | 0 | 3.107110 | -1.635191 | 0.918096 |
| 15 | 1 | 0 | 1.839895 | -2.284766 | -1.798917 |
| 16 | 1 | 0 | 2.137843 | -3.396627 | -0.458405 |
| 17 | 1 | 0 | -0.493765 | -2.971805 | -1.708078 |
| 18 | 1 | 0 | -2.592502 | -3.319117 | -0.456816 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 1 | 0 | 3.287486 | 2.290222 | 0.872560 |
| 20 | 1 | 0 | 2.561595 | 0.338321 | -2.686898 |
| 21 | 1 | 0 | -3.273727 | 0.205302 | -2.135131 |
| 22 | 1 | 0 | -3.243474 | -0.707874 | 1.933668 |
| 23 | 1 | 0 | 0.914859 | 3.568715 | -1.139534 |
| 24 | 1 | 0 | -0.092837 | 0.383829 | -1.606953 |
| 25 | 15 | 0 | -0.658728 | 2.272951 | 0.227191 |
| 26 | 6 | 0 | 0.549370 | 3.647185 | -0.111371 |
| 27 | 1 | 0 | 0.087761 | 4.631475 | 0.026037 |
| 28 | 1 | 0 | 1.403498 | 3.564655 | 0.566042 |
| 29 | 6 | 0 | -2.082290 | 2.892892 | -0.798421 |
| 30 | 1 | 0 | -2.285728 | 3.952969 | -0.609798 |
| 31 | 1 | 0 | -1.847209 | 2.755892 | -1.857882 |
| 32 | 1 | 0 | -2.985561 | 2.318740 | -0.573546 |
| 33 | 6 | 0 | -1.236333 | 2.787532 | 1.922279 |
| 34 | 1 | 0 | -1.551810 | 3.837124 | 1.943087 |
| 35 | 1 | 0 | -2.075194 | 2.157619 | 2.233023 |
| 36 | 1 | 0 | -0.424117 | 2.647732 | 2.642160 |
| 37 | 1 | 0 | -0.130293 | -4.016233 | -0.333582 |
| 38 | 1 | 0 | -1.798811 | -2.879810 | 1.070724 |
| 39 | 1 | 0 | -0.170942 | 0.098215 | 3.112591 |
| 40 | 1 | 0 | 0.793186 | -2.470314 | 1.578130 |
| 41 | 1 | 0 | -2.296783 | -1.170046 | -2.665038 |
| 42 | 1 | 0 | -3.889259 | -1.453157 | -1.907606 |
| 43 | 1 | 0 | -3.947650 | 0.441503 | 0.782035 |
| 44 | 1 | 0 | -4.398136 | -1.277092 | 0.701673 |
| 45 | 1 | 0 | 3.187877 | 0.891775 | 1.960065 |
| 46 | 1 | 0 | 4.483561 | 0.981785 | 0.740018 |
| 47 | 1 | 0 | 2.720707 | 1.972780 | -2.028918 |
| 48 | 1 | 0 | 4.090473 | 0.836826 | -1.909613 |
| 49 | 1 | 0 | 0.070260 | -0.608721 | 3.103323 |
| 50 | 8 | 0 | 0.978503 | -2.772107 | 2.525707 |
| 51 | 1 | 0 | 0.706969 | -3.697928 | 2.566429 |

HF= -1687.6977173 / Enthalpies= -1687.235657 / Free Energies= -1687.325190

NImag=1 (Imag. Freq. = -117.4253 $cm^{-1}$)

*Optimized structures for $H_2O$ and $H_2$*

**Table S21.** Coordinates and energy values of **$H_2O$**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.000000 | 0.110785 | 0.000000 |
| 2 | 1 | 0 | 0.783146 | -0.459308 | 0.000000 |
| 3 | 1 | 0 | -0.783146 | -0.426972 | 0.000000 |

HF=-76.4331183 / Enthalpies= -76.408028 / Free Energies= -76.430110
NImag=0

**Table S22.** Coordinates and energy values of **$H_2O$** (PCM).

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.000000 | 0.117519 | 0.000000 |
| 2 | 1 | 0 | 0.768221 | -0.470004 | 0.000000 |
| 3 | 1 | 0 | -0.768221 | -0.470149 | 0.000000 |

HF= -76.4383193 / Enthalpies= -76.413446 / Free Energies= -76.435537
NImag=0

**Table S23.** Coordinates and energy values of **$H_2$**.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 1 | 0 | 0.000000 | 0.000000 | 0.350000 |
| 2 | 1 | 0 | 0.000000 | 0.000000 | -0.350000 |

HF= -1.1785393 / Enthalpies= -1.165061 / Free Energies= -1.179853
NImag=0

**Table S24.** Coordinates and energy values of **$H_2$** (PCM).

$H_2$ – Hydrogen

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 1 | 0 | 0.000000 | 0.000000 | 0.371461 |
| 2 | 1 | 0 | 0.000000 | 0.000000 | -0.371461 |

HF= -1.1785836 / Enthalpies= -1.165110 / Free Energies= -1.179902
NImag=0

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