# Supporting information

# Theoretical study on the mechanism of hydrogen evolution reaction catalyzed by platinum subnanoclusters

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**Table S1.** Summary of the Gibbs free energies computed for the acid and base forms, which were used to calculate the corresponding p$K_a$ values.

| Compound | Gibbs energy in vacuo (kcal/mol) | Gibbs energy in C-PCM (kcal/mol) |
|---|---|---|
| pyridinium (Hpy$^+$) | -155873.2103 | -155926.1802 |
| pyridine (py) | -155652.7957 | -155656.2909 |
| trans-[Pt(NH$_3$)$_2$Cl(OH$_2$)]$^+$ | -482414.2236 | -482477.4001 |
| trans-[Pt(NH$_3$)$_2$Cl(OH)] | -482185.2842 | -482202.7892 |
| cis-[Pt(NH$_3$)$_2$Cl(OH$_2$)]$^+$ | -482412.0349 | -482475.2967 |
| cis-[Pt(NH$_3$)$_2$Cl(OH)] | -482179.5788 | -482200.1009 |
| triethylammonium (HNEt$_3$$^+$) | -183482.3596 | -183530.5787 |
| triethylamine (NEt$_3$) | -183254.1049 | -183252.2556 |
| pyrrolidinium (H$_2$NC$_4$H$_8$$^+$) | -133466.1196 | -133521.9867 |
| pyrrolidine (HNC$_4$H$_8$) | -133241.3212 | -133243.7227 |
| guanidinium (H$_2$NC(NH$_2$)$_2$$^+$) | -129009.9552 | -129068.5156 |
| guanidine (HNC(NH$_2$)$_2$) | -128773.5347 | -128782.6417 |

**Table S2.** Summary of the calculated and experimental p$K_a$ values for several monocationic acids used in benchmarking the individual p$K_a$ values in this study.

| Acid | Calculated p$K_a$ | Experimental p$K_a$ |
|---|---|---|
| pyridinium (Hpy$^+$) | 4.32 | 5.24 [S1] |
| trans-[Pt(NH$_3$)$_2$Cl(OH$_2$)]$^+$ | 7.77 | 5.63 [S2] |
| cis-[Pt(NH$_3$)$_2$Cl(OH$_2$)]$^+$ | 8.20 | 6.85 [S3] |
| triethylammonium (HNEt$_3$$^+$) | 9.14 | 10.75 [S1] |
| pyrrolidinium (H$_2$NC$_4$H$_8$$^+$) | 10.5 | 11.27 [S1] |
| guanidinium (H$_2$NC(NH$_2$)$_2$$^+$) | 16.0 | 13.60 [S1] |

**Table S3.** Summary of the Gibbs free energies computed for six redox couples, which were used to calculate the corresponding redox potentials.

| Compound | Gibbs energy in vacuo (kcal/mol) | Gibbs energy in C-PCM (kcal/mol) |
|---|---|---|
| $MV^{2+}$ (1,1'-dimethyl-4,4'-bipyridinium) | -360216.2137 | -360365.7523 |
| $MV^{+\bullet}$ | -360425.2045 | -360463.9381 |
| $MV^0$ | -360538.0401 | -360544.1928 |
| $I_3^-$ | -21599.9071 | -21558.53979 |
| $I_2$ | -14311.35318 | -14310.07494 |
| $I^-$ | -7206.363165 | -7265.269778 |
| $[Pt(III)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2(OH_2)_2]^{4+}$ ($\alpha$-pyrro = $\alpha$-pyrrolidonato) | -745202.2162 | -745779.6767 |
| $[Pt(II)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2]^{2+}$ | -650037.2813 | -650186.3355 |
| $\{[Pt(III)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2(OH_2)_2]Cl_2\}^{2+}$ | -1323385.037 | -1323565.791 |
| $\{[Pt(II)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2]Cl_2\}$ | -1227928.919 | -1227961.666 |
| $H_2O$ | -47935.46075 | -47940.82847 |

**Table S4.** Summary of the calculated and experimental redox potentials used in benchmarking the individual redox potentials in this study.

| Redox couple | Calculated potential (V) | Experimental potential (V vs. NHE) |
|---|---|---|
| $MV^{2+}$ / $MV^{+\bullet}$ | 4.22 | -0.450 [S4] |
| $MV^{+\bullet}$ / $MV^0$ | 3.44 | -0.816 [S4] |
| $I_2$ / $2I^-$ | 4.72 | 0.623 [S5] |
| $I_3^-$ / $3I^-$ | 4.21 | 0.536 [S6] |
| $[Pt(III)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2(OH_2)_2]^{4+}$ / $[Pt(II)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2]^{2+}$+ $2H_2O$ | 6.21[a] | 0.774 [S7] |
| $\{[Pt(III)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2(OH_2)_2]Cl_2\}^{2+}$ / $\{[Pt(II)_2(NH_3)_4(\mu\text{-}\alpha\text{-pyrro})_2]Cl_2\}$ + $2H_2O$ | 5.98 [a] | 0.774 [S7] |

[a] The two-electron one-step oxidation-reduction potential of the diaqua-coordinated Pt(III)$_2$ dimer was computed in two different models. One was computed without discharging the system, while the other was computed by making efforts to decrease the total positive charge by locating two chloride ions beside the dimeric unit. Empirically, the more realistic structures are known to be given by discharging the model systems due to the suppression of excessive Coulombic repulsion between the two positively charged platinum(II or III) coordination planes within the dimeric unit.
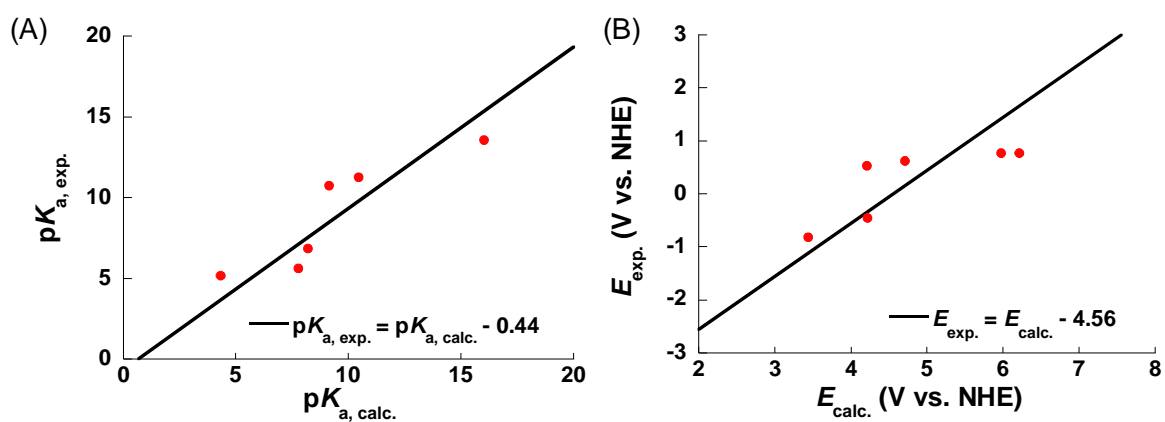
**Fig. S1** Correlations between the calculated and experimental values for the p$K_a$ values (A) and the redox potentials (B), where the red plots correspond to the values in Tables S2 and S4.

**Table S5.** Summary of the Pt-Pt bond lengths (Å) computed for the neutral $Pt^0_n$ subnanocluster models (n = 2-5). See also Fig. 2.

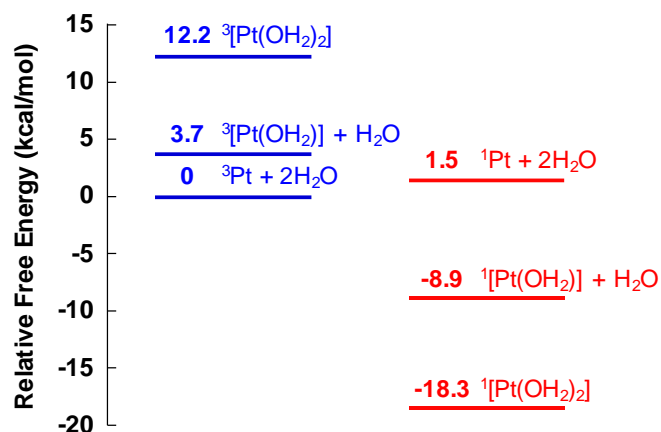|  | [Pt$_2$] | [Pt$_3$] | [Pt$_4$] | [Pt$_5$] |
|---|---|---|---|---|
| Pt1-Pt2 | 2.396 | 2.538 | 2.631 | 2.692 |
| Pt1-Pt3 |  | 2.538 | 2.631 | 2.692 |
| Pt2-Pt3 |  | 2.538 | 2.723 | - |
| Pt1-Pt4 |  |  | 2.631 | - |
| Pt2-Pt4 |  |  | 2.725 | 2.693 |
| Pt3-Pt4 |  |  | 2.721 | 2.693 |
| Pt1-Pt5 |  |  |  | 2.651 |
| Pt2-Pt5 |  |  |  | 2.727 |
| Pt3-Pt5 |  |  |  | 2.727 |
| Pt4-Pt5 |  |  |  | 2.692 |
| Averaged Pt-Pt | 2.396 | 2.538 | 2.677 | 2.690 |

**Fig. S2** Comparison of the free energies of the triplet (left) and singlet (right) states of the Pt(0) system in aqueous media, corresponding to the initial state before promoting either PT or ET.
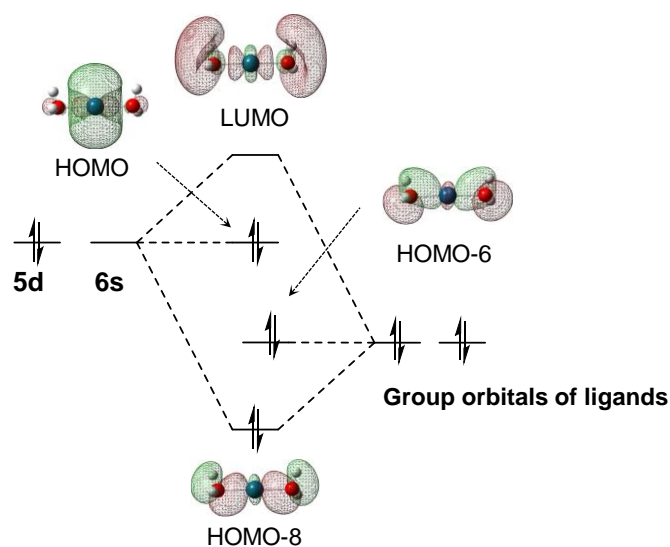


**Fig. S3** Schematic diagram for the molecular orbitals (MOs) computed for $^1[Pt(OH_2)_2]$ in aqueous media (C-PCM). The Pt-O bonds are judged to be given on the basis of the hybridization of 6s and 5d orbitals (i.e., sd-hybrid orbitals). Only a single bonding orbital is achieved so that the bond order for each Pt-O bond is regarded as 0.5. In other words, the two aqua donors provide two electron pairs as the source of donors but, by forming a non-bonding orbital derived from these donors (HOMO-6), only a single bond is achieved in total.

**Table S6.** The structure of $Pt_{13}$ (triplet) optimized at the M06 level of DFT using SDD(Pt) basis set in vacuo. The structure was defined using the Z-matrix format in Gaussian and was forced to possess a cuboctahedral geometry in its highest symmetry so that all the Pt-Pt distances were defined with a common variable, which converged at 2.785 Å. This value is nearly consistent with the crystallographically determined Pt-Pt distance for the bulk platinum (2.775 Å).[S8]
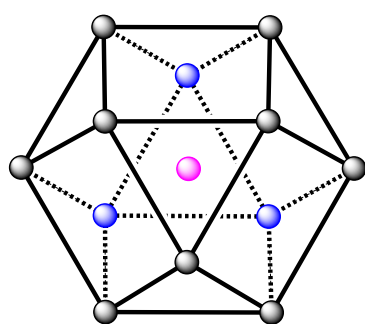


**Cuboctahedron**
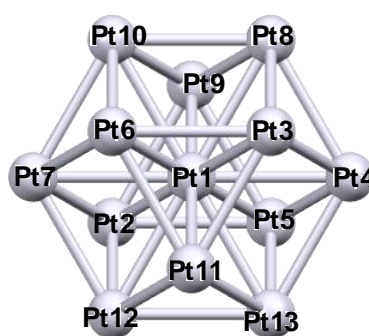
Pt-Pt = **2.785 Å** (For all Pt-Pt)

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom |
|---|---|---|---|
| Pt1 | 0.000000 | 0.000000 | 0.000000 |
| Pt2 | -1.969224 | 0.000000 | 1.969224 |
| Pt3 | 0.000000 | 1.969224 | 1.969224 |
| Pt4 | 1.969224 | 1.969224 | 0.000000 |
| Pt5 | 1.969224 | 0.000000 | -1.969224 |
| Pt6 | 0.000000 | -1.969224 | -1.969224 |
| Pt7 | -1.969224 | -1.969224 | 0.000000 |
| Pt8 | -1.969224 | 1.969224 | 0.000000 |
| Pt9 | 0.000000 | 1.969224 | -1.969224 |
| Pt10 | -1.969224 | 0.000000 | -1.969224 |
| Pt11 | 1.969224 | 0.000000 | 1.969224 |
| Pt12 | 1.969224 | -1.969224 | 0.000000 |
| Pt13 | 0.000000 | -1.969224 | 1.969224 |
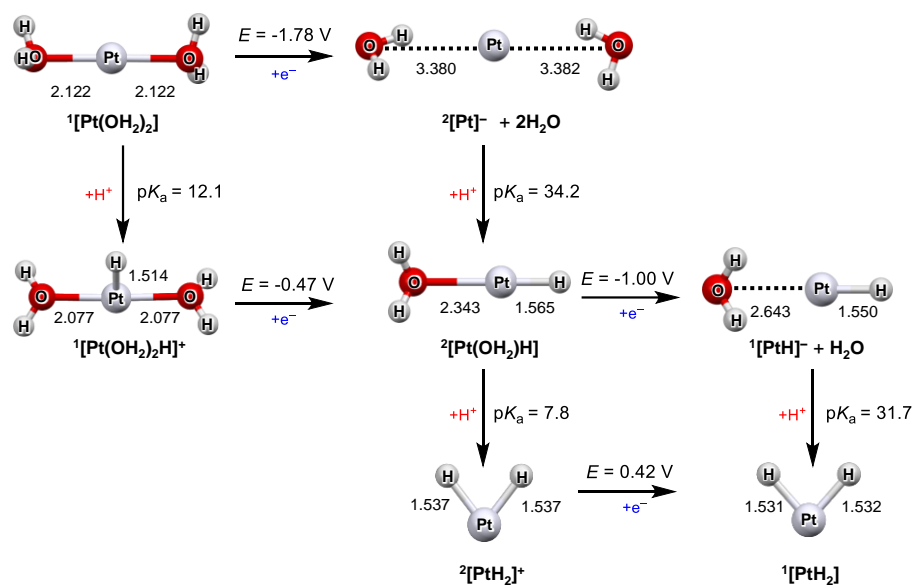
**Fig. S4** Square schemes developed for the Pt$_1$ system, where the redox potentials are given in V vs. NHE. The structural variations during the couse of reactions are also shown.
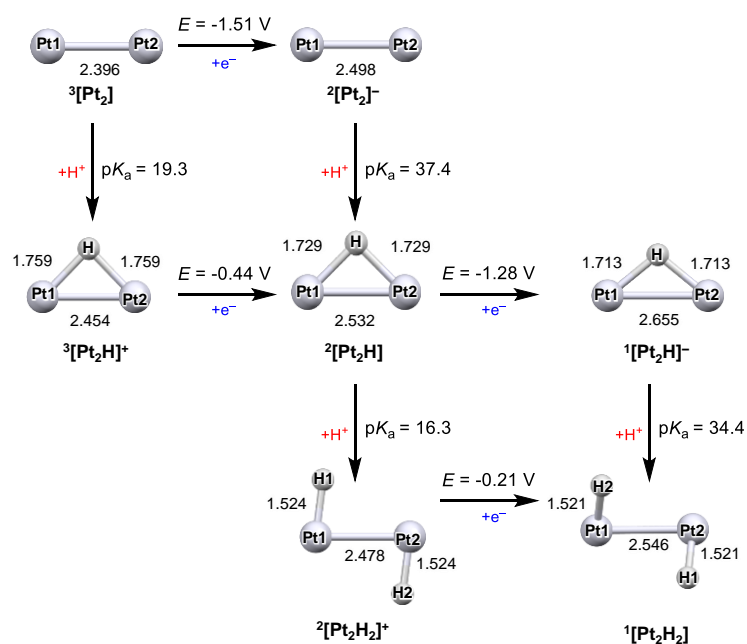


**Fig. S5** Square schemes for the Pt$_2$ system, where the redox potentials are given in V vs. NHE. The structural variations during the couse of reactions are also shown.
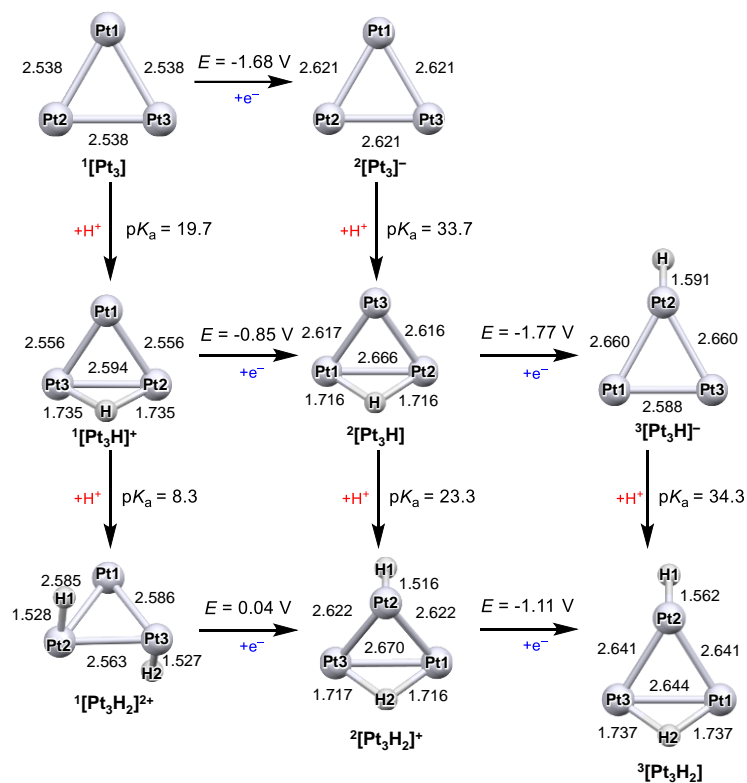
**Fig. S6** Square schemes for the Pt$_3$ system, where the redox potentials are given in V vs. NHE. The structural variations during the couse of reactions are also shown.

**Table S7.** Summary of the Gibbs free energies computed for the chemical species adopted to estimate the p$K_a$ values of [Pt$_4$H]$^+$, [Pt$_5$H]$^+$ and [Pt$_6$H]$^+$. The resulting p$K_a$ values are also summarized.

| Compound | Gibbs energy in vacuo (kcal/mol) | Gibbs energy in C-PCM (kcal/mol) |
|---|---|---|
| [Pt$_4$H]$^+$ (p$K_a$ = 27.0) | -299810.468 | -299931.584 |
| [Pt$_4$] | -299605.163 | -299630.124 |
| [Pt$_5$H]$^+$ (p$K_a$ = 26.5) | -374718.129 | -374841.590 |
| [Pt$_5$] | -374513.979 | -374540.872 |
| [Pt$_6$H]$^+$ (p$K_a$ = 28.4) | -449629.683 | -449753.421 |
| [Pt$_6$] | -449427.965 | -449450.117 |

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**Table S8.** The selected Pt-H vibrational frequencies ($cm^{-1}$) computed for some important intermediates appearing in the successive PT and ET steps for the $Pt_1$ model. The values in parentheses correspond to the oscillator strengths.

| $^1[Pt(OH_2)_2H]^+$ | | $^2[Pt(OH_2)H]$ | | $^2[PtH_2]^+$ | |
|---|---|---|---|---|---|
| 245.58[a] | (7.73) | 239.41[a] | (32.99) | 765.37[a] | (15.48) |
| 736.76[a] | (90.96) | 251.99[a] | (60.76) | 2343.45[b] | (35.58) |
| 766.80[a] | (8.42) | 337.97[a] | (234.44) | 2391.68[b] | (11.39) |
| 2422.09[b] | (44.55) | 461.31[a] | (239.80) | | |
| | | 535.63[a] | (81.49) | | |
| | | 2108.22[b] | (613.35) | | |

| $^1[PtH_2]$ | | $^1[PtH_3]^+$ | |
|---|---|---|---|
| 824.39[a] | (4.23) | 879.01[a] | (8.25) |
| 2335.85[b] | (222.55) | 893.54[a] | (7.50) |
| 2401.41[b] | (81.65) | 1002.71[a] | (31.65) |
| | | 2406.44[b] | (4.11) |
| | | 2429.42[b] | (9.20) |
| | | 2460.65[b] | (6.03) |

[a] Bending. [b] Stretching.

**Table S9.** The selected Pt-H vibrational frequencies ($cm^{-1}$) computed for some important intermediates appearing in the successive PT and ET steps for the $Pt_2$ model. The values in parentheses correspond to the oscillator strengths.

| $^3[Pt_2H]^+$ | | $^2[Pt_2H]$ | | $^2[Pt_2H_2]^+$ | |
|---|---|---|---|---|---|
| 631.72[a] | (311.20) | 680.92[a] | (2.32) | 262.52[c] | (93.60) |
| 1610.04[b] | (136.60) | 1607.57[b] | (235.94) | 2394.32[b] | (181.90) |

| $^1[Pt_2H_2]$ | | $^1[Pt_2H_3]^+$ | | $^2[Pt_2H_3]$ | |
|---|---|---|---|---|---|
| 389.42[c] | (166.15) | 346.27[c] | (110.74) | 258.3[c] | (200.58) |
| 475.42[c] | (138.58) | 530.55[c] | (22.82) | 512.12[c] | (3117.75) |
| 504.35[c] | (0.49) | 778.82[c] | (57.80) | 636.78[c] | (12.92) |
| 2362.60[b] | (91.38) | 892.72[c] | (14.26) | 885.38[a] | (2322.05) |
| 2364.77[b] | (265.61) | 2361.8[b] | (37.93) | 1376.09[b] | (49.69) |
| | | 2409.08[b] | (21.98) | 2232.41[b] | (1938.56) |
| | | 2439.87[b] | (118.01) | 2301.55[b] | (8.42) |

| $^2[Pt_2H_4]^+$ | | $^1[Pt_2H_4]$ | | $^1[Pt_2H_5]^+$ | |
|---|---|---|---|---|---|
| 237.63[c] | (172.74) | 234.85[c] | (22.15) | 218.61[c] | (41.53) |
| 351.25[c] | (217.12) | 298.73[c] | (148.31) | 369.93[c] | (102.57) |
| 397.33[c] | (23.42) | 707.09[c] | (93.08) | 648.49[c] | (43.26) |
| 491.23[c] | (179.38) | 794.13[c] | (55.64) | 703.94[c] | (8.33) |
| 535.67[c] | (0.10) | 1058.19[b] | (480.74) | 746.90[c] | (9.53) |
| 895.51[c] | (53.23) | 1784.31[b] | (91.00) | 902.06[c] | (126.26) |
| 910.19[c] | (5.81) | 1878.13[b] | (54.77) | 2243.62[b] | (36.14) |
| 2320.68[b] | (13.88) | 2108.03[b] | (456.70) | 2284.76[b] | (273.43) |
| 2329.55[b] | (197.29) | 2342.59[b] | (60.25) | 2359.55[b] | (89.09) |
| 2389.60[b] | (46.74) | | | 2401.64[b] | (30.07) |
| 2395.85[b] | (13.58) | | | 2439.57[b] | (13.86) |

[a] Sliding. [b] Stretching. [c] Bending.

**Table S10.** The Pt-H vibrational frequencies (cm$^{-1}$) computed for some important intermediates appearing in the successive PT and ET steps for the Pt$_3$ model. The values in parentheses correspond to the oscillator strengths.

| $^1$[Pt$_3$H]$^+$ | | $^2$[Pt$_3$H] | | $^1$[Pt$_3$H$_2$]$^{2+}$ | |
|---|---|---|---|---|---|
| 631.68[a] | (69.54) | 586.57[a] | (124.69) | 383.07[c] | (41.25) |
| 740.98[a] | (364.94) | 1026.53[a] | (837.48) | 466.61[c] | (17.75) |
| 1581.93[b] | (118.83) | 1465.51[b] | (120.93) | 579.00[c] | (46.51) |
| | | | | 978.66[c] | (22.42) |
| | | | | 2278.53[b] | (27.31) |
| | | | | 2323.48[b] | (28.74) |

| $^2$[Pt$_3$H$_2$]$^+$ | | [Pt$_3$H$_2$] | |
|---|---|---|---|
| 260.85[c] | (97.59) | 489.29[c] | (627.16) |
| 645.90[a] | (106.69) | 562.90[a] | (125.61) |
| 966.46[a] | (628.09) | 1053.20[a] | (218.68) |
| 1493.87[b] | (118.71) | 1459.55[b] | (215.64) |
| 2447.01[b] | (69.00) | 2060.89[b] | (435.39) |

[a] Sliding. [b] Stretching [c] Bending.

| MO 20 | s | p | d |
|---|---|---|---|
| Pt1 | 39.06 | 6.50 | 4.43 |
| Pt2 | 39.06 | 6.50 | 4.43 |
| H | 0.00 | | |

LUMO

| MO 17 | s | p | d |
|---|---|---|---|
| Pt1 | 0.00 | 0.20 | 49.80 |
| Pt2 | 0.00 | 0.20 | 49.80 |
| H | 0.00 | | |

SOMO

| MO 12 | s | p | d |
|---|---|---|---|
| Pt1 | 3.06 | 0.08 | 45.48 |
| Pt2 | 3.06 | 0.08 | 45.48 |
| H | 2.75 | | |

π-type bonding

| MO 10 | s | p | d |
|---|---|---|---|
| Pt1 | 3.22 | 0.82 | 44.63 |
| Pt2 | 3.22 | 0.82 | 44.63 |
| H | 2.67 | | |

π-type bonding

| MO 9 | s | p | d |
|---|---|---|---|
| Pt1 | 12.74 | 3.28 | 19.83 |
| Pt2 | 12.74 | 3.28 | 19.83 |
| H | 28.23 | | |

σ-type bonding

**Fig. S7** The selected $\alpha$-MOs of $^2$[Pt$_2$H] correlated with the Pt-H bond, including its SOMO. The contributions (%) for all the s-, p- and d-based atomic orbitals (AOs) of Pt and H atoms are also shown.
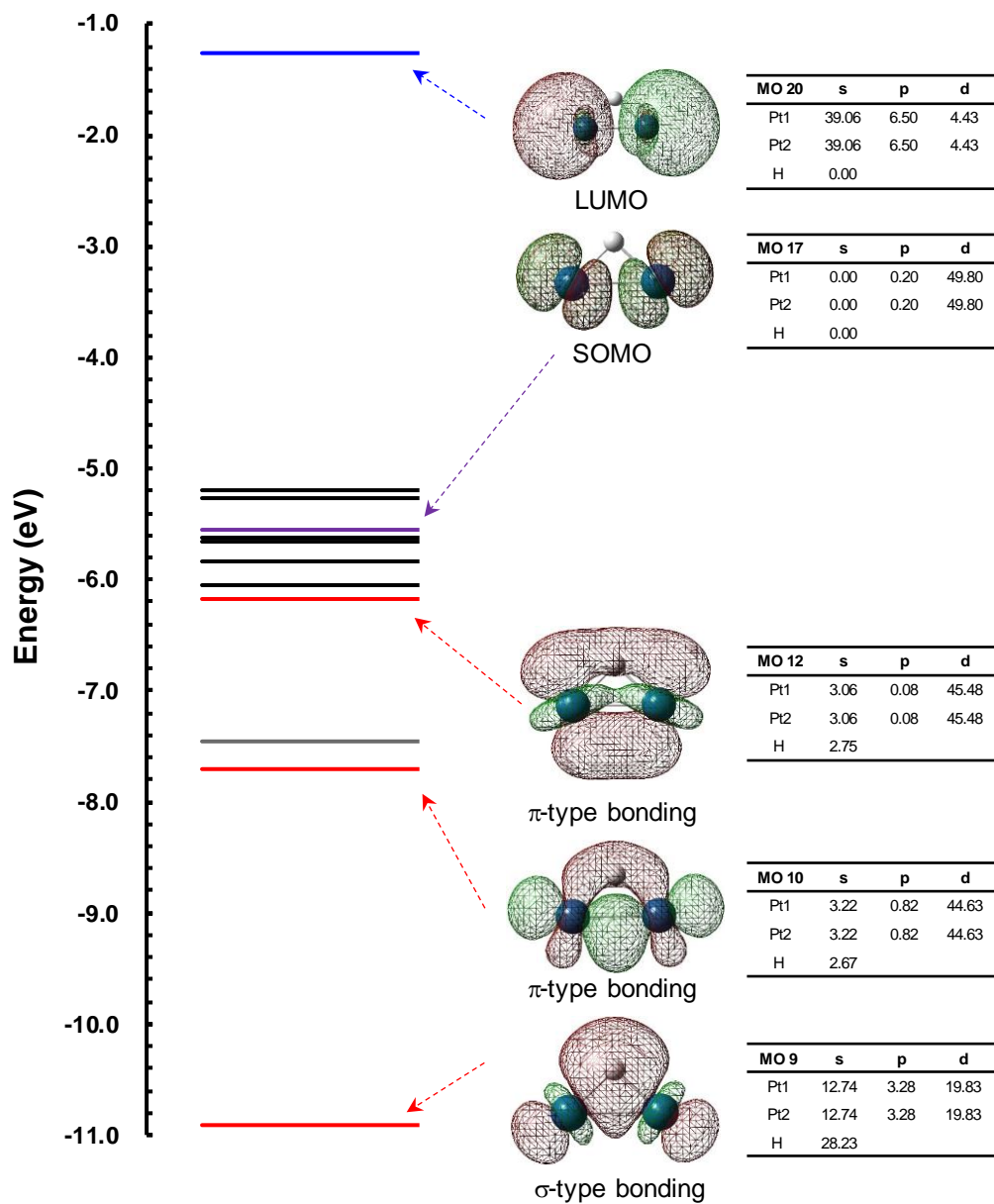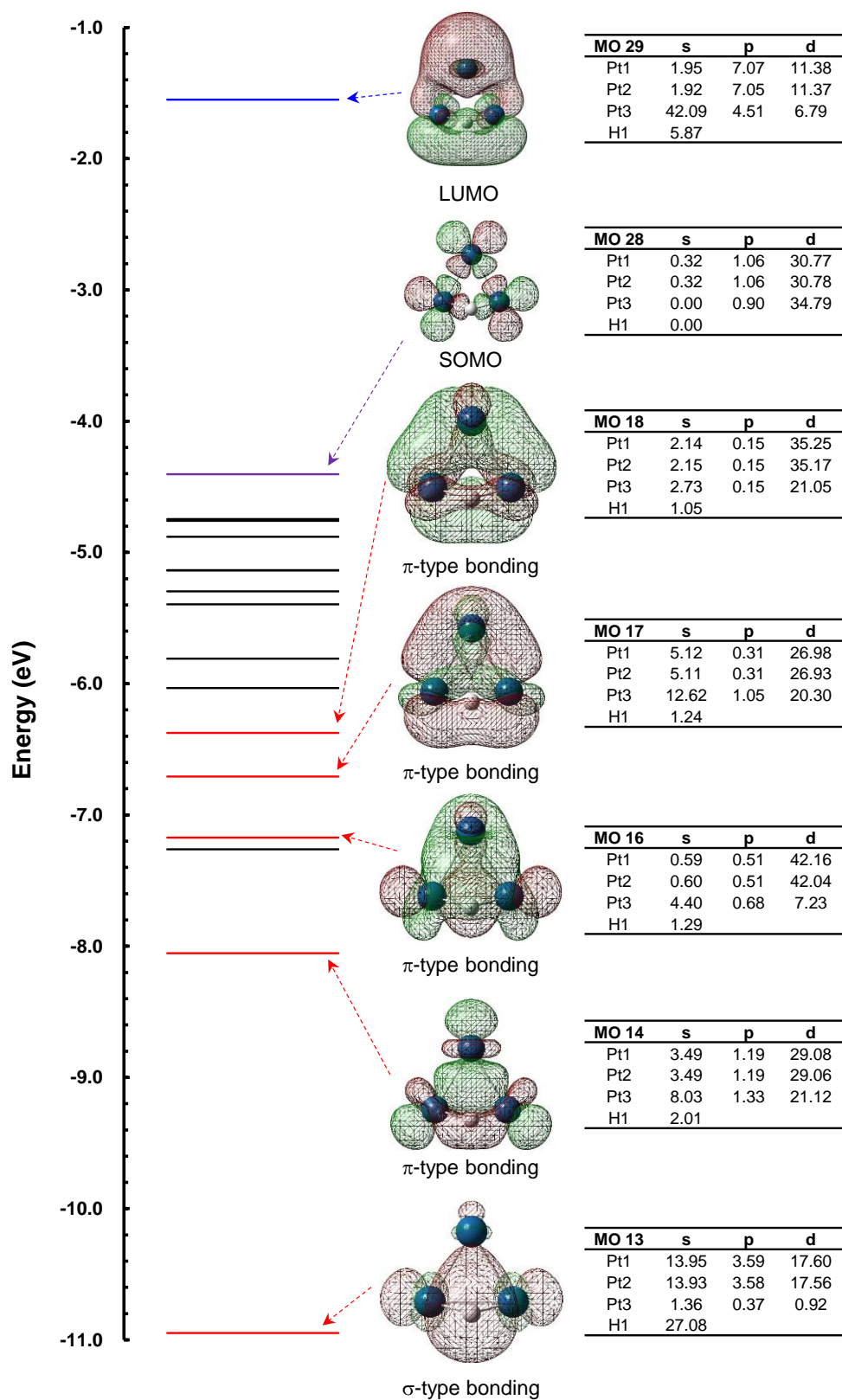
**Fig. S8** The selected α-MOs of ²[Pt₃H] correlated with the Pt-H bond, including its SOMO. The contributions (%) for all the s-, p- and d-based AOs of Pt and H atoms are also shown.

| MO 29 | s | p | d |
|---|---|---|---|
| Pt1 | 1.95 | 7.07 | 11.38 |
| Pt2 | 1.92 | 7.05 | 11.37 |
| Pt3 | 42.09 | 4.51 | 6.79 |
| H1 | 5.87 | | |

| MO 28 | s | p | d |
|---|---|---|---|
| Pt1 | 0.32 | 1.06 | 30.77 |
| Pt2 | 0.32 | 1.06 | 30.78 |
| Pt3 | 0.00 | 0.90 | 34.79 |
| H1 | 0.00 | | |

| MO 18 | s | p | d |
|---|---|---|---|
| Pt1 | 2.14 | 0.15 | 35.25 |
| Pt2 | 2.15 | 0.15 | 35.17 |
| Pt3 | 2.73 | 0.15 | 21.05 |
| H1 | 1.05 | | |

| MO 17 | s | p | d |
|---|---|---|---|
| Pt1 | 5.12 | 0.31 | 26.98 |
| Pt2 | 5.11 | 0.31 | 26.93 |
| Pt3 | 12.62 | 1.05 | 20.30 |
| H1 | 1.24 | | |

| MO 16 | s | p | d |
|---|---|---|---|
| Pt1 | 0.59 | 0.51 | 42.16 |
| Pt2 | 0.60 | 0.51 | 42.04 |
| Pt3 | 4.40 | 0.68 | 7.23 |
| H1 | 1.29 | | |

| MO 14 | s | p | d |
|---|---|---|---|
| Pt1 | 3.49 | 1.19 | 29.08 |
| Pt2 | 3.49 | 1.19 | 29.06 |
| Pt3 | 8.03 | 1.33 | 21.12 |
| H1 | 2.01 | | |

| MO 13 | s | p | d |
|---|---|---|---|
| Pt1 | 13.95 | 3.59 | 17.60 |
| Pt2 | 13.93 | 3.58 | 17.56 |
| Pt3 | 1.36 | 0.37 | 0.92 |
| H1 | 27.08 | | |

**Scheme S1.** Thermodynamic cycles for estimating the thermodynamic hydricity ($\Delta G^{\circ}_{H^-}$), where $R$ is the gas constant, $T$ is the temperature in Kelvin (298.15 K), $F$ is the Faraday constant, and $\Delta G^{\circ}_{H^+/H^-}$ is the free energy change for the reduction of $H^+$ to $H^-$ in water, reported as 34.2 kcal/mol.[S9] The computed values for $pK_a$ and redox potentials were used as follows.

$$\Delta G^{\circ}_{H^-} = \Delta G^{\circ}_{H^+} - \Delta G^{\circ}_{M\cdot/M^-} - \Delta G^{\circ}_{M^+/M\cdot} + \Delta G^{\circ}_{H^+/H^-}$$

$$\Delta G^{\circ}_{H^-} = RT\,ln(10)\,pK_a + FE^{\circ}_{M\cdot/M^-} + FE^{\circ}_{M^+/M\cdot} + \Delta G^{\circ}_{H^+/H^-}$$

**Table S11.** Summary of the thermodynamic hydricity ($\Delta G_{H^-}$) values, $pK_a$ values, and redox potentials.

| Compound (MH) | $\Delta G_{H^-}$ (kcal/mol) | $pK_a$ | Redox potential $E(M\cdot/M^-)$ (V vs. NHE) | Redox potential $E(M^+/M\cdot)$ (V vs. NHE) |
|---|---|---|---|---|
| $[Pt(OH_2)_2H]^+$ | 78.9 | 12.1 | 0.13 | 1.09 |
| $[Pt(OH_2)H]$ | 43.2 | 38.4 | -1.52 | -0.36 |
| $[PtH_2]^+$ | 85.2 | 10.8 | -0.05 | 1.62 |
| $[PtH_2]$ | 57.4 | 32.3 | -0.86 | -0.05 |
| $[PtH_3]^+$ | 92.9 | 1.5 | 0.41 | 2.04 |
| $[Pt_2H]^+$ | 67.7 | 19.3 | 0.56 | -0.25 |
| $[Pt_2H]$ | 63.3 | 37.4 | -1.51 | 0.56 |
| $[Pt_2H_2]^+$ | 78.6 | 16.3 | -0.44 | 1.40 |
| $[Pt_2H_2]$ | 41.4 | 34.4 | -1.28 | -0.44 |
| $[Pt_2H_3]^+$ | 72.8 | 10.1 | -0.21 | 1.28 |
| $[Pt_2H_3]$ | 25.3 | 23.1 | -1.55 | -0.21 |
| $[Pt_2H_4]^+$ | 51.1 | 14.6 | -0.78 | 0.65 |
| $[Pt_2H_4]$ | 28.7 | 21.8 | -0.75 | -0.78 |
| $[Pt_2H_5]^+$ | 43.6 | 4.8 | -0.32 | 0.45 |
| $[Pt_3H]^+$ | 77.0 | 19.7 | -0.63 | 1.32 |
| $[Pt_3H]$ | 26.9 | 33.7 | -1.68 | -0.63 |
| $[Pt_3H_2]^+$ | 64.2 | 23.3 | -0.85 | 0.77 |
| $[Pt_3H_2]$ | 20.6 | 34.3 | -1.77 | -0.85 |
| $[Pt_3H_3]^+$ | 28.3 | 13.8 | -1.11 | 0.04 |
| $[Pt_3H_3]$ | 19.8 | 28.1 | -1.18 | -1.11 |
| $[Pt_3H_4]^+$ | 19.3 | 7.8 | -0.33 | -0.78 |
| $[Pt_3H_4]$ | 37.5 | 24.7 | -0.99 | -0.33 |
| $[Pt_3H_5]^+$ | 25.1 | 0.6 | 0.01 | -0.44 |
| $[Pt_3H_5]$ | 33.7 | 22.4 | -1.36 | 0.01 |
| $[Pt_3H_6]^+$ | 40.4 | 8.5 | -0.08 | -0.15 |

| | | | | |
|---|---|---|---|---|
| [Pt$_3$H$_6$] | 34.9 | 12.3 | -0.62 | -0.08 |
| [Pt$_3$H$_7$]$^+$ | 50.7 | 8.5 | -0.39 | 0.60 |
| [Pt$_3$H$_7$] | 7.7 | 7.4 | -1.20 | -0.39 |

**Table S12.** Summary of the Gibbs free energies for the chemical species used to estimate the individual hydricity values.

| Compound | Gibbs energy in vacuo (kcal/mol) | Gibbs energy in C-PCM (kcal/mol) |
|---|---|---|
| $[Pt(OH_2)_2H]^+$ | -170973.510 | -171046.240 |
| $[Pt(OH_2)_2]$ | -170754.857 | -170765.154 |
| $[Pt(OH_2)_2]^+$ | -170587.600 | -170656.065 |
| $[Pt(OH_2)_2]^{2+}$ | -170239.658 | -170524.937 |
| $[Pt(OH_2)H]$ | -123181.086 | -123200.390 |
| $[Pt(OH_2)]^-$ | -122843.807 | -122883.420 |
| $[Pt(OH_2)]$ | -122801.102 | -122812.465 |
| $[Pt(OH_2)]^+$ | -122615.492 | -122714.770 |
| $[PtH_2]^+$ | -75410.179 | -75534.732 |
| $[PtH]$ | -75237.141 | -75255.396 |
| $[PtH]^+$ | -75024.790 | -75150.649 |
| $[PtH]^{2+}$ | -74585.337 | -75007.221 |
| $[PtH_2]$ | -75629.617 | -75650.249 |
| $[PtH]^-$ | -75286.293 | -75341.563 |
| $[PtH_3]^+$ | -75802.514 | -75916.866 |
| $[PtH_2]^{2+}$ | -74975.394 | -75365.620 |
| $[Pt_2H]^+$ | -149942.366 | -150073.205 |
| $[Pt_2]$ | -149762.519 | -149782.261 |
| $[Pt_2]^+$ | -149553.966 | -149663.400 |
| $[Pt_2]^{2+}$ | -149204.476 | -149563.257 |
| $[Pt_2H]$ | -150144.902 | -150168.954 |
| $[Pt_2]^-$ | -149816.087 | -149853.282 |
| $[Pt_2H_2]^+$ | -150328.911 | -150455.760 |
| $[Pt_2H]^{2+}$ | -149587.959 | -149934.857 |
| $[Pt_2H_2]$ | -150527.212 | -150556.918 |
| $[Pt_2H]^-$ | -150195.124 | -150245.427 |
| $[Pt_2H_3]^+$ | -150716.638 | -150835.346 |
| $[Pt_2H_2]^{2+}$ | -149967.838 | -150312.186 |
| $[Pt_2H_3]$ | -150893.581 | -150923.370 |
| $[Pt_2H_2]^-$ | -150576.038 | -150627.196 |
| $[Pt_2H_4]^+$ | -151086.591 | -151207.840 |
| $[Pt_2H_3]^{2+}$ | -150369.160 | -150714.444 |
| $[Pt_2H_4]$ | -151275.407 | -151306.299 |
| $[Pt_2H_3]^-$ | -150957.567 | -151012.002 |
| $[Pt_2H_5]^+$ | -151465.872 | -151577.454 |
| $[Pt_2H_4]^{2+}$ | -150759.990 | -151091.527 |
| $[Pt_3H]^+$ | -224876.000 | -225001.327 |
| $[Pt_3]$ | -224682.823 | -224709.822 |
| $[Pt_3]^+$ | -224492.047 | -224618.401 |
| $[Pt_3]^{2+}$ | -224139.876 | -224482.016 |
| $[Pt_3H]$ | -225060.524 | -225087.739 |
| $[Pt_3]^-$ | -224737.885 | -224777.113 |
| $[Pt_3H_2]^+$ | -225260.125 | -225384.096 |
| $[Pt_3H]^{2+}$ | -224551.458 | -224877.633 |
| $[Pt_3H_2]$ | -225428.924 | -225464.348 |

| | | |
|---|---|---|
| [Pt$_3$H]$^-$ | -225108.751 | -225152.964 |
| [Pt$_3$H$_3$]$^+$ | -225619.795 | -225747.751 |
| [Pt$_3$H$_2$]$^{2+}$ | -224861.645 | -225530.164 |
| [Pt$_3$H$_3$] | -225805.415 | -225846.068 |
| [Pt$_3$H$_2$]$^-$ | -225490.491 | -225543.113 |
| [Pt$_3$H$_4$]$^+$ | -225999.246 | -226121.292 |
| [Pt$_3$H$_3$]$^{2+}$ | -225326.780 | -225659.867 |
| [Pt$_3$H$_4$] | -226181.147 | -226227.522 |
| [Pt$_3$H$_3$]$^-$ | -225867.445 | -225929.139 |
| [Pt$_3$H$_5$]$^+$ | -226376.498 | -226493.014 |
| [Pt$_3$H$_4$]$^{2+}$ | -225701.952 | -226025.478 |
| [Pt$_3$H$_5$] | -226555.640 | -226597.220 |
| [Pt$_3$H$_4$]$^-$ | -226239.284 | -226302.034 |
| [Pt$_3$H$_6$]$^+$ | -226744.606 | -226873.349 |
| [Pt$_3$H$_5$]$^{2+}$ | -226080.498 | -226390.568 |
| [Pt$_3$H$_6$] | -226929.271 | -226970.314 |
| [Pt$_3$H$_5$]$^-$ | -226688.864 | -226625.964 |
| [Pt$_3$H$_7$]$^+$ | -227121.747 | -227246.550 |
| [Pt$_3$H$_6$]$^{2+}$ | -226448.308 | -226753.582 |
| [Pt$_3$H$_7$] | -227294.607 | -227323.202 |
| [Pt$_3$H$_6$]$^-$ | -226985.400 | -227048.533 |

**Table S13.** Summary of the bond lengths in $^1[Pt_3H_5]^+$ (i.e., $^1[Pt_3(H_{ontop})_2(\mu\text{-}H_{bridge})(H_2)]^+$), optimized at the M06 level of DFT using SDD(Pt) and 6-31+G**(H)  basis sets in vacuo.
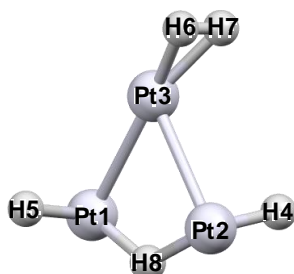


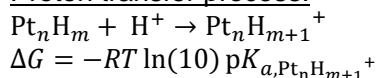|  | Bond length (Å) |
|---|---|
| Pt1-Pt3 | 2.641 |
| Pt2-Pt3 | 2.592 |
| Pt1-H5 | 1.525 |
| Pt1-H8 | 1.657 |
| Pt2-H4 | 1.519 |
| Pt2-H8 | 1.783 |
| Pt3-H6 | 1.733 |
| Pt3-H7 | 1.731 |
| H6-H7 | 0.867 |

**Scheme S2.** Free energy changes relevant to the catalytic processes of Pt nanoclusters under the applied potential of 0.0 V vs. NHE at pH 0.[S10,S11]
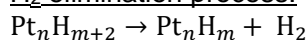
Electron transfer process:
$$Pt_nH_m + e^- \rightarrow Pt_nH_m^-$$
$$\Delta G = -F(E_{Pt_nH_m/Pt_nH_m^-})$$

Proton transfer process:
$$Pt_nH_m + H^+ \rightarrow Pt_nH_{m+1}^+$$
$$\Delta G = -RT\ln(10)\,pK_{a,Pt_nH_{m+1}^+}$$
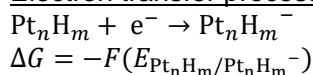
H$_2$ elimination process:
$$Pt_nH_{m+2} \rightarrow Pt_nH_m + H_2$$

a) PT-PT-ET-ET path
$$\Delta G_{H2} = RT\ln(10)(pK_{a,Pt_nH_{m+1}^+} + pK_{a,Pt_nH_{m+2}^{2+}}) + F(E_{Pt_nH_{m+2}^{2+}/Pt_nH_{m+2}^+} + E_{Pt_nH_{m+2}^+/Pt_nH_{m+2}})$$

b) PT-ET-PT-ET path
$$\Delta G_{H2} = RT\ln(10)(pK_{a,Pt_nH_{m+1}^+} + pK_{a,Pt_nH_{m+2}^+}) + F(E_{Pt_nH_{m+1}^+/Pt_nH_{m+1}} + E_{Pt_nH_{m+2}^+/Pt_nH_{m+2}})$$

c) PT-ET-ET-PT path
$$\Delta G_{H2} = RT\ln(10)(pK_{a,Pt_nH_{m+1}^+} + pK_{a,Pt_nH_{m+2}}) + F(E_{Pt_nH_{m+1}^+/Pt_nH_{m+1}} + E_{Pt_nH_{m+1}/Pt_nH_{m+1}^-})$$

d) ET-PT-PT-ET path
$$\Delta G_{H2} = RT\ln(10)(pK_{a,Pt_nH_{m+1}} + pK_{a,Pt_nH_{m+2}^+}) + F(E_{Pt_nH_m/Pt_nH_m^-} + E_{Pt_nH_{m+2}^+/Pt_nH_{m+2}})$$

e) ET-PT-ET-PT path
$$\Delta G_{H2} = RT\ln(10)(pK_{a,Pt_nH_{m+1}} + pK_{a,Pt_nH_{m+2}}) + F(E_{Pt_nH_m/Pt_nH_m^-} + E_{Pt_nH_{m+1}/Pt_nH_{m+1}^-})$$

f) ET-ET-PT-PT path
$$\Delta G_{H2} = RT\ln(10)(pK_{a,Pt_nH_{m+1}^-} + pK_{a,Pt_nH_{m+2}}) + F(E_{Pt_nH_m/Pt_nH_m^-} + E_{Pt_nH_m^-/Pt_nH_m^{2-}})$$

$^1$[Pt(OH$_2$)$_2$]  $\xrightarrow{E = -1.78\text{ V}}$  $^2$[Pt]$^-$ + 2H$_2$O
  $+e^-$

+H$^+$  p$K_a$ = 12.1    +H$^+$  p$K_a$ = 34.2

$^1$[Pt(OH$_2$)$_2$H]$^+$  $\xrightarrow{E = -0.47\text{ V}}$  $^2$[Pt(OH$_2$)H]  $\xrightarrow{E = -1.00\text{ V}}$  $^1$[PtH]$^-$ + H$_2$O
  $+e^-$    $+e^-$

+H$^+$  p$K_a$ = -46.5    +H$^+$  p$K_a$ = 7.8    +H$^+$  p$K_a$ = 31.7

$^1$[PtH$_2$]$^{2+}$    $^2$[PtH$_2$]$^+$  $\xrightarrow{E = 0.42\text{ V}}$  $^1$[PtH$_2$]  $\xrightarrow{E = -2.07\text{ V}}$  $^2$[PtH$_2$]$^-$
  $+e^-$    $+e^-$

+H$^+$  p$K_a$ = -42.0    +H$^+$  p$K_a$ = 1.5

$^2$[PtH$_3$]$^{2+}$    $^1$[PtH$_3$]$^+$  $\xrightarrow{E = -1.23\text{ V}}$  $^2$[PtH$_3$]
  $+e^-$

+H$^+$  p$K_a$ = -71.0

$^1$[PtH$_4$]$^{2+}$

**Fig. S9** Square schemes developed for the Pt$_1$ system, where each potential is given in V vs. NHE. The species highlighted by rectangles are possible intermediates during the catalysis. Arrows in red, blue and pink colors represent the exergonic pathways, while those in gray color represent the endergonic pathways under the applied potential of 0.0 V vs NHE at pH 0.

$E$ = -1.51 V

$^3[Pt_2]$ → $^2[Pt_2]^-$

+e⁻

+H⁺ | p$K_a$ = 19.3

+H⁺ | p$K_a$ = 37.4

$E$ = -0.44 V

$^3[Pt_2H]^+$ → $^2[Pt_2H]$ → $^1[Pt_2H]^-$

+e⁻    $E$ = -1.28 V    +e⁻

+H⁺ | p$K_a$ = -12.8

+H⁺ | p$K_a$ = 16.3

+H⁺ | p$K_a$ = 34.4

$E$ = 1.28 V

$^3[Pt_2H_2]^{2+}$ → $^2[Pt_2H_2]^+$ → $^1[Pt_2H_2]$ → $^2[Pt_2H_2]^-$

+e⁻   $E$ = -0.21 V   +e⁻   $E$ = -1.55 V   +e⁻

+H⁺ | p$K_a$ = -4.3

$^2[Pt_2H_3]^{2+}$

+H⁺ | p$K_a$ = 10.1

$^1[Pt_2H_3]^+$ → $^2[Pt_2H_3]$ → $^1[Pt_2H_3]^-$

+e⁻   $E$ = -0.78 V   +e⁻   $E$ = -0.75 V

+H⁺ | p$K_a$ = -6.2

$^1[Pt_2H_4]^{2+}$

+H⁺ | p$K_a$ = 14.6

$^2[Pt_2H_4]^+$ → $^1[Pt_2H_4]$ → $^1[Pt_2H_4]^-$

+e⁻   $E$ = -0.32 V   +e⁻   $E$ = -2.11 V

+H⁺ | p$K_a$ = -21.7

$^1[Pt_2H_4]^{2+}$

+H⁺ | p$K_a$ = 4.8

$^1[Pt_2H_5]^+$ → $^1[Pt_2H_5]$

+e⁻   $E$ = -1.04 V

+H⁺ | p$K_a$ = -26.9

$^1[Pt_2H_6]^{2+}$

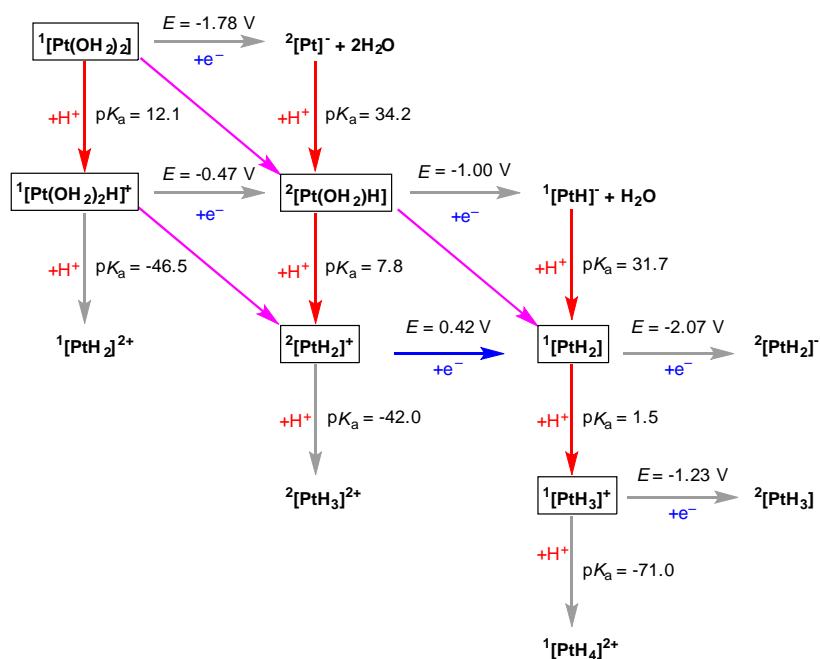**Fig. S10** Square schemes developed for the Pt$_2$ system, where each potential is given in V vs. NHE. The species highlighted by rectangles are possible intermediates during the catalysis. Arrows in red, blue and pink colors represent the exergonic pathways, while those in gray color represent the endergonic pathways under the applied potential of 0.0 V vs NHE at pH 0.
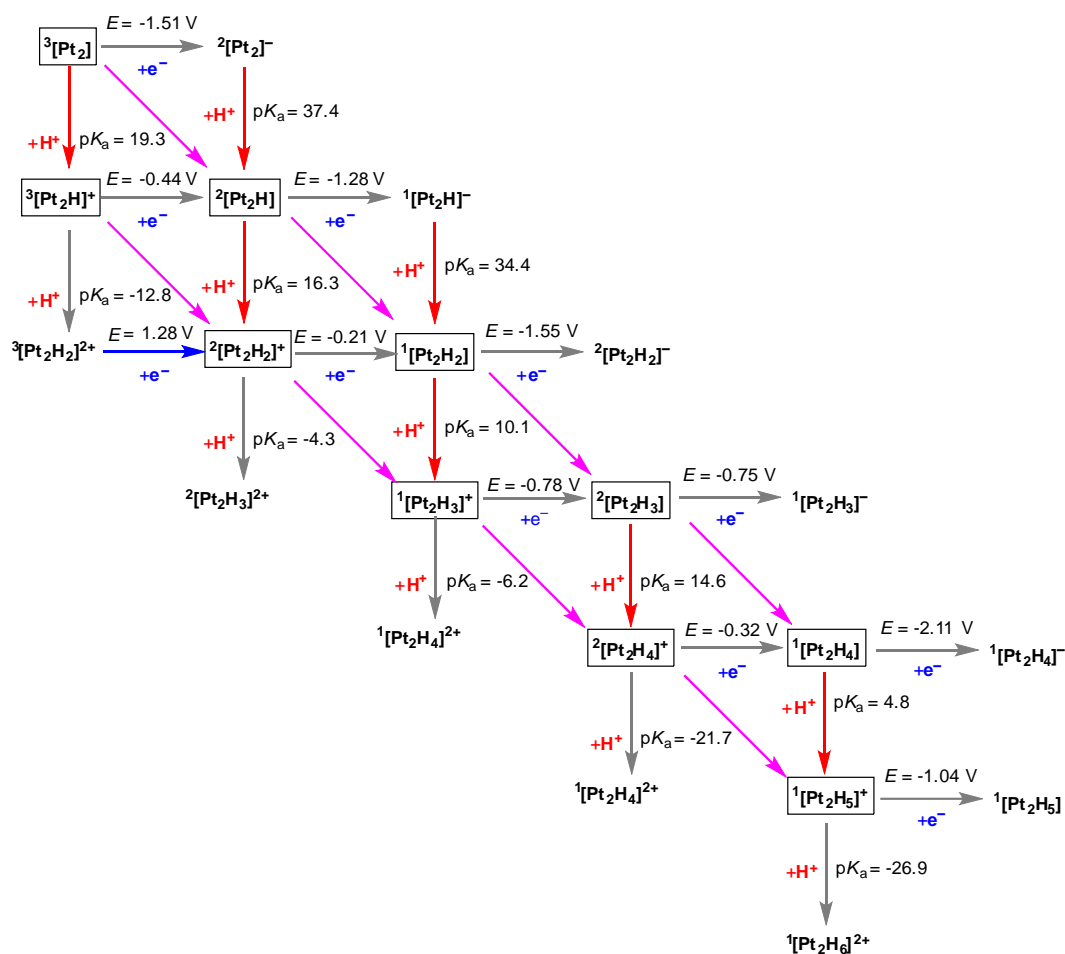
**Fig. S11** Energy diagram for the reaction steps computed for the Pt$_3$ system when the electrocatalytic HER is driven by 0.0 V vs. NHE at pH 0.

**Fig. S12** Square schemes developed for the Pt$_3$ system, where each potential is given in V vs. NHE. The species highlighted by rectangles are possible intermediates during the catalysis. Arrows in red, blue and pink colors represent the exergonic pathways, while those in gray color represent the endergonic pathways under the applied potential of 0.0 V vs NHE at pH 0.
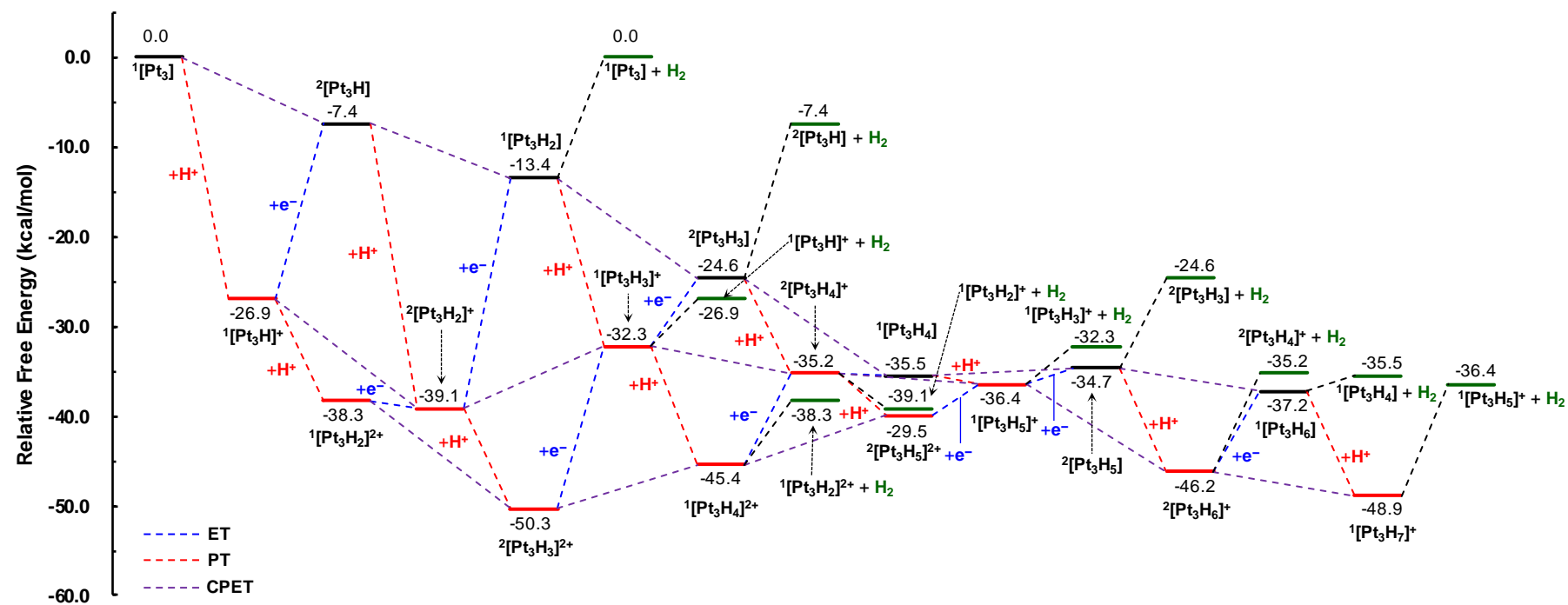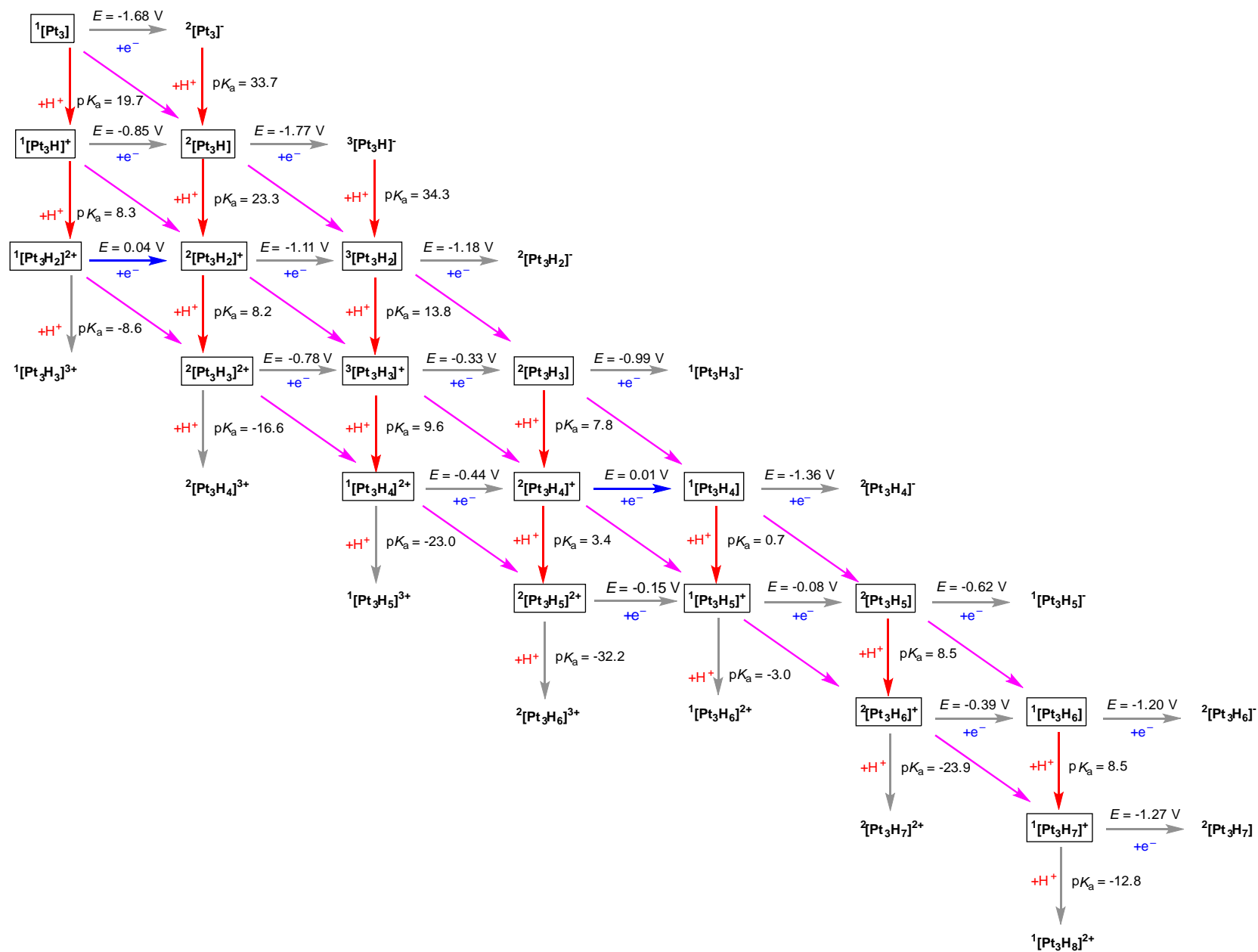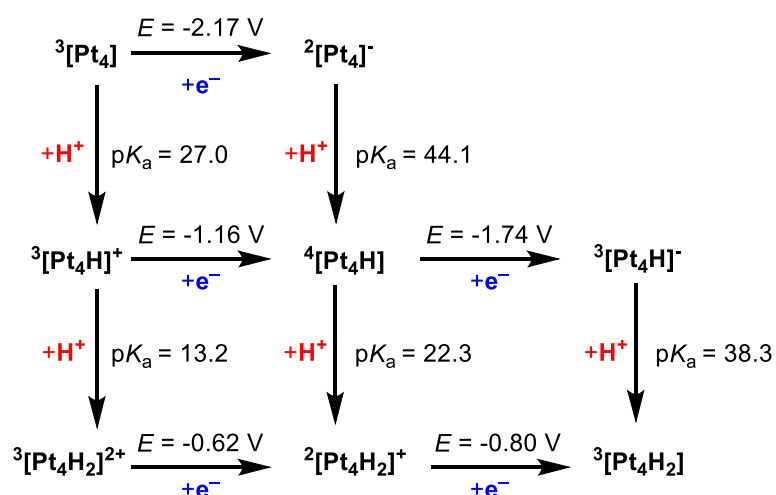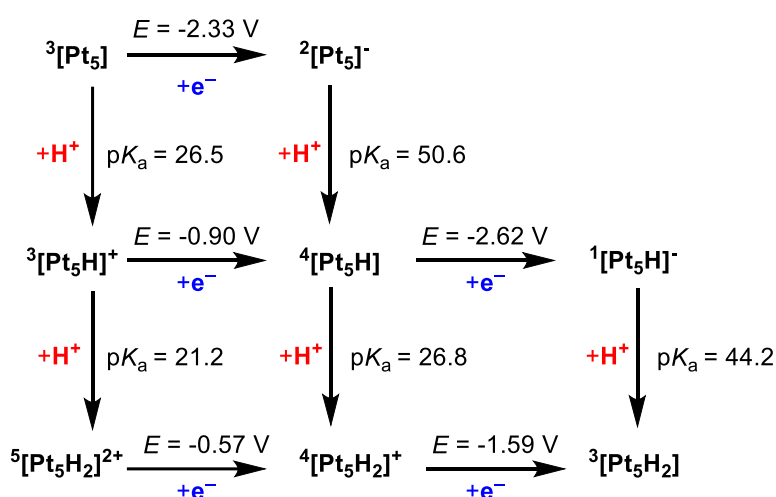
**Table S14.** Summary of the Gibbs free energies computed for the species appearing in the unfeasible reaction paths.

| Compound | Gibbs energy in vacuo (kcal/mol) | Gibbs energy in C-PCM (kcal/mol) |
|---|---|---|
| $^1[PtH_2]^{2+}$ | -74975.394 | -75365.620 |
| $^2[PtH_2]^-$ | -75651.485 | -75708.457 |
| $^2[PtH_3]^{2+}$ | -75375.290 | -75742.065 |
| $^2[PtH_3]$ | -75975.928 | -75994.609 |
| $^1[PtH_4]^{2+}$ | -75745.075 | -76084.619 |
| $^3[Pt_2H_2]^{2+}$ | -149967.964 | -150320.427 |
| $^2[Pt_2H_2]^-$ | -150329.037 | -150455.886 |
| $^2[Pt_2H_3]^{2+}$ | -150369.286 | -150714.571 |
| $^1[Pt_2H_3]^-$ | -150957.694 | -151012.129 |
| $^1[Pt_2H_4]^{2+}$ | -150760.116 | -151091.653 |
| $^1[Pt_2H_4]^-$ | -151308.062 | -151358.567 |
| $^2[Pt_2H_5]^{2+}$ | -151129.456 | -151442.943 |
| $^2[Pt_2H_5]$ | -151637.033 | -151659.556 |
| $^1[Pt_2H_6]^{2+}$ | -151504.637 | -151805.538 |
| $^2[Pt_3H_2]^-$ | -225490.680 | -225543.302 |
| $^1[Pt_3H_3]^{3+}$ | -224861.834 | -225530.353 |
| $^1[Pt_3H_3]^-$ | -225867.634 | -225929.328 |
| $^2[Pt_3H_4]^{3+}$ | -225250.483 | -225902.022 |
| $^2[Pt_3H_4]^-$ | -226239.474 | -226302.223 |
| $^1[Pt_3H_5]^{3+}$ | -225632.331 | -226258.897 |
| $^1[Pt_3H_5]^-$ | -226626.154 | -226689.054 |
| $^2[Pt_3H_6]^{3+}$ | -226007.044 | -226611.307 |
| $^1[Pt_3H_6]^{2+}$ | -226448.498 | -226753.773 |
| $^2[Pt_3H_6]^-$ | -226985.590 | -227048.724 |
| $^2[Pt_3H_7]^{2+}$ | -226817.775 | -227105.519 |
| $^2[Pt_3H_7]$ | -227294.798 | -227323.393 |
| $^1[Pt_3H_8]^{2+}$ | -227203.227 | -227493.944 |

(A) Tetraplatinum system

$E$ = -2.17 V

$^3[Pt_4]$ $\xrightarrow{\phantom{E}}$ $^2[Pt_4]^-$
        +e$^-$

+H$^+$ | p$K_a$ = 27.0     +H$^+$ | p$K_a$ = 44.1

$E$ = -1.16 V                    $E$ = -1.74 V

$^3[Pt_4H]^+$ $\xrightarrow{\phantom{E}}$ $^4[Pt_4H]$ $\xrightarrow{\phantom{E}}$ $^3[Pt_4H]^-$
            +e$^-$                      +e$^-$

+H$^+$ | p$K_a$ = 13.2     +H$^+$ | p$K_a$ = 22.3     +H$^+$ | p$K_a$ = 38.3

$^3[Pt_4H_2]^{2+}$ $\xrightarrow{E = -0.62\,V}$ $^2[Pt_4H_2]^+$ $\xrightarrow{E = -0.80\,V}$ $^3[Pt_4H_2]$
                   +e$^-$                        +e$^-$

(B) Pentaplatinum system

$E$ = -2.33 V

$^3[Pt_5]$ $\xrightarrow{\phantom{E}}$ $^2[Pt_5]^-$
        +e$^-$

+H$^+$ | p$K_a$ = 26.5     +H$^+$ | p$K_a$ = 50.6

$E$ = -0.90 V                    $E$ = -2.62 V

$^3[Pt_5H]^+$ $\xrightarrow{\phantom{E}}$ $^4[Pt_5H]$ $\xrightarrow{\phantom{E}}$ $^1[Pt_5H]^-$
            +e$^-$                      +e$^-$

+H$^+$ | p$K_a$ = 21.2     +H$^+$ | p$K_a$ = 26.8     +H$^+$ | p$K_a$ = 44.2

$^5[Pt_5H_2]^{2+}$ $\xrightarrow{E = -0.57\,V}$ $^4[Pt_5H_2]^+$ $\xrightarrow{E = -1.59\,V}$ $^3[Pt_5H_2]$
                   +e$^-$                        +e$^-$

(C) Undecaplatinum system

$E$ = -1.72 V

$^3[Pt_{11}]$ $\xrightarrow{\phantom{E}}$ $^2[Pt_{11}]^-$
          +e$^-$

+H$^+$ | p$K_a$ = 29.7     +H$^+$ | p$K_a$ = 35.6

$E$ = -1.37 V                    $E$ = -1.41 V

$^3[Pt_{11}H]^+$ $\xrightarrow{\phantom{E}}$ $^2[Pt_{11}H]$ $\xrightarrow{\phantom{E}}$ $^3[Pt_{11}H]^-$
              +e$^-$                        +e$^-$

+H$^+$ | p$K_a$ = 26.0     +H$^+$ | p$K_a$ = 32.5     +H$^+$ | p$K_a$ = 37.4

$^3[Pt_{11}H_2]^{2+}$ $\xrightarrow{E = -0.99\,V}$ $^2[Pt_{11}H_2]^+$ $\xrightarrow{E = -1.12\,V}$ $^3[Pt_{11}H_2]$
                      +e$^-$                          +e$^-$
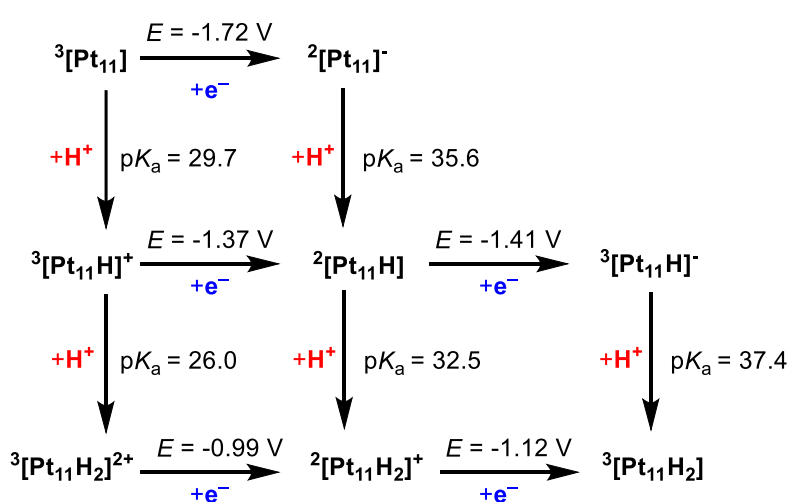
**Fig. S13** Selected square schemes for the $Pt_4$ (A), $Pt_5$ (B), and $Pt_{11}$ (C) systems, where each potential is given in V vs. NHE.

**Fig. S14** Energy diagram for the reaction steps computed for the Pt$_4$ system when the electrocatalytic HER is driven by 0.0 V vs. NHE at pH 0.



**Fig. S15** Energy diagram for the reaction steps computed for the Pt$_5$ system when the electrocatalytic HER is driven by 0.0 V vs. NHE at pH 0.
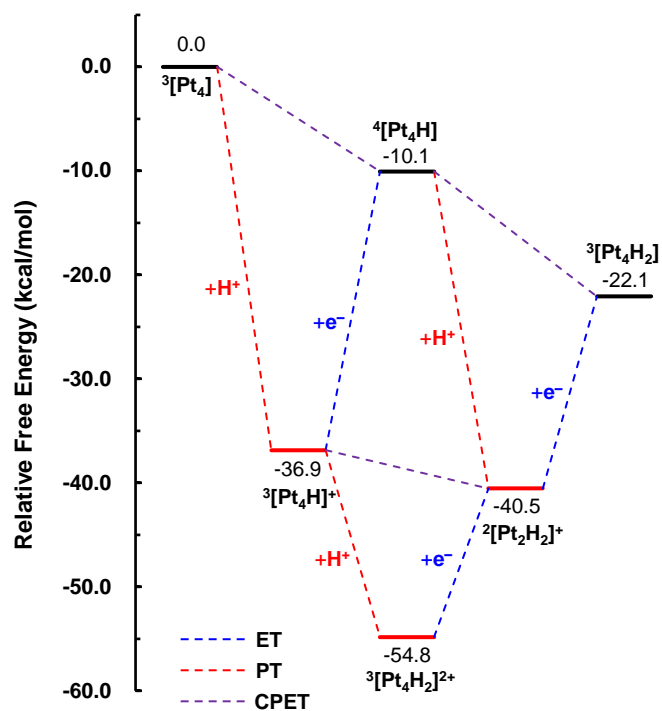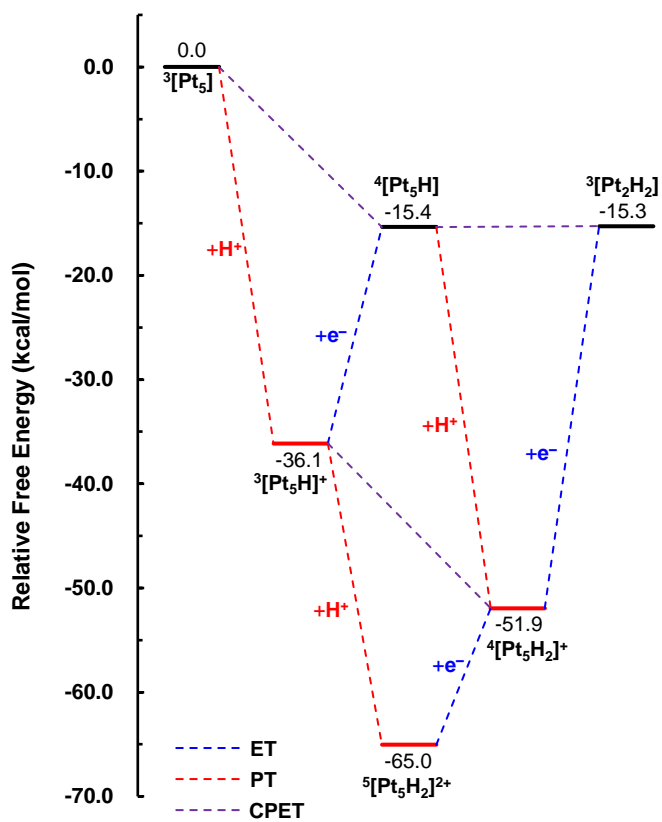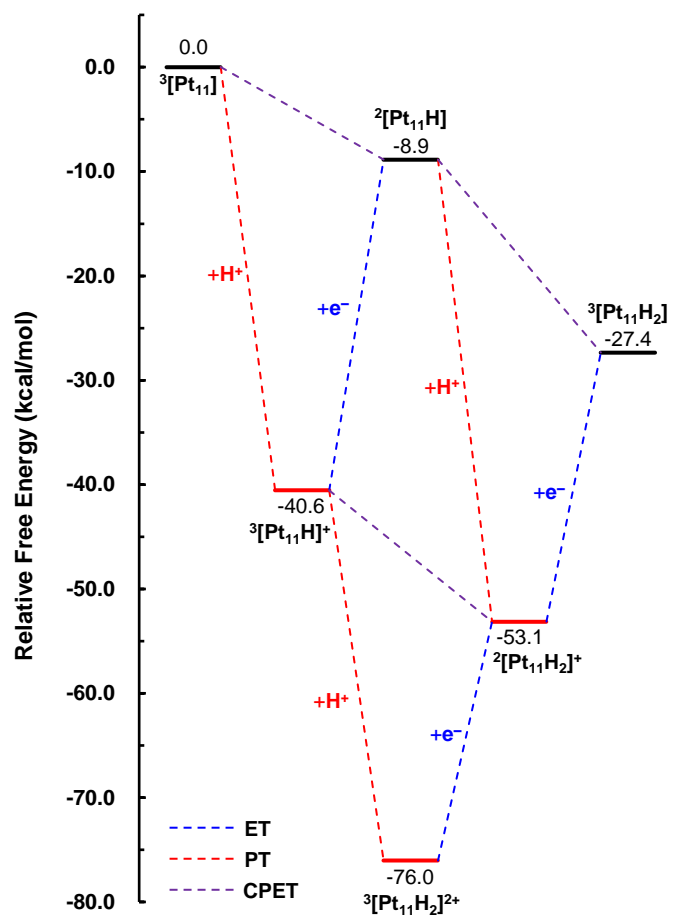
**Fig. S16** Energy diagram for the reaction steps computed for the $Pt_{11}$ system when the electrocatalytic HER is driven by 0.0 V vs. NHE at pH 0.

**Table S15.**
(A) Summary for the DFT calculation of Pt (i.e., single Pt(0) atom) in its singlet state. Computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]

[a]Part of the Gaussian output file:

```
Thermal correction to Energy=              0.001416 (Hartree/Particle)
Thermal correction to Enthalpy=            0.002360
Thermal correction to Gibbs Free Energy=   -0.017456
Sum of electronic and zero-point Energies=     -119.271079
Sum of electronic and thermal Energies=        -119.269662
Sum of electronic and thermal Enthalpies=      -119.268718
Sum of electronic and thermal Free Energies=   -119.288535
```

(B) Summary for the DFT calculation of Pt (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) basis set.[a]

[a]Part of the Gaussian output file:

```
Thermal correction to Energy=              0.001416 (Hartree/Particle)
Thermal correction to Enthalpy=            0.002360
Thermal correction to Gibbs Free Energy=   -0.017456
Sum of electronic and zero-point Energies=     -119.277578
Sum of electronic and thermal Energies=        -119.276162
Sum of electronic and thermal Enthalpies=      -119.275218
Sum of electronic and thermal Free Energies=   -119.295035
```

**Table S16.**
(A) Summary for the DFT calculation of Pt (i.e., single Pt(0) atom) in its triplet state. Computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]

[a]Part of the Gaussian output file:

```
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0027,   after    2.0000
```

```
Thermal correction to Energy=              0.001416 (Hartree/Particle)
Thermal correction to Enthalpy=            0.002360
Thermal correction to Gibbs Free Energy=   -0.018494
Sum of electronic and zero-point Energies=     -119.267154
Sum of electronic and thermal Energies=        -119.265738
Sum of electronic and thermal Enthalpies=      -119.264793
Sum of electronic and thermal Free Energies=   -119.285648
```

(B) Summary for the DFT calculation of Pt (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) basis set.[a]

[a]Part of the Gaussian output file:

```
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0032,   after    2.0000
```

```
Thermal correction to Energy=              0.001416 (Hartree/Particle)
Thermal correction to Enthalpy=             0.002360
```

Thermal correction to Gibbs Free Energy=      -0.018494
Sum of electronic and zero-point Energies=       -119.278938
Sum of electronic and thermal Energies=       -119.277522
Sum of electronic and thermal Enthalpies=       -119.276577
Sum of electronic and thermal Free Energies=        -119.297432

**Table S17.**

(A) Geometry optimized for [Pt(OH$_2$)] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.251720 | -0.000006 | 0.001290 | -0.073240 |
| O2 | -1.907902 | -0.000044 | -0.110431 | -0.780554 |
| H3 | -2.186304 | -0.776891 | 0.391646 | 0.426924 |
| H4 | -2.184669 | 0.777722 | 0.391179 | 0.426869 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -195.693879520     A.U. after   10 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000068 | 0.000450 | YES |
| RMS Force | 0.000038 | 0.000300 | YES |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 325.7599 | 517.5624 | 560.7030 |
| Red. masses -- | 5.6421 | 1.1967 | 1.0451 |
| Frc consts -- | 0.3528 | 0.1889 | 0.1936 |
| IR Inten -- | 0.2142 | 293.1672 | 0.6567 |

| | |
|---|---|
| Zero-point correction= | 0.024457 (Hartree/Particle) |
| Thermal correction to Energy= | 0.028076 |
| Thermal correction to Enthalpy= | 0.029020 |
| Thermal correction to Gibbs Free Energy= | -0.001969 |
| Sum of electronic and zero-point Energies= | -195.669423 |
| Sum of electronic and thermal Energies= | -195.665803 |
| Sum of electronic and thermal Enthalpies= | -195.664859 |
| Sum of electronic and thermal Free Energies= | -195.695849 |

(B) Summary for the DFT calculation of [Pt(OH$_2$)] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
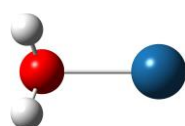


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.251720 | -0.000006 | 0.001290 | -0.097531 |
| O2 | -1.907902 | -0.000044 | -0.110431 | -0.794640 |
| H3 | -2.186304 | -0.776891 | 0.391646 | 0.446130 |
| H4 | -2.184669 | 0.777722 | 0.391179 | 0.446040 |

[a]Part of the Gaussian output file:

Zero-point correction=                          0.024227 (Hartree/Particle)
Thermal correction to Energy=              0.027895
Thermal correction to Enthalpy=            0.028839
Thermal correction to Gibbs Free Energy=    -0.002227
Sum of electronic and zero-point Energies=       -195.687502
Sum of electronic and thermal Energies=          -195.683834
Sum of electronic and thermal Enthalpies=        -195.682890
Sum of electronic and thermal Free Energies=       -195.713956

**Table S18.**

(A) Geometry optimized for [Pt(OH$_2$)] (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.292564 | -0.000006 | 0.001228 | -0.100391 | 1.989652 |
| O2 | -2.217419 | -0.000065 | -0.105082 | -0.695626 | -0.000875 |
| H3 | -2.541223 | -0.772480 | 0.372683 | 0.398026 | 0.005619 |
| H4 | -2.539411 | 0.773436 | 0.372152 | 0.397991 | 0.005604 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -195.675879145     A.U. after   17 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0029,   after    2.0000

|        Item       | Value   | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000020 | 0.000450 | YES |
| RMS    Force | 0.000011 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 188.5257 | 342.1375 | 386.0530 |
| Red. masses -- | 6.2631 | 1.1705 | 1.0440 |
| Frc consts  -- | 0.1312 | 0.0807 | 0.0917 |
| IR Inten    -- | 10.1224 | 275.5564 | 0.5286 |

Zero-point correction=                           0.023526 (Hartree/Particle)
Thermal correction to Energy=                0.027634
Thermal correction to Enthalpy=               0.028578
Thermal correction to Gibbs Free Energy=       -0.004683
Sum of electronic and zero-point Energies=          -195.652353
Sum of electronic and thermal Energies=           -195.648245
Sum of electronic and thermal Enthalpies=          -195.647301
Sum of electronic and thermal Free Energies=        -195.680562

(B) Summary for the DFT calculation of [Pt(OH$_2$)] (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]

Spin density distribution

S32
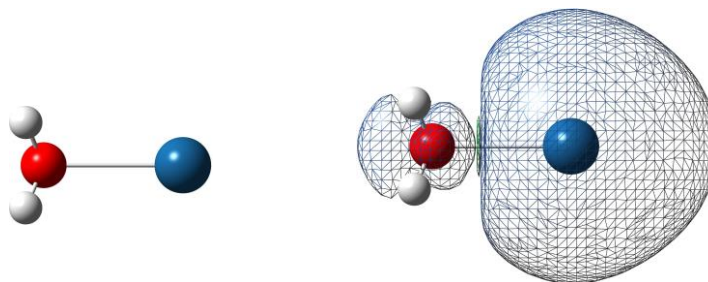
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:----------:|:-------------:|:-------------:|:-------------:|:---------------:|:------------:|
| Pt1 | 0.292564 | -0.000006 | 0.001228 | -0.085232 | 1.994503 |
| O2 | -2.217419 | -0.000065 | -0.105082 | -0.743260 | -0.006898 |
| H3 | -2.541224 | -0.772480 | 0.372683 | 0.414264 | 0.006206 |
| H4 | -2.539411 | 0.773436 | 0.372152 | 0.414228 | 0.006189 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                    0.022380 (Hartree/Particle)
Thermal correction to Energy=             0.026268
Thermal correction to Enthalpy=           0.027212
Thermal correction to Gibbs Free Energy=  -0.005778
Sum of electronic and zero-point Energies=    -195.665770
Sum of electronic and thermal Energies=       -195.661883
Sum of electronic and thermal Enthalpies=     -195.660939
Sum of electronic and thermal Free Energies=  -195.693928
```

**Table S19.**

(A) Geometry optimized for [Pt(OH$_2$)$_2$] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.000000 | 0.012942 | 0.000000 | -0.363913 |
| O2 | 2.120403 | 0.021599 | -0.080355 | -0.663227 |
| O3 | -2.120400 | 0.021573 | 0.080374 | -0.663234 |
| H4 | 2.400755 | 0.219285 | 0.823754 | 0.422759 |
| H5 | 2.363130 | -0.896794 | -0.260075 | 0.422429 |
| H6 | -2.400785 | 0.219539 | -0.823663 | 0.422758 |
| H7 | -2.363140 | -0.896867 | 0.259828 | 0.422428 |

[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -272.135881414    A.U. after    8 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000001 | 0.000450 | YES |
| RMS   Force | 0.000000 | 0.000300 | YES |

| | 1 | 2 | 3 |
|--|--|--|--|
| | A | A | A |
| Frequencies -- | 129.4163 | 149.9240 | 152.4530 |
| Red. masses -- | 1.0659 | 4.2381 | 5.0360 |
| Frc consts  -- | 0.0105 | 0.0561 | 0.0690 |
| IR Inten   -- | 67.1261 | 1.4973 | 18.0452 |

Zero-point correction=                   0.050621 (Hartree/Particle)
Thermal correction to Energy=            0.056694
Thermal correction to Enthalpy=          0.057638
Thermal correction to Gibbs Free Energy=      0.020923
Sum of electronic and zero-point Energies=      -272.085260
Sum of electronic and thermal Energies=         -272.079187
Sum of electronic and thermal Enthalpies=       -272.078243
Sum of electronic and thermal Free Energies=    -272.114958

(B) Summary for the DFT calculation of [Pt(OH$_2$)$_2$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
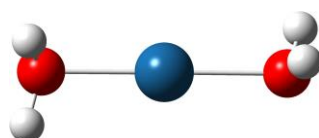


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.000000 | 0.012942 | 0.000000 | -0.375066 |
| O2 | 2.120403 | 0.021599 | -0.080355 | -0.702997 |
| O3 | -2.120400 | 0.021573 | 0.080374 | -0.703002 |

| | | | |
|---|---|---|---|
| H4 | 2.400755 | 0.219285 | 0.823754 | 0.445232 |
| H5 | 2.363130 | -0.896794 | -0.260075 | 0.445301 |
| H6 | -2.400785 | 0.219539 | -0.823663 | 0.445232 |
| H7 | -2.363140 | -0.896867 | 0.259828 | 0.445300 |

---------------------------------------------------------------------------------------------------------------------

aPart of the Gaussian output file:

Zero-point correction=                      0.049916 (Hartree/Particle)
Thermal correction to Energy=            0.055407
Thermal correction to Enthalpy=          0.056351
Thermal correction to Gibbs Free Energy=      0.020864
Sum of electronic and zero-point Energies=        -272.102315
Sum of electronic and thermal Energies=          -272.096824
Sum of electronic and thermal Enthalpies=         -272.095880
Sum of electronic and thermal Free Energies=       -272.131367

**Table S20.**

(A) Geometry optimized for [Pt(OH$_2$)$_2$] (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000076 | -0.006624 | 0.000089 | -0.246008 | 2.078949 |
| O2 | 2.680813 | -0.046405 | 0.083833 | -0.657211 | -0.052484 |
| O3 | -2.682389 | -0.049110 | -0.082614 | -0.657055 | -0.052042 |
| H4 | 2.912600 | -0.255447 | -0.827821 | 0.390591 | 0.006441 |
| H5 | 2.892766 | 0.885402 | 0.207693 | 0.389380 | 0.006404 |
| H6 | -2.909421 | -0.229144 | 0.836410 | 0.390766 | 0.006378 |
| H7 | -2.889265 | 0.879987 | -0.232944 | 0.389538 | 0.006353 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -272.080534520     A.U. after   16 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0029,   after     2.0000

```
      Item          Value    Threshold  Converged?
Maximum Force       0.000035    0.000450    YES
RMS    Force        0.000018    0.000300    YES
```

```
              1              2              3
              A              A              A
Frequencies --   50.1781        56.2938        59.7880
Red. masses --    5.9499         6.3359         1.0404
Frc consts  --    0.0088         0.0118         0.0022
IR Inten   --    3.9621         0.0964        73.1924
```

Zero-point correction=                  0.046554 (Hartree/Particle)
Thermal correction to Energy=            0.054967
Thermal correction to Enthalpy=          0.055911
Thermal correction to Gibbs Free Energy=      0.011143
Sum of electronic and zero-point Energies=        -272.033980
Sum of electronic and thermal Energies=         -272.025568
Sum of electronic and thermal Enthalpies=         -272.024624
Sum of electronic and thermal Free Energies=        -272.069392

(B) Summary for the DFT calculation of [Pt(OH$_2$)$_2$] (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
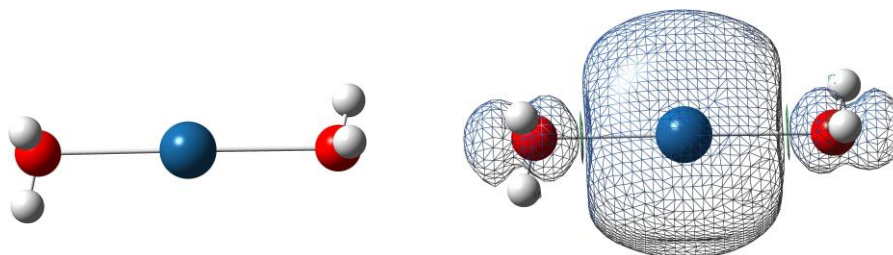


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | -0.000076 | 0.006624 | 0.000089 | -0.239548 | 2.061002 |
| O2 | -2.680814 | 0.046405 | 0.083833 | -0.698015 | -0.041048 |
| O3 | 2.682389 | 0.049110 | -0.082614 | -0.698004 | -0.040627 |
| H4 | -2.912600 | 0.255447 | -0.827821 | 0.409008 | 0.005141 |
| H5 | -2.892767 | -0.885402 | 0.207693 | 0.408661 | 0.005259 |
| H6 | 2.909421 | 0.229144 | 0.836410 | 0.409118 | 0.005078 |
| H7 | 2.889265 | -0.879987 | -0.232944 | 0.408780 | 0.005196 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.043898 (Hartree/Particle)
Thermal correction to Energy=            0.050452
Thermal correction to Enthalpy=          0.051396
Thermal correction to Gibbs Free Energy=      0.010154
Sum of electronic and zero-point Energies=      -272.048957
Sum of electronic and thermal Energies=        -272.042403
Sum of electronic and thermal Enthalpies=      -272.041459
Sum of electronic and thermal Free Energies=       -272.082702
```

**Table S21.**

(A) Geometry optimized for [Pt(OH$_2$)$_2$H]$^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 0.000002 | -0.010378 | -0.010508 | 0.452656 |
| O2 | -2.076585 | 0.024237 | 0.026691 | -0.703809 |
| O3 | 2.076558 | 0.024283 | 0.026573 | -0.703842 |
| H4 | -2.561096 | 0.455437 | -0.691428 | 0.448348 |
| H5 | -2.564671 | -0.751717 | 0.336751 | 0.448187 |
| H6 | 2.564820 | -0.750883 | 0.338288 | 0.448207 |
| H7 | 2.560994 | 0.454362 | -0.692252 | 0.448342 |
| H8 | 0.000016 | 1.014134 | 1.102170 | 0.161911 |

[a]Part of the Gaussian output file:

 SCF Done:  E(RM06) =  -272.491154440     A.U. after     9 cycles

|       Item       | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000013 | 0.000450 | YES |
| RMS    Force | 0.000005 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 99.5050 | 153.7264 | 165.7230 |
| Red. masses -- | 1.0256 | 3.9796 | 6.7347 |
| Frc consts  -- | 0.0060 | 0.0554 | 0.1090 |
| IR Inten   -- | 0.2670 | 30.0153 | 10.7210 |

 Zero-point correction=                    0.058300 (Hartree/Particle)
 Thermal correction to Energy=             0.065202
 Thermal correction to Enthalpy=           0.066146
 Thermal correction to Gibbs Free Energy=    0.027751
 Sum of electronic and zero-point Energies=     -272.432854
 Sum of electronic and thermal Energies=        -272.425953
 Sum of electronic and thermal Enthalpies=      -272.425009
 Sum of electronic and thermal Free Energies=    -272.463403

(B) Summary for the DFT calculation of [Pt(OH$_2$)$_2$H]$^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
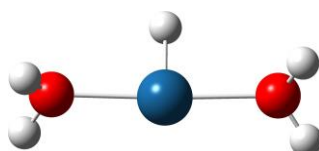


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -0.000032 | -0.015453 | 0.005027 | 0.597236 |
| O2 | -2.076387 | 0.039414 | -0.011479 | -0.726911 |

| | | | |
|---|---|---|---|
| O3 | 2.076276 | 0.018404 | -0.026710 | -0.728415 |
| H4 | -2.577189 | -0.655942 | -0.460975 | 0.451362 |
| H5 | -2.550224 | 0.330368 | 0.780506 | 0.451703 |
| H6 | 2.540169 | 0.608245 | 0.584505 | 0.450911 |
| H7 | 2.588337 | -0.790824 | -0.165124 | 0.453281 |
| H8 | 0.002311 | 1.250967 | -0.825539 | 0.050833 |

------------------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

Zero-point correction=                              0.056774 (Hartree/Particle)
Thermal correction to Energy=                0.063595
Thermal correction to Enthalpy=               0.064539
Thermal correction to Gibbs Free Energy=        0.025834
Sum of electronic and zero-point Energies=        -272.548365
Sum of electronic and thermal Energies=          -272.541544
Sum of electronic and thermal Enthalpies=         -272.540600
Sum of electronic and thermal Free Energies=        -272.579305

**Table S22.**
(A) Geometry optimized for [Pt(OH$_2$)$_2$]$^-$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000029 | -0.009691 | 0.000006 | -1.124472 | 0.999164 |
| O2 | 3.379595 | -0.011014 | -0.019629 | -0.634514 | 0.002381 |
| O3 | -3.381560 | -0.007255 | 0.018930 | -0.633150 | 0.002450 |
| H4 | 2.490733 | -0.399575 | -0.162750 | 0.356570 | -0.001217 |
| H5 | 3.133452 | 0.864196 | 0.299932 | 0.339318 | -0.000740 |
| H6 | -3.104471 | 0.860534 | -0.296598 | 0.340320 | -0.000797 |
| H7 | -2.506253 | -0.423083 | 0.164564 | 0.355928 | -0.001242 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -272.173312325     A.U. after   26 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7529,   after    0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000332 | 0.000450 | YES |
| RMS    Force | 0.000121 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 10.5605 | 23.1158 | 57.8817 |
| Red. masses -- | 8.5043 | 7.4909 | 1.0561 |
| Frc consts  -- | 0.0006 | 0.0024 | 0.0021 |
| IR Inten   -- | 1.8973 | 5.6729 | 5.5409 |

Zero-point correction=                      0.046061 (Hartree/Particle)
Thermal correction to Energy=               0.054310
Thermal correction to Enthalpy=             0.055255
Thermal correction to Gibbs Free Energy=    0.008910
Sum of electronic and zero-point Energies=      -272.127252
Sum of electronic and thermal Energies=         -272.119002
Sum of electronic and thermal Enthalpies=       -272.118058
Sum of electronic and thermal Free Energies=    -272.164402

(B) Summary for the DFT calculation of [Pt(OH$_2$)$_2$]$^-$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
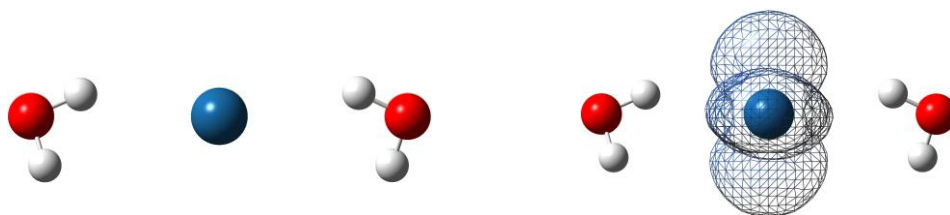


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | -0.000029 | 0.009691 | 0.000006 | -1.098556 | 0.998803 |
| O2 | -3.379595 | 0.011014 | -0.019629 | -0.660800 | 0.002752 |
| O3 | 3.381561 | 0.007255 | 0.018930 | -0.658688 | 0.002810 |
| H4 | -2.490733 | 0.399575 | -0.162750 | 0.341227 | -0.001519 |
| H5 | -3.133452 | -0.864196 | 0.299932 | 0.367714 | -0.000626 |
| H6 | 3.104471 | -0.860534 | -0.296598 | 0.367260 | -0.000692 |
| H7 | 2.506253 | 0.423083 | 0.164564 | 0.341843 | -0.001528 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                    0.044277 (Hartree/Particle)
Thermal correction to Energy=             0.050663
Thermal correction to Enthalpy=           0.051607
Thermal correction to Gibbs Free Energy=  0.011015
Sum of electronic and zero-point Energies=    -272.201489
Sum of electronic and thermal Energies=       -272.195103
Sum of electronic and thermal Enthalpies=     -272.194159
Sum of electronic and thermal Free Energies=  -272.234751
```

**Table S23.**

(A) Geometry optimized for [Pt(OH₂)H] (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

---

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.253746 | -0.000008 | -0.000256 | -0.067436 | 1.007260 |
| O2 | -2.086945 | 0.000016 | -0.093811 | -0.718780 | 0.001902 |
| H3 | -2.456807 | -0.773915 | 0.346472 | 0.409758 | -0.000116 |
| H4 | -2.456680 | 0.774056 | 0.346387 | 0.409762 | -0.000113 |
| H5 | 1.816876 | 0.000371 | 0.077613 | -0.033304 | -0.008932 |

---

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -196.304643593     A.U. after   22 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7520,   after    0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000008 | 0.000450 | YES |
| RMS    Force | 0.000003 | 0.000300 | YES |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 269.8000 | 273.1938 | 409.4547 |
| Red. masses -- | 6.4101 | 1.0175 | 1.1174 |
| Frc consts  -- | 0.2749 | 0.0447 | 0.1104 |
| IR Inten   -- | 9.0896 | 8.3313 | 244.2310 |

Zero-point correction=                   0.030999 (Hartree/Particle)
Thermal correction to Energy=            0.035428
Thermal correction to Enthalpy=          0.036372
Thermal correction to Gibbs Free Energy=     0.003251
Sum of electronic and zero-point Energies=     -196.273645
Sum of electronic and thermal Energies=        -196.269216
Sum of electronic and thermal Enthalpies=      -196.268271
Sum of electronic and thermal Free Energies=   -196.301392

(B) Summary for the DFT calculation of [Pt(OH₂)H] (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
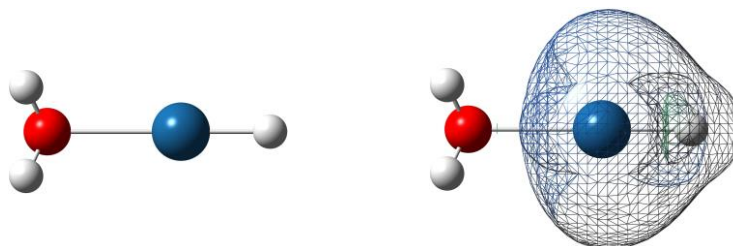


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.253746 | -0.000008 | -0.000256 | -0.011599 | 0.968458 |
| O2 | -2.086945 | 0.000016 | -0.093811 | -0.750090 | 0.005615 |
| H3 | -2.456807 | -0.773915 | 0.346472 | 0.429035 | 0.000236 |
| H4 | -2.456680 | 0.774056 | 0.346387 | 0.429034 | 0.000235 |
| H5 | 1.816876 | 0.000371 | 0.077613 | -0.096379 | 0.025455 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                       0.030386 (Hartree/Particle)
Thermal correction to Energy=            0.035036
Thermal correction to Enthalpy=           0.035980
Thermal correction to Gibbs Free Energy=     0.002433
Sum of electronic and zero-point Energies=        -196.304202
Sum of electronic and thermal Energies=          -196.299552
Sum of electronic and thermal Enthalpies=         -196.298608
Sum of electronic and thermal Free Energies=       -196.332154
```

**Table S24.**

(A) Geometry optimized for [PtH$_2$]$^+$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

--------------------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 0.000000 | 0.029677 | 0.558061 | 0.910759 |
| H2 | 0.000000 | 0.965426 | -1.157391 | 0.220970 | 0.044620 |
| H3 | 0.000000 | -0.965426 | -1.157391 | 0.220970 | 0.044620 |

--------------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -120.162864783     A.U. after    9 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7506,   after    0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000041 | 0.000450 | YES |
| RMS    Force | 0.000034 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A1 | B2 | A1 |
| Frequencies -- | 723.3082 | 2323.8583 | 2354.3568 |
| Red. masses -- | 1.0121 | 1.0120 | 1.0139 |
| Frc consts  -- | 0.3120 | 3.2198 | 3.3112 |
| IR Inten   -- | 7.3182 | 28.5319 | 81.4126 |

Zero-point correction=                     0.012306 (Hartree/Particle)
Thermal correction to Energy=              0.015242
Thermal correction to Enthalpy=            0.016186
Thermal correction to Gibbs Free Energy=      -0.010804
Sum of electronic and zero-point Energies=        -120.150559
Sum of electronic and thermal Energies=           -120.147623
Sum of electronic and thermal Enthalpies=         -120.146679
Sum of electronic and thermal Free Energies=       -120.173669

(B) Summary for the DFT calculation of [PtH$_2$]$^+$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
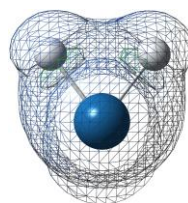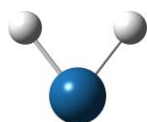


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 0.000000 | 0.000000 | 0.030446 | 0.880615 | 0.959484 |
| H2 | 0.000000 | 0.938062 | -1.187409 | 0.059692 | 0.020258 |
| H3 | 0.000000 | -0.938062 | -1.187409 | 0.059692 | 0.020258 |

[a]Part of the Gaussian output file:

Zero-point correction=                              0.012531 (Hartree/Particle)
Thermal correction to Energy=                  0.015453
Thermal correction to Enthalpy=               0.016397
Thermal correction to Gibbs Free Energy=      -0.010574
Sum of electronic and zero-point Energies=       -120.349051
Sum of electronic and thermal Energies=          -120.346129
Sum of electronic and thermal Enthalpies=        -120.345185
Sum of electronic and thermal Free Energies=     -120.372157

**Table S25.**

(A) Geometry optimized for [Pt(OH$_2$)H]$^-$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H,O) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 0.269919 | -0.000001 | -0.009562 | -1.123970 |
| O2 | -2.373284 | 0.000031 | -0.046849 | -0.499140 |
| H3 | -1.916774 | -0.761656 | 0.362073 | 0.330431 |
| H4 | -1.916414 | 0.761472 | 0.362184 | 0.330413 |
| H5 | 1.765809 | -0.000016 | 0.396388 | -0.037734 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -196.379904942    A.U. after   9 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000008 | 0.000450 | YES |
| RMS     Force | 0.000004 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 136.7257 | 386.9079 | 528.6790 |
| Red. masses -- | 8.5137 | 1.0185 | 1.0563 |
| Frc consts  -- | 0.0938 | 0.0898 | 0.1739 |
| IR Inten    -- | 31.9281 | 109.2473 | 79.5537 |

| | |
|---|---|
| Zero-point correction= | 0.030430 (Hartree/Particle) |
| Thermal correction to Energy= | 0.034792 |
| Thermal correction to Enthalpy= | 0.035736 |
| Thermal correction to Gibbs Free Energy= | 0.003001 |
| Sum of electronic and zero-point Energies= | -196.349475 |
| Sum of electronic and thermal Energies= | -196.345113 |
| Sum of electronic and thermal Enthalpies= | -196.344169 |
| Sum of electronic and thermal Free Energies= | -196.376904 |

(B) Summary for the DFT calculation of [Pt(OH$_2$)H]$^-$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H,O) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
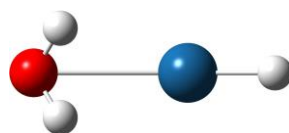


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -0.269919 | 0.000001 | -0.009562 | -1.079268 |
| O2 | 2.373284 | -0.000031 | -0.046849 | -0.547915 |
| H3 | 1.916774 | 0.761656 | 0.362074 | 0.354188 |
| H4 | 1.916414 | -0.761472 | 0.362184 | 0.354152 |
| H5 | -1.765809 | 0.000016 | 0.396388 | -0.081157 |

---------------------------------------------------------------------------------------------------------------------

Zero-point correction=                          0.029198 (Hartree/Particle)
Thermal correction to Energy=              0.033238
Thermal correction to Enthalpy=            0.034182
Thermal correction to Gibbs Free Energy=      0.002193
Sum of electronic and zero-point Energies=        -196.437199
Sum of electronic and thermal Energies=          -196.433160
Sum of electronic and thermal Enthalpies=        -196.432216
Sum of electronic and thermal Free Energies=       -196.464205

**Table S26.**

(A) Geometry optimized for [PtH$_2$] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.000000 | 0.000000 | 0.028644 | -0.134731 |
| H2 | 0.000000 | 1.006612 | -1.117129 | 0.067366 |
| H3 | 0.000000 | -1.006612 | -1.117129 | 0.067366 |

------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -120.513288164    A.U. after    7 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000056 | 0.000450 | YES |
| RMS    Force | 0.000046 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A1 | B2 | A1 |
| Frequencies -- | 736.4392 | 2317.4162 | 2380.1545 |
| Red. masses -- | 1.0123 | 1.0123 | 1.0136 |
| Frc consts  -- | 0.3235 | 3.2032 | 3.3833 |
| IR Inten    -- | 1.9471 | 44.3644 | 2.6241 |

Zero-point correction=                   0.012380 (Hartree/Particle)
Thermal correction to Energy=            0.015311
Thermal correction to Enthalpy=          0.016255
Thermal correction to Gibbs Free Energy=      -0.010077
Sum of electronic and zero-point Energies=      -120.500909
Sum of electronic and thermal Energies=         -120.497977
Sum of electronic and thermal Enthalpies=       -120.497033
Sum of electronic and thermal Free Energies=      -120.523365

(B) Summary for the DFT calculation of [PtH$_2$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]



------------------------------------------------------------------------------------------------------
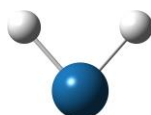
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.000000 | 0.000000 | 0.028644 | 0.034948 |
| H2 | 0.000000 | 1.006612 | -1.117129 | -0.017474 |
| H3 | 0.000000 | -1.006612 | -1.117129 | -0.017474 |

------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

Zero-point correction=                   0.012670 (Hartree/Particle)

Thermal correction to Energy=                   0.015575
Thermal correction to Enthalpy=                  0.016519
Thermal correction to Gibbs Free Energy=        -0.009776
Sum of electronic and zero-point Energies=      -120.533798
Sum of electronic and thermal Energies=         -120.530894
Sum of electronic and thermal Enthalpies=       -120.529949
Sum of electronic and thermal Free Energies=    -120.556245

**Table S27.** (A) Geometry optimized for [PtH$_3$]$^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 0.036926 | -0.000056 | 0.000157 | 0.318046 |
| H2 | -0.967191 | -0.010631 | 1.144811 | 0.227438 |
| H3 | -0.958650 | -0.990723 | -0.588988 | 0.227342 |
| H4 | -0.954381 | 1.005758 | -0.568081 | 0.227174 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -120.797360578     A.U. after     1 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000295 | 0.000450 | YES |
| RMS    Force | 0.000159 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 817.6731 | 837.2736 | 889.7916 |
| Red. masses -- | 1.0097 | 1.0097 | 1.0167 |
| Frc consts  -- | 0.3978 | 0.4170 | 0.4743 |
| IR Inten   -- | 3.1825 | 3.2143 | 19.2045 |

| | |
|---|---|
| Zero-point correction= | 0.022152 (Hartree/Particle) |
| Thermal correction to Energy= | 0.025183 |
| Thermal correction to Enthalpy= | 0.026127 |
| Thermal correction to Gibbs Free Energy= | -0.001635 |
| Sum of electronic and zero-point Energies= | -120.775208 |
| Sum of electronic and thermal Energies= | -120.772178 |
| Sum of electronic and thermal Enthalpies= | -120.771233 |
| Sum of electronic and thermal Free Energies= | -120.798996 |

(B) Summary for the DFT calculation of [PtH$_3$]$^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]



Top view          Side view
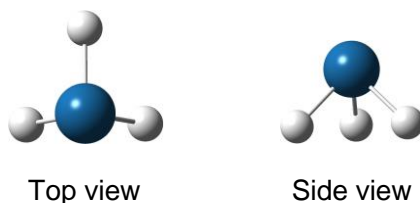
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 0.036926 | -0.000056 | 0.000157 | 0.706114 |
| H2 | -0.967191 | -0.010631 | 1.144811 | 0.097975 |
| H3 | -0.958650 | -0.990723 | -0.588988 | 0.098004 |
| H4 | -0.954381 | 1.005758 | -0.568081 | 0.097906 |

--------------------------------------------------------------------------------------------------------------------

Zero-point correction=                                0.022945 (Hartree/Particle)
Thermal correction to Energy=                   0.025928
Thermal correction to Enthalpy=                 0.026872
Thermal correction to Gibbs Free Energy=      -0.000828
Sum of electronic and zero-point Energies=           -120.957453
Sum of electronic and thermal Energies=             -120.954470
Sum of electronic and thermal Enthalpies=           -120.953526
Sum of electronic and thermal Free Energies=         -120.981227

**Table S28.** (A) Geometry optimized for [Pt$_2$] (triplet) computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.000000 | 0.000000 | 1.198356 | 0.000000 | 1.000000 |
| Pt2 | 0.000000 | 0.000000 | -1.198356 | 0.000000 | 1.000000 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -238.634690825     A.U. after    9 cycles
Annihilation of the first spin contaminant:
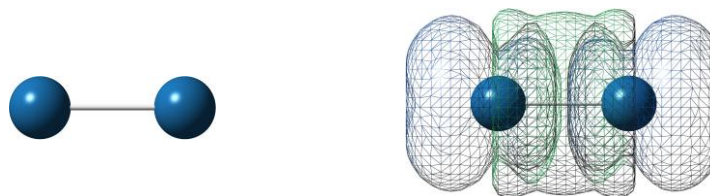S**2 before annihilation    2.0186,   after    2.0001

```
      Item           Value   Threshold  Converged?
Maximum Force        0.000000    0.000450    YES
RMS    Force         0.000000    0.000300    YES
```

```
            1
          SGG
Frequencies --   217.8236
Red. masses --    194.9648
Frc consts  --    5.4502
IR Inten    --    0.0000
```

```
Zero-point correction=                  0.000496 (Hartree/Particle)
Thermal correction to Energy=           0.003390
Thermal correction to Enthalpy=         0.004334
Thermal correction to Gibbs Free Energy=    -0.027074
Sum of electronic and zero-point Energies=     -238.634195
Sum of electronic and thermal Energies=        -238.631301
Sum of electronic and thermal Enthalpies=      -238.630357
Sum of electronic and thermal Free Energies=   -238.661765
```

(B) Summary for the DFT calculation of [Pt$_2$] (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) basis set. Computed by the single-point calculation for its optimized structure in vacuo.[a]



Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.000000 | 0.000000 | 1.198356 | 0.000000 | 1.000000 |
| Pt2 | 0.000000 | 0.000000 | -1.198356 | 0.000000 | 1.000000 |

```
Zero-point correction=                          0.000534 (Hartree/Particle)
Thermal correction to Energy=             0.003403
Thermal correction to Enthalpy=           0.004347
Thermal correction to Gibbs Free Energy=       -0.026998
Sum of electronic and zero-point Energies=        -238.665695
Sum of electronic and thermal Energies=           -238.662825
Sum of electronic and thermal Enthalpies=         -238.661881
Sum of electronic and thermal Free Energies=        -238.693227
```

**Table S29.**
(A) Geometry optimized for [Pt$_2$H]$^+$ (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

--------------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 1.226753 | -0.008031 | 0.448765 | 1.009741 |
| Pt2 | 0.000000 | -1.226753 | -0.008031 | 0.448765 | 1.009741 |
| H3 | 0.000000 | 0.000000 | 1.252770 | 0.102471 | -0.019483 |

--------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -238.924501406    A.U. after   24 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0181,   after    2.0002

```
      Item          Value    Threshold  Converged?
Maximum Force        0.000356   0.000450    YES
RMS    Force         0.000211   0.000300    YES


                 1             2             3
                A1            B2            A1
Frequencies --   199.8507       735.2953       1598.5905
Red. masses --   138.4448         1.0132         1.0126
Frc consts  --     3.2579         0.3227         1.5246
IR Inten    --     0.0074        21.8725         0.2653
```
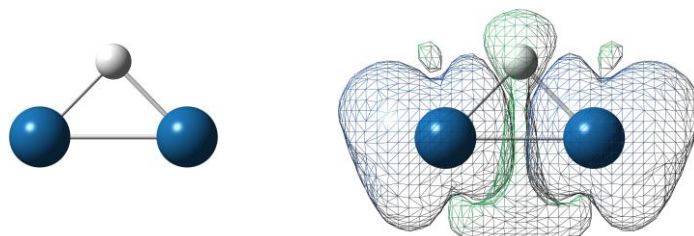
Zero-point correction=                   0.005772 (Hartree/Particle)
Thermal correction to Energy=            0.009268
Thermal correction to Enthalpy=          0.010212
Thermal correction to Gibbs Free Energy=     -0.023869
Sum of electronic and zero-point Energies=       -238.918729
Sum of electronic and thermal Energies=          -238.915233
Sum of electronic and thermal Enthalpies=        -238.914289
Sum of electronic and thermal Free Energies=     -238.948370

(B) Summary for the DFT calculation of [Pt$_2$H]$^+$ (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]

Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 1.226753 | -0.008031 | 0.513062 | 1.013779 |
| Pt2 | 0.000000 | -1.226753 | -0.008031 | 0.513062 | 1.013779 |
| H3 | 0.000000 | 0.000000 | 1.252771 | -0.026125 | -0.027558 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.005580 (Hartree/Particle)
Thermal correction to Energy=               0.009108
Thermal correction to Enthalpy=             0.010052
Thermal correction to Gibbs Free Energy=    -0.024058
Sum of electronic and zero-point Energies=       -239.127237
Sum of electronic and thermal Energies=          -239.123709
Sum of electronic and thermal Enthalpies=        -239.122765
Sum of electronic and thermal Free Energies=     -239.156875
```

**Table S30.**

(A) Geometry optimized for [Pt$_2$]$^-$ (doublet) computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 0.000000 | 1.248630 | -0.500000 | 0.500000 |
| Pt2 | 0.000000 | 0.000000 | -1.248630 | -0.500000 | 0.500000 |

[a]Part of the Gaussian output file:

```
SCF Done:  E(UM06) = -238.720204752     A.U. after   14 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7998,  after     0.7504

      Item           Value    Threshold  Converged?
Maximum Force       0.000001    0.000450    YES
RMS    Force        0.000001    0.000300    YES


            1
          SGG
Frequencies --   186.5738
Red. masses --    194.9648
Frc consts  --     3.9986
IR Inten    --     0.0000


Zero-point correction=                  0.000425 (Hartree/Particle)
Thermal correction to Energy=              0.003368
Thermal correction to Enthalpy=            0.004312
Thermal correction to Gibbs Free Energy=   -0.026927
Sum of electronic and zero-point Energies=     -238.719780
Sum of electronic and thermal Energies=        -238.716837
Sum of electronic and thermal Enthalpies=      -238.715893
Sum of electronic and thermal Free Energies=    -238.747132
```
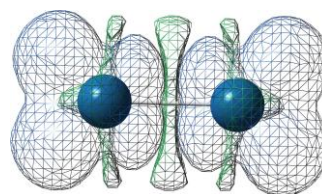
(B) Summary for the DFT calculation of [Pt$_2$]$^-$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) basis set. Computed by the single-point calculation for its optimized structure in vacuo.[a]



Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 0.000000 | 1.248630 | -0.500000 | 0.500000 |

| Pt2 | 0.000000 | 0.000000 | -1.248630 | -0.500000 | 0.500000 |

---

<sup>a</sup>Part of the Gaussian output file:

```
Zero-point correction=                        0.000416 (Hartree/Particle)
Thermal correction to Energy=            0.003365
Thermal correction to Enthalpy=          0.004309
Thermal correction to Gibbs Free Energy=    -0.026948
Sum of electronic and zero-point Energies=       -238.779042
Sum of electronic and thermal Energies=          -238.776093
Sum of electronic and thermal Enthalpies=        -238.775149
Sum of electronic and thermal Free Energies=      -238.806406
```

**Table S31.**

(A) Geometry optimized for [Pt$_2$H] (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 0.000000 | 1.266181 | -0.007503 | -0.027717 | 0.501234 |
| Pt2 | 0.000000 | -1.266181 | -0.007503 | -0.027717 | 0.501234 |
| H3 | 0.000000 | 0.000000 | 1.170424 | 0.055433 | -0.002468 |

------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -239.247524200    A.U. after   15 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7585,   after    0.7500

|       Item       |   Value   | Threshold | Converged? |
|------------------|-----------|-----------|------------|
| Maximum Force    | 0.000159  | 0.000450  | YES        |
| RMS   Force      | 0.000151  | 0.000300  | YES        |

|                  |     1     |     2     |     3     |
|------------------|-----------|-----------|-----------|
|                  |    A1     |    B2     |    A1     |
| Frequencies --   | 181.0064  | 741.6041  | 1580.3253 |
| Red. masses --   | 132.8387  | 1.0127    | 1.0129    |
| Frc consts  --   | 2.5643    | 0.3281    | 1.4904    |
| IR Inten   --    | 0.0004    | 11.9880   | 18.2817   |

Zero-point correction=                  0.005702 (Hartree/Particle)
Thermal correction to Energy=            0.009226
Thermal correction to Enthalpy=          0.010170
Thermal correction to Gibbs Free Energy=    -0.023608
Sum of electronic and zero-point Energies=      -239.241822
Sum of electronic and thermal Energies=         -239.238298
Sum of electronic and thermal Enthalpies=       -239.237354
Sum of electronic and thermal Free Energies=    -239.271132

(B) Summary for the DFT calculation of [Pt$_2$H] (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
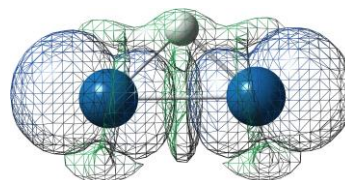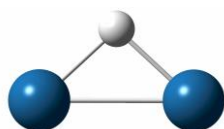




Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 1.266181 | -0.007503 | 0.011562 | 0.502536 |
| Pt2 | 0.000000 | -1.266181 | -0.007503 | 0.011562 | 0.502536 |
| H3 | 0.000000 | 0.000000 | 1.170424 | -0.023124 | -0.005072 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.005585 (Hartree/Particle)
Thermal correction to Energy=               0.009162
Thermal correction to Enthalpy=             0.010106
Thermal correction to Gibbs Free Energy=    -0.023796
Sum of electronic and zero-point Energies=       -239.280079
Sum of electronic and thermal Energies=          -239.276502
Sum of electronic and thermal Enthalpies=        -239.275558
Sum of electronic and thermal Free Energies=     -239.309461
```

**Table S32.**

(A) Geometry optimized for $[Pt_2H_2]^+$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 1.238860 | 0.000000 | 0.338947 | 0.513201 |
| Pt2 | 0.000000 | -1.238860 | 0.000000 | 0.338947 | 0.513201 |
| H3 | 1.511627 | 1.049044 | 0.000000 | 0.161053 | -0.013201 |
| H4 | -1.511627 | -1.049044 | 0.000000 | 0.161053 | -0.013201 |

[a]Part of the Gaussian output file:

```
SCF Done:  E(UM06) =  -239.548271053     A.U. after   10 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7549,   after    0.7500
```

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000032 | 0.000450 | YES |
| RMS    Force | 0.000019 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | AG | AU | AG |
| Frequencies -- | 194.4210 | 219.0035 | 508.4820 |
| Red. masses -- | 179.7780 | 1.0130 | 1.0143 |
| Frc consts  -- | 4.0038 | 0.0286 | 0.1545 |
| IR Inten   -- | 0.0000 | 2.7339 | 0.0000 |

```
Zero-point correction=                   0.014245 (Hartree/Particle)
Thermal correction to Energy=            0.018610
Thermal correction to Enthalpy=          0.019554
Thermal correction to Gibbs Free Energy=      -0.016097
Sum of electronic and zero-point Energies=     -239.534026
Sum of electronic and thermal Energies=        -239.529661
Sum of electronic and thermal Enthalpies=      -239.528717
Sum of electronic and thermal Free Energies=   -239.564368
```
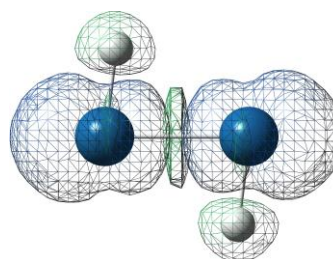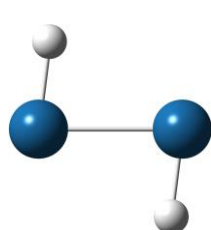
(B) Summary for the DFT calculation of $[Pt_2H_2]^+$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]

Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 0.000000 | 1.238860 | 0.000000 | 0.477566 | 0.514252 |
| Pt2 | 0.000000 | -1.238860 | 0.000000 | 0.477566 | 0.514252 |
| H3 | 1.511627 | 1.049044 | 0.000000 | 0.022434 | -0.014252 |
| H4 | -1.511627 | -1.049044 | 0.000000 | 0.022434 | -0.014252 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                    0.011963 (Hartree/Particle)
Thermal correction to Energy=             0.015829
Thermal correction to Enthalpy=           0.016773
Thermal correction to Gibbs Free Energy=  -0.018112
Sum of electronic and zero-point Energies=      -239.736440
Sum of electronic and thermal Energies=         -239.732574
Sum of electronic and thermal Enthalpies=       -239.731630
Sum of electronic and thermal Free Energies=    -239.766515
```

**Table S33.**
(A) Geometry optimized for [Pt₂H]⁻ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

----------------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 0.000000 | 1.327729 | -0.006893 | -0.515820 |
| Pt2 | 0.000000 | -1.327729 | -0.006893 | -0.515820 |
| H3 | 0.000000 | 0.000000 | 1.075304 | 0.031640 |

----------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -239.328043980    A.U. after   12 cycles

|       Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000026 | 0.000450 | YES |
| RMS    Force | 0.000024 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A1 | B2 | A1 |
| Frequencies -- | 142.2125 | 988.4580 | 1360.8039 |
| Red. masses -- | 109.1582 | 1.0121 | 1.0145 |
| Frc consts  -- | 1.3007 | 0.5826 | 1.1069 |
| IR Inten   -- | 0.0132 | 208.3272 | 36.6561 |

Zero-point correction=                   0.005676 (Hartree/Particle)
Thermal correction to Energy=            0.009213
Thermal correction to Enthalpy=          0.010157
Thermal correction to Gibbs Free Energy=      -0.023122
Sum of electronic and zero-point Energies=       -239.322368
Sum of electronic and thermal Energies=          -239.318831
Sum of electronic and thermal Enthalpies=        -239.317887
Sum of electronic and thermal Free Energies=       -239.351166

(B) Summary for the DFT calculation of [Pt₂H]⁻ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]



----------------------------------------------------------------------------------------------------------------
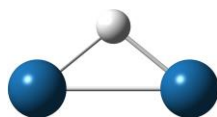
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 0.000000 | 1.327729 | -0.006893 | -0.479384 |
| Pt2 | 0.000000 | -1.327729 | -0.006893 | -0.479384 |
| H3 | 0.000000 | 0.000000 | 1.075304 | -0.041231 |

----------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

Zero-point correction=                   0.005152 (Hartree/Particle)
Thermal correction to Energy=            0.008707

Thermal correction to Enthalpy=               0.009651
Thermal correction to Gibbs Free Energy=      -0.023651
Sum of electronic and zero-point Energies=       -239.402524
Sum of electronic and thermal Energies=          -239.398970
Sum of electronic and thermal Enthalpies=        -239.398026
Sum of electronic and thermal Free Energies=     -239.431328

**Table S34.**

(A) Geometry optimized for [Pt$_2$H$_2$] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.272794 | 0.013960 | 0.011154 | -0.076738 |
| Pt2 | 1.272800 | -0.013959 | 0.011151 | -0.076793 |
| H3 | 1.136593 | 1.219041 | -0.869931 | 0.076769 |
| H4 | -1.137003 | -1.219117 | -0.869873 | 0.076761 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -239.863367375     A.U. after   10 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000011 | 0.000450 | YES |
| RMS    Force | 0.000007 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 173.2425 | 247.7200 | 390.0014 |
| Red. masses -- | 117.0366 | 1.0136 | 1.0151 |
| Frc consts  -- | 2.0696 | 0.0366 | 0.0910 |
| IR Inten    -- | 0.0823 | 8.5593 | 13.2721 |

| | |
|---|---|
| Zero-point correction= | 0.013508 (Hartree/Particle) |
| Thermal correction to Energy= | 0.018045 |
| Thermal correction to Enthalpy= | 0.018989 |
| Thermal correction to Gibbs Free Energy= | -0.017014 |
| Sum of electronic and zero-point Energies= | -239.849859 |
| Sum of electronic and thermal Energies= | -239.845322 |
| Sum of electronic and thermal Enthalpies= | -239.844378 |
| Sum of electronic and thermal Free Energies= | -239.880382 |

(B) Summary for the DFT calculation of [Pt$_2$H$_2$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
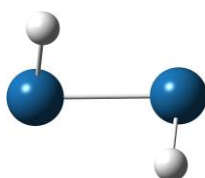


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.272794 | -0.013960 | -0.011154 | 0.023924 |
| Pt2 | 1.272800 | 0.013959 | -0.011151 | 0.023884 |
| H3 | 1.136593 | -1.219041 | 0.869931 | -0.023896 |
| H4 | -1.137003 | 1.219117 | 0.869873 | -0.023912 |

Zero-point correction=                              0.014208 (Hartree/Particle)
Thermal correction to Energy=                0.018485
Thermal correction to Enthalpy=              0.019429
Thermal correction to Gibbs Free Energy=      -0.016163
Sum of electronic and zero-point Energies=        -239.897351
Sum of electronic and thermal Energies=           -239.893074
Sum of electronic and thermal Enthalpies=         -239.892130
Sum of electronic and thermal Free Energies=       -239.927721

**Table S35.**

(A) Geometry optimized for [$Pt_2H_2$] (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.283919 | 0.019395 | -0.001905 | -0.051685 | 0.934055 |
| Pt2 | 1.283915 | 0.019399 | 0.001905 | -0.051674 | 0.934155 |
| H3 | 1.426271 | -1.512987 | -0.133769 | 0.051673 | 0.065912 |
| H4 | -1.425990 | -1.513007 | 0.133768 | 0.051687 | 0.065878 |

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -239.829065901    A.U. after   14 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0097,   after    2.0000

|  | Item | Value | Threshold | Converged? |
|---|---|---|---|---|
| Maximum Force | | 0.000017 | 0.000450 | YES |
| RMS    Force | | 0.000013 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 165.2987 | 250.0044 | 255.9441 |
| Red. masses -- | 93.4637 | 1.0178 | 1.0209 |
| Frc consts -- | 1.5046 | 0.0375 | 0.0394 |
| IR Inten   -- | 0.1216 | 0.5095 | 72.3789 |

Zero-point correction=                     0.012787 (Hartree/Particle)
Thermal correction to Energy=              0.017402
Thermal correction to Enthalpy=            0.018346
Thermal correction to Gibbs Free Energy=      -0.018939
Sum of electronic and zero-point Energies=      -239.816279
Sum of electronic and thermal Energies=        -239.811664
Sum of electronic and thermal Enthalpies=      -239.810719
Sum of electronic and thermal Free Energies=      -239.848005

(B) Summary for the DFT calculation of [$Pt_2H_2$] (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
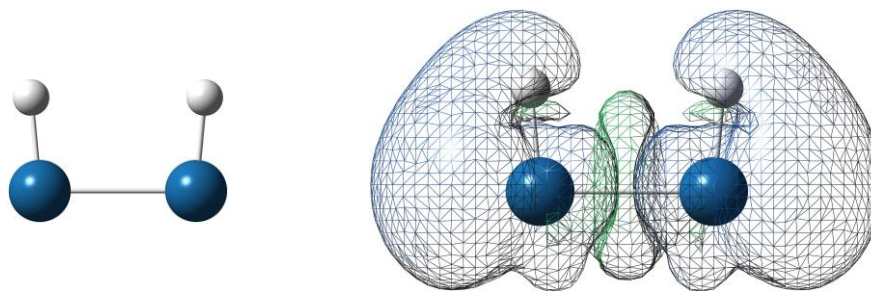


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -1.283919 | -0.019395 | 0.001905 | 0.067327 | 0.951315 |
| Pt2 | 1.283915 | -0.019399 | -0.001905 | 0.067314 | 0.951371 |
| H3 | 1.426271 | 1.512987 | 0.133769 | -0.067326 | 0.048664 |
| H4 | -1.425990 | 1.513007 | -0.133768 | -0.067315 | 0.048650 |

[a]Part of the Gaussian output file:

Zero-point correction=                            0.013695 (Hartree/Particle)
Thermal correction to Energy=                0.017982
Thermal correction to Enthalpy=              0.018926
Thermal correction to Gibbs Free Energy=    -0.017823
Sum of electronic and zero-point Energies=        -239.865362
Sum of electronic and thermal Energies=            -239.861075
Sum of electronic and thermal Enthalpies=         -239.860131
Sum of electronic and thermal Free Energies=       -239.896880

**Table S36.**

(A) Geometry optimized for $[Pt_2H_3]^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.301080 | -0.016624 | -0.004077 | 0.289815 |
| Pt2 | 1.289310 | 0.020464 | -0.013743 | 0.172941 |
| H3 | -1.167517 | 1.486967 | 0.128295 | 0.154561 |
| H4 | 1.165828 | -1.486960 | -0.171592 | 0.188501 |
| H5 | 0.919679 | -0.299498 | 1.433301 | 0.194182 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -240.170289993     A.U. after    9 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000005 | 0.000450 | YES |
| RMS    Force | 0.000002 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 162.2882 | 278.2278 | 352.7894 |
| Red. masses -- | 140.2332 | 1.0115 | 1.0145 |
| Frc consts  -- | 2.1761 | 0.0461 | 0.0744 |
| IR Inten    -- | 0.7037 | 2.4306 | 0.7758 |

| | |
|---|---|
| Zero-point correction= | 0.022742 (Hartree/Particle) |
| Thermal correction to Energy= | 0.027410 |
| Thermal correction to Enthalpy= | 0.028354 |
| Thermal correction to Gibbs Free Energy= | -0.008026 |
| Sum of electronic and zero-point Energies= | -240.147548 |
| Sum of electronic and thermal Energies= | -240.142880 |
| Sum of electronic and thermal Enthalpies= | -240.141936 |
| Sum of electronic and thermal Free Energies= | -240.178316 |

(B) Summary for the DFT calculation of $[Pt_2H_3]^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
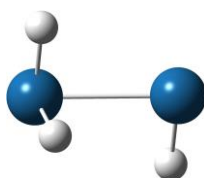


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.301080 | 0.016624 | -0.004077 | 0.310485 |
| Pt2 | -1.289311 | -0.020464 | -0.013743 | 0.525964 |
| H3 | 1.167517 | -1.486967 | 0.128295 | 0.015031 |
| H4 | -1.165828 | 1.486960 | -0.171592 | 0.071597 |

| H5 | -0.919679 | 0.299498 | 1.433301 | 0.076922 |

---------------------------------------------------------------------------------------------------------------------

aPart of the Gaussian output file:

Zero-point correction=                      0.022623 (Hartree/Particle)
Thermal correction to Energy=            0.026771
Thermal correction to Enthalpy=          0.027715
Thermal correction to Gibbs Free Energy=      -0.007807
Sum of electronic and zero-point Energies=        -240.338865
Sum of electronic and thermal Energies=        -240.334716
Sum of electronic and thermal Enthalpies=        -240.333772
Sum of electronic and thermal Free Energies=        -240.369294

**Table S37.**

(A) Geometry optimized for $[Pt_2H_3]^+$ (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.346786 | -0.022848 | 0.000026 | 0.367918 | 1.337671 |
| Pt2 | 1.332084 | 0.033077 | 0.000048 | 0.162005 | 0.468098 |
| H3 | -1.723994 | 1.485015 | -0.001184 | 0.131177 | 0.119958 |
| H4 | 1.436547 | -1.143254 | 0.971418 | 0.169445 | 0.037191 |
| H5 | 1.434238 | -1.139579 | -0.976024 | 0.169455 | 0.037083 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -240.135240026    A.U. after   20 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0056,   after    2.0000

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000027 | 0.000450 | YES |
| RMS    Force | 0.000014 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 131.3499 | 237.9701 | 322.0693 |
| Red. masses -- | 158.2149 | 1.0119 | 1.0159 |
| Frc consts  -- | 1.6083 | 0.0338 | 0.0621 |
| IR Inten    -- | 0.0632 | 4.3474 | 31.2413 |

Zero-point correction=                    0.021276 (Hartree/Particle)
Thermal correction to Energy=             0.026338
Thermal correction to Enthalpy=           0.027282
Thermal correction to Gibbs Free Energy=     -0.011003
Sum of electronic and zero-point Energies=       -240.113964
Sum of electronic and thermal Energies=          -240.108902
Sum of electronic and thermal Enthalpies=        -240.107958
Sum of electronic and thermal Free Energies=     -240.146243

(B) Summary for the DFT calculation of $[Pt_2H_3]^+$ (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
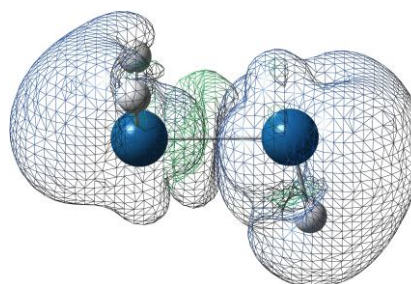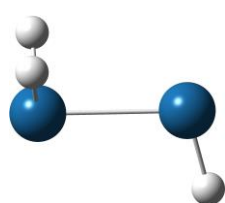


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 1.346786 | -0.022848 | -0.000026 | 0.530516 | 1.425639 |
| Pt2 | -1.332084 | 0.033077 | -0.000048 | 0.456583 | 0.461043 |
| H3 | 1.723994 | 1.485015 | 0.001184 | -0.053646 | 0.074825 |
| H4 | -1.436547 | -1.143254 | -0.971418 | 0.033249 | 0.019289 |
| H5 | -1.434238 | -1.139579 | 0.976024 | 0.033299 | 0.019205 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                       0.021539 (Hartree/Particle)
Thermal correction to Energy=                0.025792
Thermal correction to Enthalpy=              0.026736
Thermal correction to Gibbs Free Energy=    -0.010019
Sum of electronic and zero-point Energies=       -240.313971
Sum of electronic and thermal Energies=          -240.309717
Sum of electronic and thermal Enthalpies=        -240.308773
Sum of electronic and thermal Free Energies=     -240.345529
```

**Table S38.**

(A) Geometry optimized for $[Pt_2H_2]^-$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.285131 | -0.024095 | -0.008101 | -0.454178 | 0.470148 |
| Pt2 | 1.285131 | 0.024095 | -0.008101 | -0.454178 | 0.470147 |
| H3 | -2.080438 | 1.160945 | 0.631896 | -0.045822 | 0.029852 |
| H4 | 2.080437 | -1.160943 | 0.631902 | -0.045822 | 0.029852 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -239.939660900     A.U. after   15 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7568,   after    0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000015 | 0.000450 | YES |
| RMS   Force | 0.000012 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 151.1778 | 308.7638 | 374.4260 |
| Red. masses -- | 157.3315 | 1.0179 | 1.0160 |
| Frc consts  -- | 2.1186 | 0.0572 | 0.0839 |
| IR Inten   -- | 0.1565 | 8.9129 | 221.7697 |

Zero-point correction=                  0.012535 (Hartree/Particle)
Thermal correction to Energy=            0.017000
Thermal correction to Enthalpy=          0.017944
Thermal correction to Gibbs Free Energy=     -0.018531
Sum of electronic and zero-point Energies=     -239.927126
Sum of electronic and thermal Energies=        -239.922661
Sum of electronic and thermal Enthalpies=      -239.921717
Sum of electronic and thermal Free Energies=   -239.958191

(B) Summary for the DFT calculation of $[Pt_2H_2]^-$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
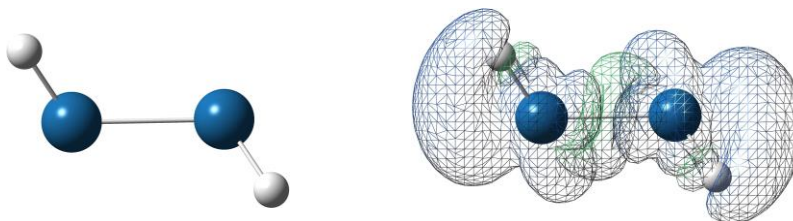


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.285131 | -0.024095 | -0.008101 | -0.396568 | 0.477811 |
| Pt2 | 1.285131 | 0.024095 | -0.008101 | -0.396568 | 0.477811 |
| H3 | -2.080438 | 1.160945 | 0.631896 | -0.103432 | 0.022189 |
| H4 | 2.080437 | -1.160943 | 0.631902 | -0.103432 | 0.022189 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.011009 (Hartree/Particle)
Thermal correction to Energy=             0.015524
Thermal correction to Enthalpy=           0.016468
Thermal correction to Gibbs Free Energy=   -0.020592
Sum of electronic and zero-point Energies=    -240.008116
Sum of electronic and thermal Energies=       -240.003601
Sum of electronic and thermal Enthalpies=     -240.002657
Sum of electronic and thermal Free Energies=   -240.039716
```

**Table S39.**

(A) Geometry optimized for [Pt$_2$H$_3$] (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

--------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -1.348904 | 0.023101 | -0.011037 | -0.097098 | 0.438203 |
| Pt2 | 1.348904 | -0.023101 | -0.011067 | -0.097098 | 0.438204 |
| H3 | -1.686081 | -1.441552 | 0.338297 | 0.050320 | 0.072634 |
| H4 | 1.686105 | 1.441548 | 0.338260 | 0.050319 | 0.072635 |
| H5 | 0.000014 | 0.000005 | 1.047580 | 0.093557 | -0.021676 |

--------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -240.452690069     A.U. after   11 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7567,   after    0.7500

|    Item    | Value | Threshold | Converged? |
|------------|-------|-----------|------------|
| Maximum Force | 0.000015 | 0.000450 | YES |
| RMS    Force | 0.000008 | 0.000300 | YES |

|                  | 1 | 2 | 3 |
|------------------|---|---|---|
|                  | A | A | A |
| Frequencies -- | 124.1834 | 255.5022 | 319.4248 |
| Red. masses -- | 91.2798 | 1.0122 | 1.0153 |
| Frc consts  -- | 0.8294 | 0.0389 | 0.0610 |
| IR Inten   -- | 0.0413 | 42.0979 | 15.2640 |

Zero-point correction=                    0.020135 (Hartree/Particle)
Thermal correction to Energy=             0.024934
Thermal correction to Enthalpy=           0.025878
Thermal correction to Gibbs Free Energy=      -0.011537
Sum of electronic and zero-point Energies=      -240.432556
Sum of electronic and thermal Energies=         -240.427756
Sum of electronic and thermal Enthalpies=       -240.426812
Sum of electronic and thermal Free Energies=      -240.464227

(B) Summary for the DFT calculation of [Pt$_2$H$_3$] (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
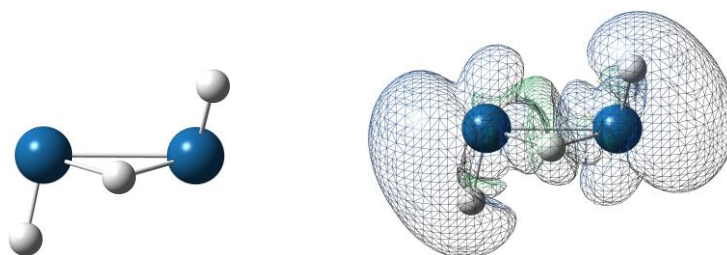


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 1.348904 | -0.023101 | -0.011037 | 0.037893 | 0.463017 |
| Pt2 | -1.348904 | 0.023101 | -0.011067 | 0.037892 | 0.463017 |
| H3 | 1.686081 | 1.441552 | 0.338297 | -0.048348 | 0.048130 |
| H4 | -1.686105 | -1.441548 | 0.338260 | -0.048348 | 0.048131 |
| H5 | -0.000014 | -0.000005 | 1.047580 | 0.020911 | -0.022294 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                         0.019228 (Hartree/Particle)
Thermal correction to Energy=             0.024356
Thermal correction to Enthalpy=           0.025300
Thermal correction to Gibbs Free Energy=    -0.013035
Sum of electronic and zero-point Energies=       -240.479437
Sum of electronic and thermal Energies=        -240.474309
Sum of electronic and thermal Enthalpies=       -240.473364
Sum of electronic and thermal Free Energies=      -240.511700
```

**Table S40.**

(A) Geometry optimized for [Pt$_2$H$_4$]$^+$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 1.342138 | 0.031591 | 0.002330 | 0.170860 | 0.424054 |
| Pt2 | -1.342202 | -0.031595 | 0.002356 | 0.170130 | 0.423425 |
| H3 | -1.432718 | 1.052254 | -1.071875 | 0.165349 | 0.036503 |
| H4 | -1.490126 | 1.206094 | 0.888628 | 0.164157 | 0.039700 |
| H5 | 1.493460 | -1.205328 | 0.889127 | 0.164158 | 0.039786 |
| H6 | 1.434328 | -1.052718 | -1.071387 | 0.165346 | 0.036532 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) = -240.769095492     A.U. after   12 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7542,   after     0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000094 | 0.000450 | YES |
| RMS    Force | 0.000044 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 130.6384 | 248.0115 | 330.1053 |
| Red. masses -- | 130.7612 | 1.0141 | 1.0179 |
| Frc consts  -- | 1.3148 | 0.0368 | 0.0653 |
| IR Inten    -- | 0.0090 | 2.6921 | 27.5614 |

Zero-point correction=                      0.029508 (Hartree/Particle)
Thermal correction to Energy=               0.034965
Thermal correction to Enthalpy=             0.035909
Thermal correction to Gibbs Free Energy=       -0.002713
Sum of electronic and zero-point Energies=      -240.739587
Sum of electronic and thermal Energies=         -240.734130
Sum of electronic and thermal Enthalpies=       -240.733186
Sum of electronic and thermal Free Energies=       -240.771808

(B) Summary for the DFT calculation of [Pt$_2$H$_4$]$^+$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
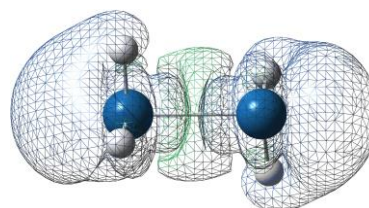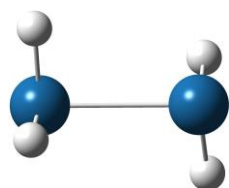


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.342138 | 0.031591 | -0.002330 | 0.436925 | 0.453702 |
| Pt2 | 1.342202 | -0.031595 | -0.002356 | 0.436901 | 0.453461 |
| H3 | 1.432718 | 1.052254 | 1.071875 | 0.033029 | 0.022147 |
| H4 | 1.490127 | 1.206094 | -0.888628 | 0.030093 | 0.024256 |
| H5 | -1.493460 | -1.205328 | -0.889127 | 0.030038 | 0.024291 |
| H6 | -1.434328 | -1.052718 | 1.071387 | 0.033014 | 0.022143 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.030597 (Hartree/Particle)
Thermal correction to Energy=               0.035742
Thermal correction to Enthalpy=             0.036686
Thermal correction to Gibbs Free Energy=    -0.001285
Sum of electronic and zero-point Energies=   -240.933150
Sum of electronic and thermal Energies=      -240.928005
Sum of electronic and thermal Enthalpies=    -240.927061
Sum of electronic and thermal Free Energies=  -240.965032
```

**Table S41.**

(A) Geometry optimized for [Pt$_2$H$_3$]$^-$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.347138 | 0.022422 | -0.000045 | -0.471261 |
| Pt2 | -1.300790 | -0.007139 | 0.000012 | -0.476382 |
| H3 | 1.519657 | -1.502503 | 0.003034 | -0.017348 |
| H4 | -2.567541 | 0.152584 | -0.895211 | -0.017510 |
| H5 | -2.567240 | 0.157851 | 0.894767 | -0.017499 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) = -240.555412636    A.U. after   10 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000026 | 0.000450 | YES |
| RMS    Force | 0.000013 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 134.8871 | 257.3980 | 289.9574 |
| Red. masses -- | 78.8338 | 1.0181 | 1.0216 |
| Frc consts  -- | 0.8451 | 0.0397 | 0.0506 |
| IR Inten    -- | 1.2963 | 3.3095 | 4.3159 |

Zero-point correction=                       0.020196 (Hartree/Particle)
Thermal correction to Energy=               0.025286
Thermal correction to Enthalpy=              0.026230
Thermal correction to Gibbs Free Energy=       -0.010784
Sum of electronic and zero-point Energies=        -240.535216
Sum of electronic and thermal Energies=        -240.530127
Sum of electronic and thermal Enthalpies=        -240.529182
Sum of electronic and thermal Free Energies=        -240.566196

(B) Summary for the DFT calculation of [Pt$_2$H$_3$]$^-$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
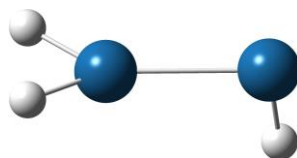


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.347138 | -0.022422 | 0.000045 | -0.342541 |
| Pt2 | -1.300790 | 0.007139 | -0.000012 | -0.496276 |
| H3 | 1.519658 | 1.502503 | -0.003034 | -0.087981 |
| H4 | -2.567541 | -0.152584 | 0.895211 | -0.036608 |

| H5 | -2.567240 | -0.157851 | -0.894767 | -0.036593 |

---
[a]Part of the Gaussian output file:

```
Zero-point correction=                         0.019568 (Hartree/Particle)
Thermal correction to Energy=            0.024254
Thermal correction to Enthalpy=          0.025198
Thermal correction to Gibbs Free Energy=      -0.011069
Sum of electronic and zero-point Energies=          -240.622306
Sum of electronic and thermal Energies=             -240.617620
Sum of electronic and thermal Enthalpies=           -240.616676
Sum of electronic and thermal Free Energies=        -240.652944
```

**Table S42.**

(A) Geometry optimized for [Pt$_2$H$_4$] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.425914 | 0.000105 | -0.000978 | 0.044652 |
| Pt2 | 1.368390 | 0.010847 | -0.017088 | -0.286577 |
| H3 | 2.003959 | -0.720741 | 1.171123 | 0.086191 |
| H4 | 2.938982 | 0.088269 | -0.180291 | 0.004749 |
| H5 | -0.234470 | 0.801734 | 0.713679 | 0.074957 |
| H6 | -0.221637 | -1.023491 | -0.295337 | 0.076028 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -241.067710043     A.U. after    9 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000016 | 0.000450 | YES |
| RMS    Force | 0.000009 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 116.2221 | 163.4490 | 232.7914 |
| Red. masses -- | 4.4924 | 1.2083 | 1.0735 |
| Frc consts  -- | 0.0358 | 0.0190 | 0.0343 |
| IR Inten    -- | 0.0846 | 2.6343 | 3.7245 |

| | |
|---|---|
| Zero-point correction= | 0.026754 (Hartree/Particle) |
| Thermal correction to Energy= | 0.032419 |
| Thermal correction to Enthalpy= | 0.033363 |
| Thermal correction to Gibbs Free Energy= | -0.004996 |
| Sum of electronic and zero-point Energies= | -241.040956 |
| Sum of electronic and thermal Energies= | -241.035291 |
| Sum of electronic and thermal Enthalpies= | -241.034347 |
| Sum of electronic and thermal Free Energies= | -241.072706 |

(B) Summary for the DFT calculation of [Pt$_2$H$_4$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
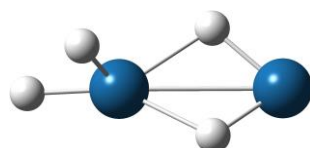


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.425914 | -0.000105 | -0.000978 | 0.276169 |
| Pt2 | -1.368390 | -0.010847 | -0.017088 | -0.243578 |
| H3 | -2.003959 | 0.720741 | 1.171123 | 0.029571 |
| H4 | -2.938982 | -0.088269 | -0.180291 | -0.061469 |

| | | | |
|---|---|---|---|
| H5 | 0.234470 | -0.801734 | 0.713680 | -0.000863 |
| H6 | 0.221637 | 1.023491 | -0.295337 | 0.000170 |

---

<sup>a</sup>Part of the Gaussian output file:

Zero-point correction=              0.025863 (Hartree/Particle)
Thermal correction to Energy=       0.030497
Thermal correction to Enthalpy=     0.031441
Thermal correction to Gibbs Free Energy=   -0.004978
Sum of electronic and zero-point Energies=   -241.091094
Sum of electronic and thermal Energies=   -241.086460
Sum of electronic and thermal Enthalpies=   -241.085515
Sum of electronic and thermal Free Energies=   -241.121935

**Table S43.**
(A) Geometry optimized for [Pt$_2$H$_5$]$^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.383864 | 0.023024 | -0.013151 | 0.070125 |
| Pt2 | 1.324515 | -0.018078 | -0.005083 | 0.076203 |
| H3 | -1.189221 | -1.473730 | -0.226816 | 0.157528 |
| H4 | 2.656956 | -0.172813 | 0.764264 | 0.169462 |
| H5 | 1.585599 | 1.445878 | 0.303709 | 0.192136 |
| H6 | 2.605558 | 0.158507 | -0.846678 | 0.175640 |
| H7 | -1.029741 | -0.343654 | 1.427781 | 0.158905 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -241.379934781     A.U. after     9 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000005 | 0.000450 | YES |
| RMS    Force | 0.000002 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 59.7068 | 131.4257 | 149.6052 |
| Red. masses -- | 1.0314 | 24.6469 | 1.0304 |
| Frc consts  -- | 0.0022 | 0.2508 | 0.0136 |
| IR Inten    -- | 1.8650 | 3.4775 | 2.5034 |

Zero-point correction=                          0.036874 (Hartree/Particle)
Thermal correction to Energy=              0.043323
Thermal correction to Enthalpy=            0.044267
Thermal correction to Gibbs Free Energy=      0.003704
Sum of electronic and zero-point Energies=       -241.343061
Sum of electronic and thermal Energies=          -241.336612
Sum of electronic and thermal Enthalpies=        -241.335668
Sum of electronic and thermal Free Energies=      -241.376231

(B) Summary for the DFT calculation of [Pt$_2$H$_5$]$^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
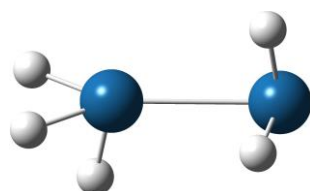


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.383864 | -0.023024 | -0.013151 | 0.290005 |
| Pt2 | -1.324516 | 0.018078 | -0.005083 | 0.382161 |

| | | | |
|---|---|---|---|
| H3 | 1.189221 | 1.473730 | -0.226816 | 0.037334 |
| H4 | -2.656956 | 0.172813 | 0.764264 | 0.076948 |
| H5 | -1.585599 | -1.445878 | 0.303709 | 0.094809 |
| H6 | -2.605558 | -0.158507 | -0.846678 | 0.083661 |
| H7 | 1.029741 | 0.343654 | 1.427781 | 0.035082 |

---------------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

Zero-point correction=                        0.035199 (Hartree/Particle)
Thermal correction to Energy=            0.039975
Thermal correction to Enthalpy=           0.040919
Thermal correction to Gibbs Free Energy=        0.004020
Sum of electronic and zero-point Energies=        -241.522869
Sum of electronic and thermal Energies=         -241.518092
Sum of electronic and thermal Enthalpies=        -241.517148
Sum of electronic and thermal Free Energies=        -241.554048

**Table S44.** (A) Geometry optimized for [Pt$_3$] (singlet) computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.000000 | 0.000000 | 1.465265 | 0.000042 |
| Pt2 | 0.000000 | 1.269029 | -0.732632 | -0.000021 |
| Pt3 | 0.000000 | -1.269029 | -0.732632 | -0.000021 |

[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -358.022287090    A.U. after   12 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000009 | 0.000450 | YES |
| RMS    Force | 0.000008 | 0.000300 | YES |

| | 1 | 2 | 3 |
|---|---|---|---|
| | B2 | A1 | A1 |
| Frequencies -- | 135.1878 | 135.9220 | 216.6090 |
| Red. masses -- | 194.9648 | 194.9648 | 194.9648 |
| Frc consts  -- | 2.0993 | 2.1222 | 5.3896 |
| IR Inten   -- | 0.0179 | 0.0171 | 0.0000 |

Zero-point correction=                      0.001111 (Hartree/Particle)
Thermal correction to Energy=              0.005816
Thermal correction to Enthalpy=            0.006761
Thermal correction to Gibbs Free Energy=      -0.032587
Sum of electronic and zero-point Energies=       -358.021176
Sum of electronic and thermal Energies=          -358.016471
Sum of electronic and thermal Enthalpies=        -358.015526
Sum of electronic and thermal Free Energies=      -358.054874

(B) Summary for the DFT calculation of [Pt$_3$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) basis set. Computed by the single-point calculation for its optimized structure in vacuo.[a]
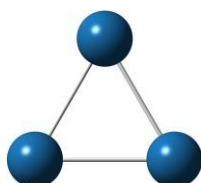


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.000000 | 0.000000 | 1.465265 | 0.013892 |
| Pt2 | 0.000000 | 1.269029 | -0.732632 | -0.006946 |
| Pt3 | 0.000000 | -1.269029 | -0.732632 | -0.006946 |

[a]Part of the Gaussian output file:

Zero-point correction=                                       0.000935 (Hartree/Particle)
Thermal correction to Energy=                     0.005783
Thermal correction to Enthalpy=                   0.006727
Thermal correction to Gibbs Free Energy=      -0.033287
Sum of electronic and zero-point Energies=            -358.063675
Sum of electronic and thermal Energies=               -358.058827
Sum of electronic and thermal Enthalpies=             -358.057883
Sum of electronic and thermal Free Energies=          -358.097897

**Table S45.**
(A) Geometry optimized for [Pt$_3$H]$^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

-----------------------------------------------------------------------------------------------------------------------
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.004835 | 1.472607 | 0.000000 | 0.452799 |
| Pt2 | 0.004835 | -0.730402 | 1.297123 | 0.186227 |
| Pt3 | 0.004835 | -0.730402 | -1.297123 | 0.186227 |
| H4 | -1.131430 | -0.920585 | 0.000000 | 0.174746 |
-----------------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -358.334744238    A.U. after   15 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000027 | 0.000450 | YES |
| RMS    Force | 0.000017 | 0.000300 | YES |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A" | A' | A' |
| Frequencies -- | 123.3697 | 132.7000 | 205.8472 |
| Red. masses -- | 92.3183 | 35.1823 | 153.9849 |
| Frc consts  -- | 0.8279 | 0.3650 | 3.8443 |
| IR Inten   -- | 0.0486 | 0.0510 | 0.1395 |

| | |
|---|---|
| Zero-point correction= | 0.006770 (Hartree/Particle) |
| Thermal correction to Energy= | 0.012031 |
| Thermal correction to Enthalpy= | 0.012975 |
| Thermal correction to Gibbs Free Energy= | -0.027973 |
| Sum of electronic and zero-point Energies= | -358.327975 |
| Sum of electronic and thermal Energies= | -358.322714 |
| Sum of electronic and thermal Enthalpies= | -358.321769 |
| Sum of electronic and thermal Free Energies= | -358.362717 |

(B) Summary for the DFT calculation of [Pt$_3$H]$^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
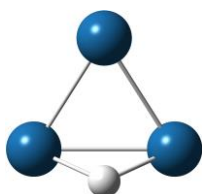


-----------------------------------------------------------------------------------------------------------------------
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.004835 | 1.472607 | 0.000000 | 0.403967 |
| Pt2 | 0.004835 | -0.730402 | 1.297123 | 0.264352 |
| Pt3 | 0.004835 | -0.730402 | -1.297123 | 0.264352 |
| H4 | -1.131430 | -0.920585 | 0.000000 | 0.067330 |

---

| | |
|---|---|
| Zero-point correction= | 0.007927 (Hartree/Particle) |
| Thermal correction to Energy= | 0.012811 |
| Thermal correction to Enthalpy= | 0.013756 |
| Thermal correction to Gibbs Free Energy= | -0.026374 |
| Sum of electronic and zero-point Energies= | -358.528137 |
| Sum of electronic and thermal Energies= | -358.523252 |
| Sum of electronic and thermal Enthalpies= | -358.522308 |
| Sum of electronic and thermal Free Energies= | -358.562438 |

**Table S46.**
(A) Geometry optimized for [Pt$_3$H$_2$]$^{2+}$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.500173 | 0.050926 | 0.000001 | 0.709185 |
| Pt2 | 0.699386 | -1.306022 | -0.016783 | 0.375927 |
| Pt3 | 0.787643 | 1.255536 | 0.016780 | 0.376989 |
| H4 | 0.473813 | -1.145789 | 1.485526 | 0.269007 |
| H5 | 0.551398 | 1.111447 | -1.485354 | 0.268893 |

aPart of the Gaussian output file:

SCF Done:  E(RM06) =  -358.438585159     A.U. after   19 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000033 | 0.000450 | YES |
| RMS    Force | 0.000013 | 0.000300 | YES |

| | 1 | 2 | 3 |
|---|---|---|---|
| | A | A | A |
| Frequencies -- | 99.0790 | 148.7613 | 188.1281 |
| Red. masses -- | 151.0925 | 146.1678 | 1.7528 |
| Frc consts  -- | 0.8739 | 1.9058 | 0.0365 |
| IR Inten   -- | 0.0326 | 0.2043 | 2.4526 |

Zero-point correction=                      0.014963 (Hartree/Particle)
Thermal correction to Energy=               0.021177
Thermal correction to Enthalpy=             0.022121
Thermal correction to Gibbs Free Energy=    -0.020623
Sum of electronic and zero-point Energies=      -358.423622
Sum of electronic and thermal Energies=         -358.417408
Sum of electronic and thermal Enthalpies=       -358.416464
Sum of electronic and thermal Free Energies=    -358.459208

(B) Summary for the DFT calculation of [Pt$_3$H$_2$]$^{2+}$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
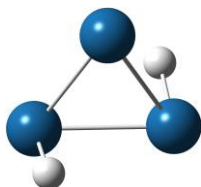


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.500173 | -0.050926 | 0.000001 | 0.651376 |
| Pt2 | -0.699386 | 1.306022 | -0.016783 | 0.586833 |
| Pt3 | -0.787643 | -1.255537 | 0.016780 | 0.584605 |
| H4 | -0.473813 | 1.145789 | 1.485526 | 0.088948 |

| H5 | -0.551398 | -1.111447 | -1.485354 | 0.088239 |

---

Zero-point correction=                       0.016675 (Hartree/Particle)
Thermal correction to Energy=                0.022506
Thermal correction to Enthalpy=              0.023450
Thermal correction to Gibbs Free Energy=    -0.020756
Sum of electronic and zero-point Energies=      -358.964771
Sum of electronic and thermal Energies=         -358.958940
Sum of electronic and thermal Enthalpies=       -358.957996
Sum of electronic and thermal Free Energies=    -359.002202

**Table S47.**
(A) Geometry optimized for [Pt₃]⁻ (doublet) computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]

---

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.000000 | 0.000000 | 1.512940 | -0.333598 | 0.333403 |
| Pt2 | 0.000000 | 1.310659 | -0.756470 | -0.333201 | 0.333298 |
| Pt3 | 0.000000 | -1.310659 | -0.756470 | -0.333201 | 0.333298 |

---

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -358.108821796    A.U. after   18 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.8011,   after    0.7516

```
        Item           Value    Threshold  Converged?
Maximum Force         0.000084    0.000450    YES
RMS    Force          0.000055    0.000300    YES
```

```
                 1              2              3
               A1             B2             A1
Frequencies --  116.4495        117.5342        182.2504
Red. masses --  194.9648        194.9648        194.9648
Frc consts  --   1.5577          1.5868          3.8154
IR Inten    --   0.0055          0.0060          0.0000
```

Zero-point correction=                    0.000948 (Hartree/Particle)
Thermal correction to Energy=             0.005775
Thermal correction to Enthalpy=           0.006719
Thermal correction to Gibbs Free Energy=     -0.033794
Sum of electronic and zero-point Energies=       -358.107874
Sum of electronic and thermal Energies=          -358.103047
Sum of electronic and thermal Enthalpies=        -358.102103
Sum of electronic and thermal Free Energies=       -358.142616

(B) Summary for the DFT calculation of [Pt₃]⁻ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) basis set. Computed by the single-point calculation for its optimized structure in vacuo.[a]
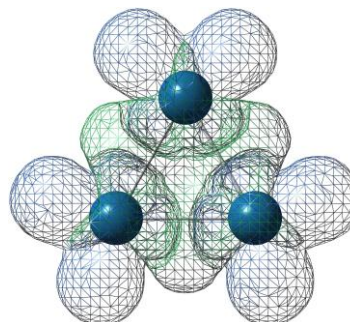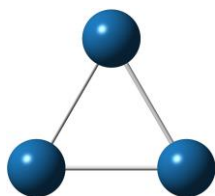


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000000 | 0.000000 | 1.512940 | -0.342966 | 0.333347 |
| Pt2 | 0.000000 | 1.310659 | -0.756470 | -0.328517 | 0.333327 |
| Pt3 | 0.000000 | -1.310659 | -0.756470 | -0.328517 | 0.333327 |

[a]Part of the Gaussian output file:

Zero-point correction=                               0.001018 (Hartree/Particle)
Thermal correction to Energy=                0.005796
Thermal correction to Enthalpy=            0.006740
Thermal correction to Gibbs Free Energy=       -0.033631
Sum of electronic and zero-point Energies=        -358.170482
Sum of electronic and thermal Energies=         -358.165704
Sum of electronic and thermal Enthalpies=        -358.164760
Sum of electronic and thermal Free Energies=       -358.205130

**Table S48.**
(A) Geometry optimized for [Pt₃H] (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 1.333683 | 0.744415 | -0.007522 | -0.068518 | 0.295885 |
| Pt2 | -1.331904 | 0.747468 | -0.007517 | -0.068619 | 0.296279 |
| Pt3 | -0.001803 | -1.506235 | 0.002139 | 0.034710 | 0.418173 |
| H4 | 0.001868 | 1.119404 | 1.006184 | 0.102427 | -0.010337 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -358.628344916     A.U. after   17 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7766,   after     0.7504

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000039 | 0.000450 | YES |
| RMS     Force | 0.000021 | 0.000300 | YES |

|   | 1 | 2 | 3 |
|---|---|---|---|
|   | A | A | A |
| Frequencies -- | 121.4088 | 121.7904 | 179.1907 |
| Red. masses -- | 81.4714 | 173.5041 | 87.4319 |
| Frc consts  -- | 0.7075 | 1.5163 | 1.6541 |
| IR Inten   -- | 0.0273 | 0.0166 | 0.0345 |

Zero-point correction=                       0.007157 (Hartree/Particle)
Thermal correction to Energy=                0.012394
Thermal correction to Enthalpy=              0.013338
Thermal correction to Gibbs Free Energy=     -0.028430
Sum of electronic and zero-point Energies=          -358.621188
Sum of electronic and thermal Energies=             -358.615951
Sum of electronic and thermal Enthalpies=           -358.615007
Sum of electronic and thermal Free Energies=        -358.656775

(B) Summary for the DFT calculation of [Pt₃H] (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
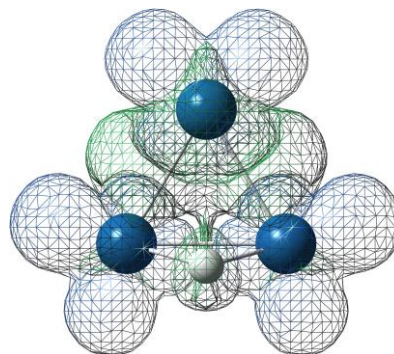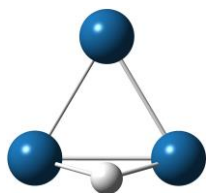


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -1.333683 | -0.744415 | -0.007522 | -0.002306 | 0.294242 |
| Pt2 | 1.331904 | -0.747468 | -0.007517 | -0.002722 | 0.294563 |
| Pt3 | 0.001803 | 1.506235 | 0.002139 | -0.016425 | 0.422391 |
| H4 | -0.001867 | -1.119404 | 1.006184 | 0.021452 | -0.011196 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.007961 (Hartree/Particle)
Thermal correction to Energy=            0.012996
Thermal correction to Enthalpy=          0.013940
Thermal correction to Gibbs Free Energy=     -0.027541
Sum of electronic and zero-point Energies=        -358.664643
Sum of electronic and thermal Energies=           -358.659607
Sum of electronic and thermal Enthalpies=         -358.658663
Sum of electronic and thermal Free Energies=       -358.700145
```

**Table S49.**
(A) Geometry optimized for [$Pt_3H_2$]$^+$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.339223 | 0.746045 | -0.006695 | 0.221818 | 0.405628 |
| Pt2 | 0.008249 | -1.503486 | 0.019413 | 0.228002 | 0.210962 |
| Pt3 | 1.330955 | 0.760152 | -0.006696 | 0.221579 | 0.405211 |
| H4 | 0.007285 | -1.311426 | -1.484545 | 0.185095 | -0.008656 |
| H5 | -0.005834 | 1.099988 | 1.014807 | 0.143505 | -0.013146 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -358.953915912     A.U. after   16 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7690,   after    0.7502

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000099 | 0.000450 | YES |
| RMS    Force | 0.000054 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 122.6933 | 123.8674 | 181.7961 |
| Red. masses -- | 175.7266 | 105.7940 | 141.0728 |
| Frc consts  -- | 1.5586 | 0.9564 | 2.7470 |
| IR Inten   -- | 0.0365 | 0.0092 | 0.0878 |

Zero-point correction=                       0.014822 (Hartree/Particle)
Thermal correction to Energy=               0.020536
Thermal correction to Enthalpy=             0.021480
Thermal correction to Gibbs Free Energy=      -0.020944
Sum of electronic and zero-point Energies=        -358.939094
Sum of electronic and thermal Energies=          -358.933380
Sum of electronic and thermal Enthalpies=         -358.932436
Sum of electronic and thermal Free Energies=       -358.974859

(B) Summary for the DFT calculation of [$Pt_3H_2$]$^+$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
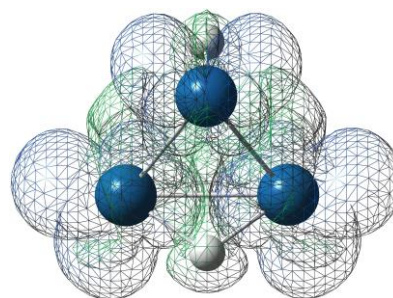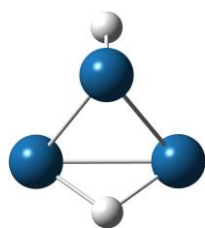


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.339223 | -0.746045 | 0.006695 | 0.262428 | 0.407747 |
| Pt2 | 0.008249 | 1.503486 | -0.019413 | 0.399360 | 0.205903 |
| Pt3 | 1.330955 | -0.760152 | 0.006696 | 0.261889 | 0.407117 |
| H4 | 0.007285 | 1.311427 | 1.484545 | 0.041542 | -0.007634 |
| H5 | -0.005834 | -1.099988 | -1.014807 | 0.034781 | -0.013133 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                       0.014179 (Hartree/Particle)
Thermal correction to Energy=                0.019680
Thermal correction to Enthalpy=              0.020624
Thermal correction to Gibbs Free Energy=    -0.021778
Sum of electronic and zero-point Energies=        -359.136463
Sum of electronic and thermal Energies=           -359.130962
Sum of electronic and thermal Enthalpies=         -359.130018
Sum of electronic and thermal Free Energies=      -359.172420
```

**Table S50.**

(A) Geometry optimized for [Pt$_3$H]$^-$ (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -0.786694 | -1.293875 | 0.003421 | -0.293703 | 0.547110 |
| Pt2 | 1.537870 | -0.000656 | -0.020892 | -0.350290 | 0.819362 |
| Pt3 | -0.785439 | 1.294560 | 0.003433 | -0.293840 | 0.547368 |
| H4 | 2.672478 | -0.002243 | 1.094989 | -0.062167 | 0.086160 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -358.705447229     A.U. after   20 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0261,   after    2.0003

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000083 | 0.000450 | YES |
| RMS    Force | 0.000033 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|--|---|---|---|
|  | A | A | A |
| Frequencies -- | 100.5139 | 118.9367 | 178.9134 |
| Red. masses -- | 155.3180 | 147.2512 | 161.8191 |
| Frc consts  -- | 0.9245 | 1.2273 | 3.0519 |
| IR Inten   -- | 0.0808 | 0.1020 | 0.0070 |

Zero-point correction=                    0.007911 (Hartree/Particle)
Thermal correction to Energy=             0.013220
Thermal correction to Enthalpy=           0.014164
Thermal correction to Gibbs Free Energy=       -0.028182
Sum of electronic and zero-point Energies=       -358.697536
Sum of electronic and thermal Energies=          -358.692227
Sum of electronic and thermal Enthalpies=        -358.691283
Sum of electronic and thermal Free Energies=       -358.733630

(B) Summary for the DFT calculation of [Pt₃H]⁻ (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]



Spin density distribution
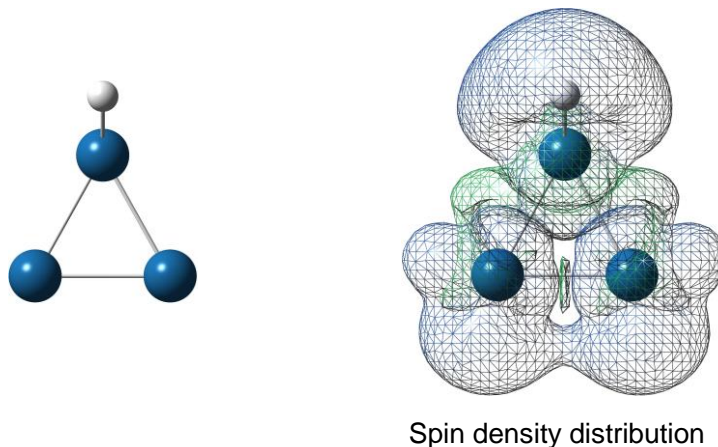
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -0.786694 | -1.293875 | 0.003421 | -0.187468 | 0.574760 |
| Pt2 | 1.537870 | -0.000656 | -0.020892 | -0.484836 | 0.768778 |
| Pt3 | -0.785439 | 1.294560 | 0.003433 | -0.187409 | 0.574944 |
| H4 | 2.672478 | -0.002243 | 1.094989 | -0.140287 | 0.081518 |

[a]Part of the Gaussian output file:

Zero-point correction=                             0.006551 (Hartree/Particle)
Thermal correction to Energy=               0.011665
Thermal correction to Enthalpy=             0.012609
Thermal correction to Gibbs Free Energy=       -0.029698
Sum of electronic and zero-point Energies=         -358.767838
Sum of electronic and thermal Energies=         -358.762724
Sum of electronic and thermal Enthalpies=         -358.761780
Sum of electronic and thermal Free Energies=         -358.804087

**Table S51.**
(A) Geometry optimized for [Pt$_3$H$_2$] (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.002090 | -0.765408 | -1.322144 | -0.040272 | 0.515970 |
| Pt2 | 0.002090 | 1.520916 | 0.000000 | -0.012322 | 0.833445 |
| Pt3 | 0.002090 | -0.765408 | 1.322144 | -0.040272 | 0.515970 |
| H4 | -1.409325 | 2.190060 | 0.000000 | 0.028414 | 0.099207 |
| H5 | 0.920178 | -1.417855 | 0.000000 | 0.064453 | 0.035408 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -359.221878232    A.U. after   12 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0171,   after    2.0001

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000012 | 0.000450 | YES |
| RMS    Force | 0.000006 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A" | A' | A' |
| Frequencies -- | 114.1921 | 123.3901 | 175.9252 |
| Red. masses -- | 75.0186 | 107.4582 | 123.8172 |
| Frc consts  -- | 0.5764 | 0.9639 | 2.2578 |
| IR Inten   -- | 0.1733 | 0.0076 | 0.0242 |

Zero-point correction=                   0.014300 (Hartree/Particle)
Thermal correction to Energy=            0.020071
Thermal correction to Enthalpy=          0.021016
Thermal correction to Gibbs Free Energy=     -0.021980
Sum of electronic and zero-point Energies=      -359.207579
Sum of electronic and thermal Energies=         -359.201807
Sum of electronic and thermal Enthalpies=       -359.200863
Sum of electronic and thermal Free Energies=      -359.243858

(B) Summary for the DFT calculation of [Pt$_3$H$_2$] (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
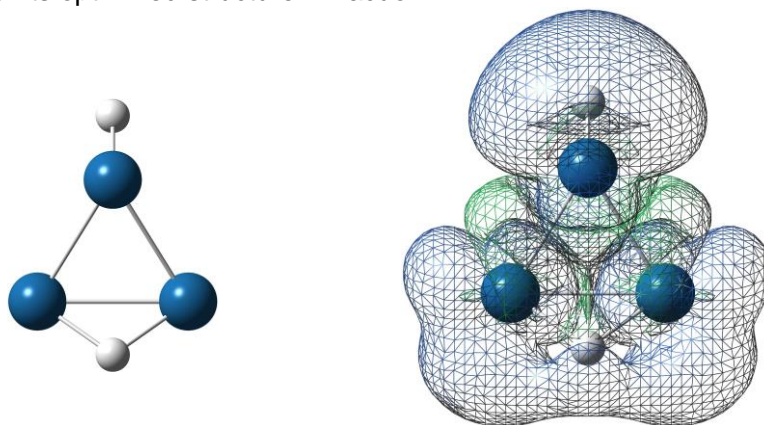


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -0.002090 | -0.765408 | 1.322144 | 0.084662 | 0.542208 |
| Pt2 | -0.002090 | 1.520917 | 0.000000 | -0.061169 | 0.828172 |
| Pt3 | -0.002090 | -0.765408 | -1.322144 | 0.084662 | 0.542208 |
| H4 | 1.409325 | 2.190060 | 0.000000 | -0.090031 | 0.069346 |
| H5 | -0.920178 | -1.417855 | 0.000000 | -0.018125 | 0.018066 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.013360 (Hartree/Particle)
Thermal correction to Energy=            0.018054
Thermal correction to Enthalpy=           0.018998
Thermal correction to Gibbs Free Energy=    -0.022415
Sum of electronic and zero-point Energies=      -359.264535
Sum of electronic and thermal Energies=         -359.259840
Sum of electronic and thermal Enthalpies=       -359.258896
Sum of electronic and thermal Free Energies=      -359.300309
```

**Table S52.** (A) Geometry optimized for [Pt$_3$H$_3$]$^{2+}$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -1.343638 | -0.724172 | -0.017908 | 0.438895 | 0.344684 |
| Pt2 | 1.301012 | -0.797765 | -0.017899 | 0.438209 | 0.344745 |
| Pt3 | 0.042680 | 1.521590 | 0.016667 | 0.402906 | 0.339886 |
| H4 | -1.237211 | -0.644871 | 1.494779 | 0.237744 | -0.009816 |
| H5 | 0.036596 | 1.385371 | -1.496411 | 0.244520 | -0.009694 |
| H6 | 1.196412 | -0.713469 | 1.494568 | 0.237726 | -0.009804 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -359.069076472     A.U. after   12 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7596,   after    0.7501

|       Item       |   Value   | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000103 | 0.000450 | YES |
| RMS    Force | 0.000040 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 120.1574 | 120.8592 | 183.8488 |
| Red. masses -- | 123.0569 | 122.7060 | 161.3926 |
| Frc consts  -- | 1.0468 | 1.0560 | 3.2141 |
| IR Inten   -- | 0.1466 | 0.1589 | 0.0068 |

Zero-point correction=                    0.024013 (Hartree/Particle)
Thermal correction to Energy=             0.030237
Thermal correction to Enthalpy=           0.031182
Thermal correction to Gibbs Free Energy=    -0.012004
Sum of electronic and zero-point Energies=      -359.045063
Sum of electronic and thermal Energies=         -359.038839
Sum of electronic and thermal Enthalpies=       -359.037895
Sum of electronic and thermal Free Energies=      -359.081080

(B) Summary for the DFT calculation of [Pt$_3$H$_3$]$^{2+}$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
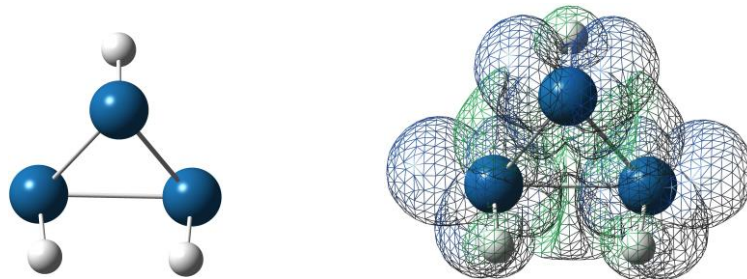


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -1.343638 | -0.724172 | -0.017908 | 0.626816 | 0.346610 |
| Pt2 | 1.301012 | -0.797765 | -0.017899 | 0.619361 | 0.346322 |
| Pt3 | 0.042680 | 1.521590 | 0.016667 | 0.563288 | 0.334571 |
| H4 | -1.237212 | -0.644870 | 1.494779 | 0.064111 | -0.009172 |
| H5 | 0.036596 | 1.385371 | -1.496411 | 0.061824 | -0.009174 |
| H6 | 1.196412 | -0.713469 | 1.494568 | 0.064599 | -0.009157 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                       0.023237 (Hartree/Particle)
Thermal correction to Energy=                0.029947
Thermal correction to Enthalpy=              0.030891
Thermal correction to Gibbs Free Energy=    -0.014015
Sum of electronic and zero-point Energies=    -359.574636
Sum of electronic and thermal Energies=       -359.567927
Sum of electronic and thermal Enthalpies=     -359.566983
Sum of electronic and thermal Free Energies=  -359.611889
```

**Table S53.** (A) Geometry optimized for [$Pt_3H_3$]$^+$ (triplet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

--------------------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 0.788036 | -1.324861 | 0.000565 | 0.097398 | 0.463869 |
| Pt2 | 0.779368 | 1.329599 | 0.000639 | 0.097238 | 0.463630 |
| Pt3 | -1.577490 | -0.004704 | -0.021790 | 0.375161 | 0.925727 |
| H4 | -1.722647 | -0.010816 | 1.516128 | 0.110237 | 0.099916 |
| H5 | 1.380696 | 0.003996 | -0.968264 | 0.144879 | 0.038588 |
| H6 | 1.128733 | 0.004181 | 1.057807 | 0.175088 | 0.008271 |

--------------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -359.530476843     A.U. after   14 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0141,   after    2.0001

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000125 | 0.000450 | YES |
| RMS    Force | 0.000058 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|--|---|---|---|
|  | A | A | A |
| Frequencies -- | 41.8729 | 128.4558 | 139.7419 |
| Red. masses -- | 2.6874 | 149.0452 | 1.6130 |
| Frc consts  -- | 0.0028 | 1.4490 | 0.0186 |
| IR Inten   -- | 6.4377 | 0.1512 | 2.9452 |

Zero-point correction=                 0.020155 (Hartree/Particle)
Thermal correction to Energy=             0.026709
Thermal correction to Enthalpy=            0.027653
Thermal correction to Gibbs Free Energy=     -0.017552
Sum of electronic and zero-point Energies=       -359.510322
Sum of electronic and thermal Energies=         -359.503768
Sum of electronic and thermal Enthalpies=        -359.502824
Sum of electronic and thermal Free Energies=       -359.548029

(B) Summary for the DFT calculation of [Pt$_3$H$_3$]$^+$ (triplet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]



Spin density distribution
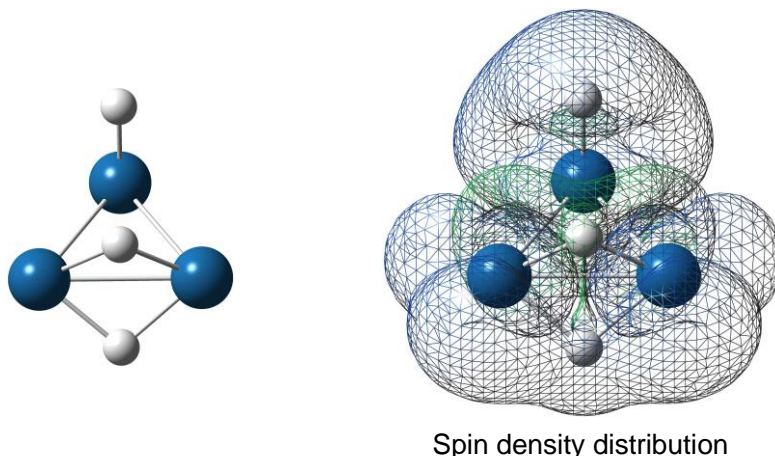
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.788036 | -1.324861 | 0.000565 | 0.262278 | 0.473414 |
| Pt2 | 0.779368 | 1.329599 | 0.000639 | 0.262455 | 0.472953 |
| Pt3 | -1.577491 | -0.004704 | -0.021790 | 0.416173 | 0.955229 |
| H4 | -1.722648 | -0.010816 | 1.516128 | -0.057363 | 0.072126 |
| H5 | 1.380696 | 0.003996 | -0.968264 | 0.039408 | 0.024799 |
| H6 | 1.128733 | 0.004181 | 1.057807 | 0.077049 | 0.001478 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                     0.019334 (Hartree/Particle)
Thermal correction to Energy=              0.024724
Thermal correction to Enthalpy=            0.025668
Thermal correction to Gibbs Free Energy=   -0.016823
Sum of electronic and zero-point Energies=    -359.715783
Sum of electronic and thermal Energies=       -359.710393
Sum of electronic and thermal Enthalpies=     -359.709449
Sum of electronic and thermal Free Energies=  -359.751941
```

**Table S54.** (A) Geometry optimized for [Pt$_3$H$_3$] (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

---

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.248664 | 1.479747 | -0.006333 | -0.041086 | 0.485638 |
| Pt2 | -1.485985 | -0.558085 | -0.008050 | -0.140101 | 0.230636 |
| Pt3 | 1.274594 | -0.920891 | 0.021917 | 0.011404 | 0.237926 |
| H4 | -1.171240 | 0.816677 | 0.874052 | 0.088363 | -0.002075 |
| H5 | 1.232730 | -0.828250 | -1.500651 | 0.077532 | 0.010337 |
| H6 | -2.968784 | -0.048570 | 0.038943 | 0.003887 | 0.037538 |

---

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -359.828574188     A.U. after   14 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7646,   after    0.7501

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000013 | 0.000450 | YES |
| RMS    Force | 0.000005 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 94.1234 | 113.7023 | 168.2943 |
| Red. masses -- | 60.3370 | 38.3147 | 47.6245 |
| Frc consts  -- | 0.3149 | 0.2918 | 0.7947 |
| IR Inten   -- | 1.0653 | 1.1445 | 0.2366 |

Zero-point correction=                      0.021303 (Hartree/Particle)
Thermal correction to Energy=               0.027831
Thermal correction to Enthalpy=             0.028775
Thermal correction to Gibbs Free Energy=        -0.015260
Sum of electronic and zero-point Energies=       -359.807271
Sum of electronic and thermal Energies=          -359.800744
Sum of electronic and thermal Enthalpies=        -359.799799
Sum of electronic and thermal Free Energies=       -359.843834

(B) Summary for the DFT calculation of [Pt$_3$H$_3$] (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
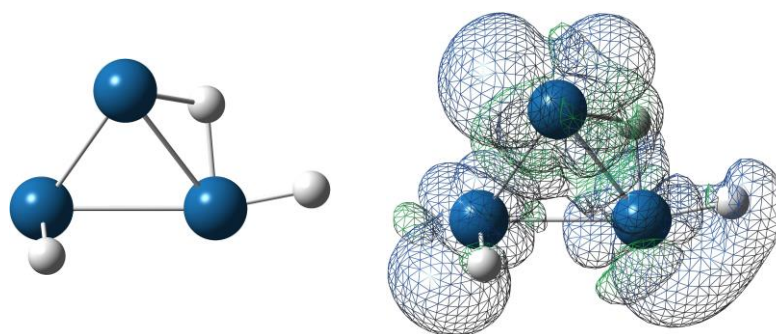


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -0.248664 | 1.479747 | 0.006333 | 0.071941 | 0.545429 |
| Pt2 | 1.485985 | -0.558085 | 0.008050 | -0.139030 | 0.227354 |
| Pt3 | -1.274594 | -0.920891 | -0.021917 | 0.168998 | 0.212861 |
| H4 | 1.171241 | 0.816677 | -0.874052 | 0.021127 | -0.010299 |
| H5 | -1.232730 | -0.828250 | 1.500651 | -0.031488 | 0.002484 |
| H6 | 2.968785 | -0.048570 | -0.038943 | -0.091549 | 0.022172 |

[a]Part of the Gaussian output file:

Zero-point correction=                         0.020003 (Hartree/Particle)
Thermal correction to Energy=              0.027006
Thermal correction to Enthalpy=            0.027950
Thermal correction to Gibbs Free Energy=      -0.017857
Sum of electronic and zero-point Energies=        -359.870757
Sum of electronic and thermal Energies=           -359.863755
Sum of electronic and thermal Enthalpies=         -359.862811
Sum of electronic and thermal Free Energies=       -359.908618

**Table S55.** (A) Geometry optimized for [Pt₃H₄]²⁺ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | -1.511534 | 0.724034 | -0.018925 | 0.396982 |
| Pt2 | 0.000296 | -1.465671 | 0.016468 | 0.371483 |
| Pt3 | 1.511233 | 0.724457 | -0.018927 | 0.397115 |
| H4 | 0.000428 | -1.336714 | -1.495052 | 0.235504 |
| H5 | -1.482891 | 0.587501 | 1.492513 | 0.240933 |
| H6 | -0.000033 | 1.500564 | 0.177956 | 0.117008 |
| H7 | 1.482862 | 0.588662 | 1.492582 | 0.240975 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -359.673445554    A.U. after   10 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000038 | 0.000450 | YES |
| RMS    Force | 0.000016 | 0.000300 | YES |

|   | 1 | 2 | 3 |
|---|---|---|---|
|   | A | A | A |
| Frequencies -- | 71.7655 | 129.8129 | 157.6130 |
| Red. masses -- | 68.7265 | 148.7793 | 122.5770 |
| Frc consts  -- | 0.2085 | 1.4772 | 1.7941 |
| IR Inten   -- | 0.0597 | 0.2370 | 0.0003 |

Zero-point correction=                    0.030734 (Hartree/Particle)
Thermal correction to Energy=             0.037468
Thermal correction to Enthalpy=           0.038412
Thermal correction to Gibbs Free Energy=      -0.005510
Sum of electronic and zero-point Energies=       -359.642712
Sum of electronic and thermal Energies=          -359.635977
Sum of electronic and thermal Enthalpies=        -359.635033
Sum of electronic and thermal Free Energies=       -359.678955

(B) Summary for the DFT calculation of [Pt₃H₄]²⁺ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
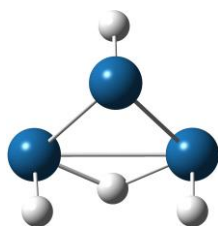


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 1.511534 | -0.724034 | -0.018925 | 0.613993 |

| | | | |
|---|---|---|---|
| Pt2 | -0.000296 | 1.465671 | 0.016468 | 0.553536 |
| Pt3 | -1.511233 | -0.724457 | -0.018927 | 0.614329 |
| H4 | -0.000428 | 1.336714 | -1.495052 | 0.059875 |
| H5 | 1.482891 | -0.587501 | 1.492514 | 0.069533 |
| H6 | 0.000033 | -1.500564 | 0.177956 | 0.019193 |
| H7 | -1.482862 | -0.588662 | 1.492583 | 0.069540 |

------------------------------------------------------------------------------------------------------------------

aPart of the Gaussian output file:

Zero-point correction=                           0.026485 (Hartree/Particle)
Thermal correction to Energy=              0.032868
Thermal correction to Enthalpy=             0.033813
Thermal correction to Gibbs Free Energy=        -0.009055
Sum of electronic and zero-point Energies=        -360.158987
Sum of electronic and thermal Energies=         -360.152604
Sum of electronic and thermal Enthalpies=        -360.151660
Sum of electronic and thermal Free Energies=        -360.194527

**Table S56.** (A) Geometry optimized for [Pt$_3$H$_4$]$^+$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 2.337841 | -0.412141 | 0.011451 | 0.176345 | 0.123578 |
| Pt2 | -0.002262 | 0.803726 | 0.003691 | 0.112069 | 0.688051 |
| Pt3 | -2.320420 | -0.412806 | -0.019390 | 0.123896 | 0.170843 |
| H4 | 2.767218 | 1.026681 | -0.245625 | 0.145533 | 0.000241 |
| H5 | 1.111500 | -0.053476 | -1.082578 | 0.111108 | -0.002273 |
| H6 | -2.164373 | -0.306687 | 1.493127 | 0.169384 | 0.006500 |
| H7 | -2.896771 | 0.988694 | 0.166450 | 0.161665 | 0.013059 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -360.143421946     A.U. after   15 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7581,   after     0.7500

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000061 | 0.000450 | YES |
| RMS    Force | 0.000029 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|--|---|---|---|
|  | A | A | A |
| Frequencies -- | 20.7795 | 124.2488 | 163.3892 |
| Red. masses -- | 58.6626 | 84.0290 | 29.7262 |
| Frc consts  -- | 0.0149 | 0.7643 | 0.4676 |
| IR Inten   -- | 0.0478 | 0.0676 | 0.2671 |

Zero-point correction=                      0.029235 (Hartree/Particle)
Thermal correction to Energy=                0.036631
Thermal correction to Enthalpy=              0.037575
Thermal correction to Gibbs Free Energy=     -0.009301
Sum of electronic and zero-point Energies=      -360.114187
Sum of electronic and thermal Energies=         -360.106791
Sum of electronic and thermal Enthalpies=       -360.105847
Sum of electronic and thermal Free Energies=       -360.152723

(B) Summary for the DFT calculation of [Pt$_3$H$_4$]$^+$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
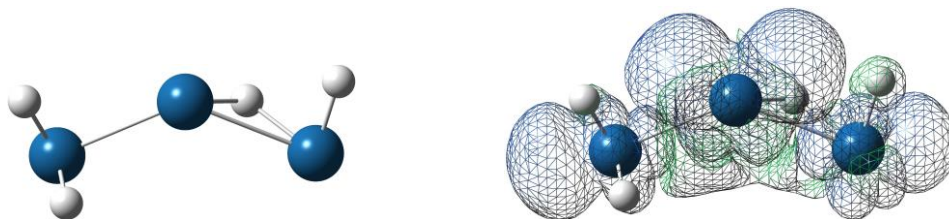


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 2.337842 | -0.412141 | 0.011451 | 0.319537 | 0.108166 |
| Pt2 | -0.002262 | 0.803726 | 0.003691 | 0.128814 | 0.710051 |
| Pt3 | -2.320420 | -0.412806 | -0.019390 | 0.434090 | 0.181079 |
| H4 | 2.767219 | 1.026681 | -0.245625 | 0.022976 | -0.004660 |
| H5 | 1.111500 | -0.053476 | -1.082578 | 0.015346 | -0.004923 |
| H6 | -2.164373 | -0.306687 | 1.493127 | 0.042206 | 0.003821 |
| H7 | -2.896771 | 0.988695 | 0.166450 | 0.037031 | 0.006467 |

[a]Part of the Gaussian output file:

Zero-point correction=                             0.027219 (Hartree/Particle)
Thermal correction to Energy=                 0.033173
Thermal correction to Enthalpy=              0.034117
Thermal correction to Gibbs Free Energy=      -0.009062
Sum of electronic and zero-point Energies=        -360.310935
Sum of electronic and thermal Energies=          -360.304981
Sum of electronic and thermal Enthalpies=        -360.304037
Sum of electronic and thermal Free Energies=      -360.347216

**Table S57.** (A) Geometry optimized for [Pt$_3$H$_4$] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | -0.931784 | -1.225300 | -0.020610 | -0.023579 |
| Pt2 | 1.617616 | -0.121996 | 0.015534 | -0.136486 |
| Pt3 | -0.711745 | 1.329508 | -0.002603 | -0.090270 |
| H4 | 2.901456 | 0.700703 | 0.314870 | 0.040597 |
| H5 | -0.851514 | -1.079990 | 1.493195 | 0.101677 |
| H6 | 2.219856 | 0.261434 | -1.334526 | 0.083855 |
| H7 | -2.248648 | 1.505344 | 0.125461 | 0.024206 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -360.436583637     A.U. after   12 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000009 | 0.000450 | YES |
| RMS    Force | 0.000003 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|--|---|---|---|
|  | A | A | A |
| Frequencies -- | 93.7121 | 116.2374 | 170.5473 |
| Red. masses -- | 70.1319 | 49.6869 | 1.3408 |
| Frc consts  -- | 0.3629 | 0.3955 | 0.0230 |
| IR Inten    -- | 1.7505 | 0.3756 | 7.0155 |

Zero-point correction=                    0.030401 (Hartree/Particle)
Thermal correction to Energy=             0.037632
Thermal correction to Enthalpy=           0.038576
Thermal correction to Gibbs Free Energy=     -0.006017
Sum of electronic and zero-point Energies=       -360.406183
Sum of electronic and thermal Energies=          -360.398952
Sum of electronic and thermal Enthalpies=        -360.398008
Sum of electronic and thermal Free Energies=     -360.442601

(B) Summary for the DFT calculation of [Pt$_3$H$_4$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
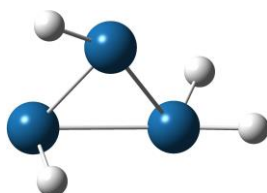


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | -0.931784 | -1.225300 | -0.020610 | 0.257085 |
| Pt2 | 1.617616 | -0.121996 | 0.015534 | -0.047477 |

| | | | |
|---|---|---|---|
| Pt3 | -0.711745 | 1.329508 | -0.002603 | -0.134612 |
| H4 | 2.901456 | 0.700703 | 0.314870 | -0.029679 |
| H5 | -0.851514 | -1.079990 | 1.493195 | 0.005224 |
| H6 | 2.219856 | 0.261434 | -1.334526 | 0.014759 |
| H7 | -2.248648 | 1.505344 | 0.125461 | -0.065300 |

--------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

```
Zero-point correction=                    0.029563 (Hartree/Particle)
Thermal correction to Energy=             0.037248
Thermal correction to Enthalpy=           0.038192
Thermal correction to Gibbs Free Energy=  -0.007936
Sum of electronic and zero-point Energies=     -360.479005
Sum of electronic and thermal Energies=        -360.471320
Sum of electronic and thermal Enthalpies=      -360.470376
Sum of electronic and thermal Free Energies=   -360.516505
```

**Table S58.** (A) Geometry optimized for $[Pt_3H_5]^{2+}$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | -2.402254 | -0.359782 | 0.004070 | 0.274897 | 0.229907 |
| Pt2 | -0.000308 | 0.676265 | -0.012229 | 0.342113 | 0.526671 |
| Pt3 | 2.402257 | -0.360591 | -0.001257 | 0.276509 | 0.230743 |
| H4 | -0.001762 | 0.439348 | 1.488926 | 0.206483 | -0.013913 |
| H5 | -2.581041 | 0.481366 | -1.256425 | 0.223587 | 0.006401 |
| H6 | 2.655543 | 0.694731 | -1.075551 | 0.222957 | 0.006586 |
| H7 | 2.656058 | 0.839960 | 0.910423 | 0.226813 | 0.006707 |
| H8 | -2.705052 | 0.985107 | 0.667037 | 0.226641 | 0.006898 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -360.282590140     A.U. after   15 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation     0.7570,   after     0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000022 | 0.000450 | YES |
| RMS    Force | 0.000008 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 33.2859 | 123.3457 | 172.8621 |
| Red. masses -- | 71.5479 | 67.2562 | 56.0912 |
| Frc consts  -- | 0.0467 | 0.6029 | 0.9875 |
| IR Inten   -- | 0.1120 | 0.0089 | 1.2002 |

| | |
|---|---|
| Zero-point correction= | 0.038679 (Hartree/Particle) |
| Thermal correction to Energy= | 0.046561 |
| Thermal correction to Enthalpy= | 0.047506 |
| Thermal correction to Gibbs Free Energy= | 0.000384 |
| Sum of electronic and zero-point Energies= | -360.243911 |
| Sum of electronic and thermal Energies= | -360.236029 |
| Sum of electronic and thermal Enthalpies= | -360.235085 |
| Sum of electronic and thermal Free Energies= | -360.282206 |

(B) Summary for the DFT calculation of $[Pt_3H_5]^{2+}$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
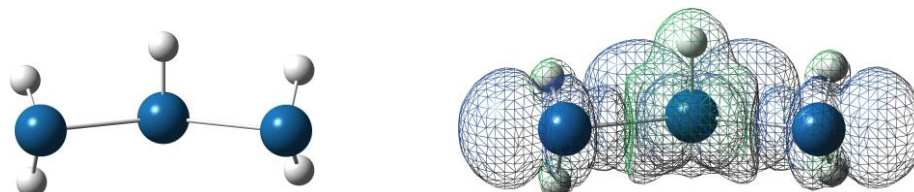


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | -2.402254 | -0.359782 | 0.004070 | 0.565048 | 0.206050 |
| Pt2 | -0.000308 | 0.676265 | -0.012229 | 0.524082 | 0.596025 |
| Pt3 | 2.402257 | -0.360591 | -0.001257 | 0.565803 | 0.204553 |
| H4 | -0.001762 | 0.439348 | 1.488926 | 0.063919 | -0.015142 |
| H5 | -2.581041 | 0.481366 | -1.256426 | 0.068952 | 0.001921 |
| H6 | 2.655543 | 0.694731 | -1.075551 | 0.068369 | 0.001713 |
| H7 | 2.656058 | 0.839960 | 0.910423 | 0.072242 | 0.002436 |
| H8 | -2.705052 | 0.985107 | 0.667037 | 0.071586 | 0.002443 |

[a]Part of the Gaussian output file:

Zero-point correction=                          0.036111 (Hartree/Particle)
Thermal correction to Energy=              0.042157
Thermal correction to Enthalpy=            0.043101
Thermal correction to Gibbs Free Energy=      -0.000046
Sum of electronic and zero-point Energies=      -360.740178
Sum of electronic and thermal Energies=         -360.734132
Sum of electronic and thermal Enthalpies=       -360.733188
Sum of electronic and thermal Free Energies=      -360.776335

**Table S59.** (A) Geometry optimized for [Pt$_3$H$_5$]$^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | -1.645226 | 0.594489 | 0.018873 | 0.172017 |
| Pt2 | 1.500022 | 0.814295 | -0.017873 | 0.194090 |
| Pt3 | 0.113577 | -1.375855 | -0.002231 | 0.096535 |
| H4 | 1.436097 | 0.619493 | 1.487426 | 0.165869 |
| H5 | -1.507966 | 0.413043 | -1.489336 | 0.152407 |
| H6 | 1.370381 | -2.510478 | -0.376839 | 0.069410 |
| H7 | 1.357719 | -2.475034 | 0.489426 | 0.075702 |
| H8 | -0.189224 | 1.384485 | -0.014651 | 0.073971 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -360.755349193    A.U. after    9 cycles

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000026 | 0.000450 | YES |
| RMS    Force | 0.000009 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 65.8270 | 145.3063 | 168.2850 |
| Red. masses -- | 45.9970 | 53.6170 | 39.3795 |
| Frc consts  -- | 0.1174 | 0.6670 | 0.6571 |
| IR Inten    -- | 0.3011 | 0.1951 | 0.1524 |

| | |
|---|---|
| Zero-point correction= | 0.038200 (Hartree/Particle) |
| Thermal correction to Energy= | 0.045774 |
| Thermal correction to Enthalpy= | 0.046719 |
| Thermal correction to Gibbs Free Energy= | 0.001437 |
| Sum of electronic and zero-point Energies= | -360.717149 |
| Sum of electronic and thermal Energies= | -360.709575 |
| Sum of electronic and thermal Enthalpies= | -360.708631 |
| Sum of electronic and thermal Free Energies= | -360.753912 |

(B) Summary for the DFT calculation of [Pt$_3$H$_5$]$^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
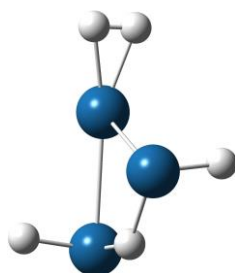
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|---|---|---|---|---|
| Pt1 | 1.645226 | -0.594489 | 0.018873 | 0.400621 |
| Pt2 | -1.500022 | -0.814295 | -0.017873 | 0.438860 |
| Pt3 | -0.113577 | 1.375855 | -0.002231 | 0.043531 |
| H4 | -1.436098 | -0.619494 | 1.487426 | 0.037351 |
| H5 | 1.507966 | -0.413043 | -1.489336 | 0.022401 |
| H6 | -1.370381 | 2.510479 | -0.376839 | 0.022653 |
| H7 | -1.357719 | 2.475034 | 0.489427 | 0.026529 |
| H8 | 0.189224 | -1.384485 | -0.014651 | 0.008052 |

[a]Part of the Gaussian output file:

Zero-point correction=                           0.035154 (Hartree/Particle)
Thermal correction to Energy=                0.041623
Thermal correction to Enthalpy=              0.042568
Thermal correction to Gibbs Free Energy=      -0.001059
Sum of electronic and zero-point Energies=        -360.903379
Sum of electronic and thermal Energies=           -360.896910
Sum of electronic and thermal Enthalpies=         -360.895966
Sum of electronic and thermal Free Energies=       -360.939593

**Table S60.** (A) Geometry optimized for [$Pt_3H_5$] (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.832878 | -1.290539 | 0.009628 | -0.097021 | 0.363338 |
| Pt2 | 0.757369 | 1.380192 | -0.011234 | -0.031348 | 0.485076 |
| Pt3 | -1.575650 | -0.039229 | -0.011636 | -0.205014 | 0.067807 |
| H4 | -0.357711 | 1.431612 | 1.109048 | 0.060116 | 0.038599 |
| H5 | 1.858177 | -1.776496 | -1.037452 | 0.081580 | 0.026280 |
| H6 | -2.286709 | -0.956426 | 0.999049 | 0.076923 | 0.000445 |
| H7 | -2.561442 | -1.032028 | -0.691888 | 0.047635 | 0.013692 |
| H8 | 2.209071 | -1.599758 | 0.654057 | 0.067130 | 0.004762 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -361.037576411     A.U. after   14 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7553,   after    0.7500

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000015 | 0.000450 | YES |
| RMS    Force | 0.000006 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 105.1944 | 112.5263 | 154.3591 |
| Red. masses -- | 24.6215 | 47.0978 | 40.2101 |
| Frc consts  -- | 0.1605 | 0.3514 | 0.5645 |
| IR Inten   -- | 1.8633 | 1.6913 | 0.1023 |

Zero-point correction=                      0.035900 (Hartree/Particle)
Thermal correction to Energy=               0.044035
Thermal correction to Enthalpy=             0.044979
Thermal correction to Gibbs Free Energy=    -0.001818
Sum of electronic and zero-point Energies=      -361.001676
Sum of electronic and thermal Energies=         -360.993541
Sum of electronic and thermal Enthalpies=       -360.992597
Sum of electronic and thermal Free Energies=    -361.039394

(B) Summary for the DFT calculation of [Pt₃H₅] (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
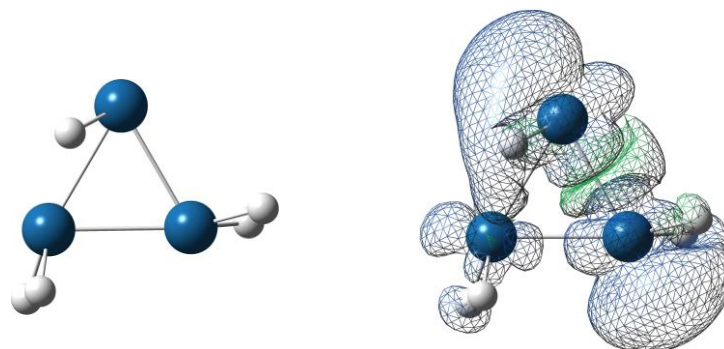
Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.832878 | -1.290539 | 0.009628 | 0.029661 | 0.330918 |
| Pt2 | 0.757369 | 1.380192 | -0.011234 | 0.163860 | 0.562182 |
| Pt3 | -1.575650 | -0.039229 | -0.011636 | -0.178481 | 0.059310 |
| H4 | -0.357711 | 1.431612 | 1.109048 | -0.036375 | 0.020190 |
| H5 | 1.858177 | -1.776497 | -1.037452 | 0.015659 | 0.018130 |
| H6 | -2.286709 | -0.956426 | 0.999050 | 0.019903 | -0.001194 |
| H7 | -2.561442 | -1.032028 | -0.691888 | -0.018689 | 0.010204 |
| H8 | 2.209071 | -1.599758 | 0.654057 | 0.004461 | 0.000260 |

[a]Part of the Gaussian output file:

Zero-point correction=                                0.033700 (Hartree/Particle)
Thermal correction to Energy=                 0.041436
Thermal correction to Enthalpy=               0.042380
Thermal correction to Gibbs Free Energy=      -0.004661
Sum of electronic and zero-point Energies=          -361.067294
Sum of electronic and thermal Energies=             -361.059558
Sum of electronic and thermal Enthalpies=           -361.058614
Sum of electronic and thermal Free Energies=        -361.105655

**Table S61.** (A) Geometry optimized for $[Pt_3H_6]^+$ (doublet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

--------------------------------------------------------------------------------------------------------------

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|------------|---------------|---------------|---------------|-----------------|--------------|
| Pt1 | 0.664090 | 1.397156 | -0.022978 | 0.015940 | 0.437264 |
| Pt2 | 1.000890 | -1.224497 | 0.021736 | -0.008755 | 0.429407 |
| Pt3 | -1.719801 | -0.162844 | 0.020067 | 0.188097 | 0.010401 |
| H4 | 2.522377 | -1.520466 | 0.140874 | 0.110889 | 0.028611 |
| H5 | 2.000039 | 2.184031 | 0.074910 | 0.107156 | 0.022356 |
| H6 | -1.510242 | -0.011164 | -1.480777 | 0.166001 | -0.000884 |
| H7 | -1.046257 | -1.557421 | -0.267053 | 0.110584 | -0.000156 |
| H8 | 0.841722 | 1.602569 | 1.482997 | 0.149153 | 0.033990 |
| H9 | 1.468379 | -1.463059 | -1.419257 | 0.160934 | 0.039011 |

--------------------------------------------------------------------------------------------------------------

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) =  -361.344897883     A.U. after   12 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    0.7546,   after    0.7500

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000035 | 0.000450 | YES |
| RMS    Force | 0.000012 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|--|---|---|---|
|  | A | A | A |
| Frequencies -- | 70.1436 | 96.0618 | 139.2028 |
| Red. masses -- | 29.2034 | 33.4561 | 1.0520 |
| Frc consts  -- | 0.0847 | 0.1819 | 0.0120 |
| IR Inten   -- | 0.4227 | 0.2370 | 2.0082 |

Zero-point correction=                      0.043328 (Hartree/Particle)
Thermal correction to Energy=               0.052295
Thermal correction to Enthalpy=             0.053239
Thermal correction to Gibbs Free Energy=       0.004368
Sum of electronic and zero-point Energies=       -361.301570
Sum of electronic and thermal Energies=        -361.292603
Sum of electronic and thermal Enthalpies=       -361.291659
Sum of electronic and thermal Free Energies=      -361.340530

(B) Summary for the DFT calculation of $[Pt_3H_6]^+$ (doublet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
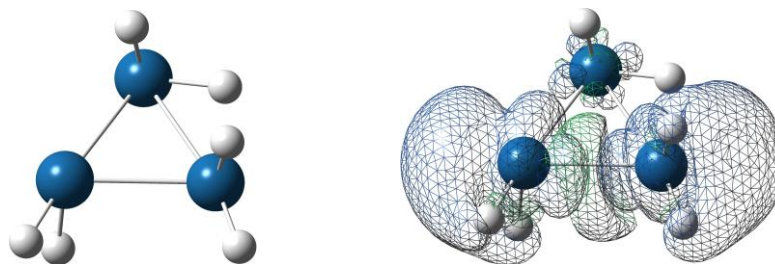


Spin density distribution

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | -0.664090 | 1.397156 | 0.022978 | 0.216640 | 0.475944 |
| Pt2 | -1.000890 | -1.224497 | -0.021736 | 0.152817 | 0.435242 |
| Pt3 | 1.719801 | -0.162844 | -0.020067 | 0.524182 | 0.012840 |
| H4 | -2.522378 | -1.520466 | -0.140874 | -0.008060 | 0.021699 |
| H5 | -2.000039 | 2.184031 | -0.074910 | -0.016296 | 0.012336 |
| H6 | 1.510242 | -0.011164 | 1.480778 | 0.039619 | -0.000323 |
| H7 | 1.046257 | -1.557421 | 0.267053 | -0.001996 | -0.000027 |
| H8 | -0.841722 | 1.602570 | -1.482997 | 0.040178 | 0.020335 |
| H9 | -1.468379 | -1.463059 | 1.419257 | 0.052916 | 0.021955 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                    0.042853 (Hartree/Particle)
Thermal correction to Energy=             0.049918
Thermal correction to Enthalpy=           0.050862
Thermal correction to Gibbs Free Energy=  0.005661
Sum of electronic and zero-point Energies=      -361.508503
Sum of electronic and thermal Energies=         -361.501439
Sum of electronic and thermal Enthalpies=       -361.500494
Sum of electronic and thermal Free Energies=    -361.545695
```

**Table S62.** (A) Geometry optimized for [Pt$_3$H$_6$] (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 1.471662 | 0.759121 | -0.007450 | -0.128459 |
| Pt2 | -1.383579 | 0.803225 | 0.008087 | -0.267027 |
| Pt3 | -0.016187 | -1.565584 | -0.008883 | -0.035230 |
| H4 | -1.834588 | 2.285256 | 0.183529 | 0.046116 |
| H5 | 0.620295 | 0.610793 | 1.290631 | 0.115913 |
| H6 | -0.795815 | -2.302700 | 1.089704 | 0.079873 |
| H7 | -0.812741 | -2.742006 | -0.631018 | 0.056050 |
| H8 | 0.038398 | 1.432573 | -0.710760 | 0.094127 |
| H9 | -2.823391 | 0.968652 | -0.578907 | 0.038637 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -361.639358932    A.U. after    8 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|-----------|
| Maximum Force | 0.000021 | 0.000450 | YES |
| RMS    Force | 0.000005 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 84.8221 | 102.7516 | 134.4904 |
| Red. masses -- | 6.1509 | 30.3637 | 1.6873 |
| Frc consts  -- | 0.0261 | 0.1889 | 0.0180 |
| IR Inten   -- | 3.0801 | 2.8152 | 3.1229 |

Zero-point correction=                      0.042406 (Hartree/Particle)
Thermal correction to Energy=               0.051105
Thermal correction to Enthalpy=             0.052050
Thermal correction to Gibbs Free Energy=    0.004546
Sum of electronic and zero-point Energies=    -361.596953
Sum of electronic and thermal Energies=       -361.588254
Sum of electronic and thermal Enthalpies=     -361.587309
Sum of electronic and thermal Free Energies=  -361.634813

(B) Summary for the DFT calculation of [Pt$_3$H$_6$] (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
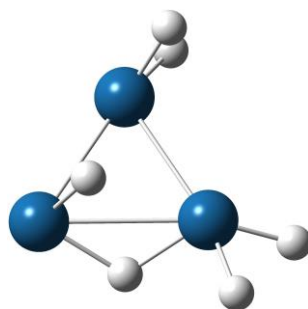
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | -1.471662 | -0.759121 | -0.007450 | 0.195899 |
| Pt2 | 1.383579 | -0.803225 | 0.008087 | -0.294343 |
| Pt3 | 0.016187 | 1.565584 | -0.008883 | 0.040175 |
| H4 | 1.834589 | -2.285257 | 0.183529 | 0.000146 |
| H5 | -0.620295 | -0.610793 | 1.290631 | 0.041887 |
| H6 | 0.795815 | 2.302701 | 1.089704 | 0.018839 |
| H7 | 0.812741 | 2.742007 | -0.631018 | -0.007326 |
| H8 | -0.038398 | -1.432573 | -0.710760 | 0.033909 |
| H9 | 2.823391 | -0.968652 | -0.578907 | -0.029186 |

[a]Part of the Gaussian output file:

Zero-point correction=                          0.042598 (Hartree/Particle)
Thermal correction to Energy=              0.049929
Thermal correction to Enthalpy=            0.050873
Thermal correction to Gibbs Free Energy=      0.006059
Sum of electronic and zero-point Energies=        -361.663680
Sum of electronic and thermal Energies=           -361.656349
Sum of electronic and thermal Enthalpies=         -361.655405
Sum of electronic and thermal Free Energies=       -361.700219

**Table S63.** (A) Geometry optimized for [Pt$_3$H$_7$]$^+$ (singlet) computed at the M06 level of DFT using SDD(Pt) and 6-31+G**(H) basis sets in vacuo.[a]

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | 0.773389 | -1.345244 | -0.006307 | -0.174324 |
| Pt2 | -1.722823 | 0.061734 | -0.016721 | 0.206229 |
| Pt3 | 0.891578 | 1.325079 | -0.017168 | -0.059335 |
| H4 | -1.375110 | -0.230271 | 1.437783 | 0.174722 |
| H5 | 0.383706 | -2.643756 | -0.739191 | 0.169529 |
| H6 | 2.394914 | 1.715160 | -0.121006 | 0.092661 |
| H7 | 1.436382 | 1.004842 | 1.378979 | 0.152049 |
| H8 | 0.621819 | -2.536254 | 0.953909 | 0.186583 |
| H9 | -1.102894 | 1.470788 | 0.362375 | 0.106338 |
| H10 | 2.153973 | -2.022950 | -0.137537 | 0.145548 |

[a]Part of the Gaussian output file:

SCF Done:  E(RM06) =  -361.957231798     A.U. after   11 cycles

| Item | Value | Threshold | Converged? |
|------|-------|-----------|------------|
| Maximum Force | 0.000045 | 0.000450 | YES |
| RMS     Force | 0.000015 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|--|---|---|---|
|  | A | A | A |
| Frequencies -- | 78.2956 | 97.5002 | 141.4567 |
| Red. masses -- | 49.4884 | 31.3282 | 6.5894 |
| Frc consts  -- | 0.1787 | 0.1755 | 0.0777 |
| IR Inten   -- | 0.4805 | 0.7426 | 3.0669 |

Zero-point correction=                       0.053574 (Hartree/Particle)
Thermal correction to Energy=                0.062368
Thermal correction to Enthalpy=              0.063312
Thermal correction to Gibbs Free Energy=     0.015690
Sum of electronic and zero-point Energies=       -361.903658
Sum of electronic and thermal Energies=          -361.894864
Sum of electronic and thermal Enthalpies=        -361.893920
Sum of electronic and thermal Free Energies=     -361.941542

(B) Summary for the DFT calculation of [Pt$_3$H$_7$]$^+$ (singlet) with solvation in water taken into consideration (C-PCM), at the M06 level of DFT with SDD(Pt) and 6-31+G**(H) basis sets. Computed by the single-point calculation for its optimized structure in vacuo.[a]
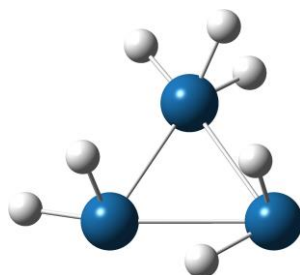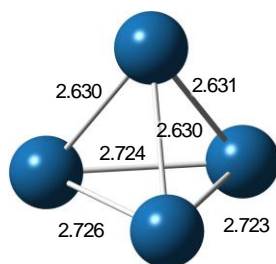
| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge |
|------------|---------------|---------------|---------------|-----------------|
| Pt1 | -0.773389 | 1.345244 | -0.006307 | 0.072245 |
| Pt2 | 1.722823 | -0.061734 | -0.016721 | 0.569487 |
| Pt3 | -0.891578 | -1.325080 | -0.017168 | 0.041644 |
| H4 | 1.375110 | 0.230272 | 1.437783 | 0.050832 |
| H5 | -0.383706 | 2.643756 | -0.739191 | 0.090191 |
| H6 | -2.394914 | -1.715160 | -0.121006 | -0.028801 |
| H7 | -1.436383 | -1.004842 | 1.378979 | 0.052672 |
| H8 | -0.621819 | 2.536254 | 0.953909 | 0.109143 |
| H9 | 1.102894 | -1.470788 | 0.362375 | -0.004157 |
| H10 | -2.153973 | 2.022950 | -0.137537 | 0.046745 |

[a]Part of the Gaussian output file:

```
Zero-point correction=                      0.050589 (Hartree/Particle)
Thermal correction to Energy=               0.059266
Thermal correction to Enthalpy=             0.060210
Thermal correction to Gibbs Free Energy=    0.011828
Sum of electronic and zero-point Energies=     -362.101667
Sum of electronic and thermal Energies=        -362.092990
Sum of electronic and thermal Enthalpies=      -362.092046
Sum of electronic and thermal Free Energies=   -362.140428
```

**Table S64.** Geometry optimized for [Pt₄] (triplet) computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.ᵃ



---

| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Pt1 | 0.009231 | 0.016437 | -1.581504 | -0.093861 | 0.624393 |
| Pt2 | 1.487076 | 0.499599 | 0.539706 | 0.032194 | 0.457629 |
| Pt3 | -0.309863 | -1.546171 | 0.511132 | 0.029994 | 0.459661 |
| Pt4 | -1.186443 | 1.030134 | 0.530666 | 0.031674 | 0.458318 |

---

ᵃPart of the Gaussian output file:

SCF Done:  E(UM06) =  -477.412674205     A.U. after   23 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0240,   after    2.0003

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000125 | 0.000450 | YES |
| RMS    Force | 0.000068 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 57.0764 | 60.0329 | 126.1458 |
| Red. masses -- | 194.9648 | 194.9648 | 194.9648 |
| Frc consts  -- | 0.3742 | 0.4140 | 1.8279 |
| IR Inten   -- | 0.0054 | 0.0038 | 0.0003 |

**Table S65.** Geometry optimized for [Pt$_5$] (triplet) computed at the M06 level of DFT using SDD(Pt) basis set in vacuo.[a]
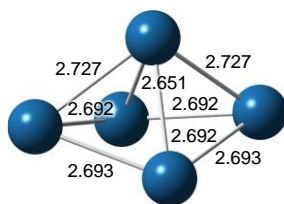


| Atom Label | X in angstrom | Y in angstrom | Z in angstrom | Mulliken Charge | Spin Density |
|---|---|---|---|---|---|
| Pt1 | 0.000035 | 1.458268 | 0.673682 | 0.040690 | 0.382949 |
| Pt2 | -2.187471 | 0.000935 | 0.091261 | 0.021538 | 0.311228 |
| Pt3 | 2.187098 | 0.000951 | 0.091443 | 0.021451 | 0.311848 |
| Pt4 | 0.000059 | -1.455097 | 0.680610 | 0.040679 | 0.382330 |
| Pt5 | 0.000279 | -0.005057 | -1.536997 | -0.124358 | 0.611644 |

[a]Part of the Gaussian output file:

SCF Done:  E(UM06) = -596.784114941     A.U. after   29 cycles
Annihilation of the first spin contaminant:
S**2 before annihilation    2.0403,   after     2.0009

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000121 | 0.000450 | YES |
| RMS    Force | 0.000071 | 0.000300 | YES |

|  | 1 | 2 | 3 |
|---|---|---|---|
|  | A | A | A |
| Frequencies -- | 43.4295 | 73.8195 | 76.2746 |
| Red. masses -- | 194.9648 | 194.9648 | 194.9648 |
| Frc consts  -- | 0.2167 | 0.6260 | 0.6683 |
| IR Inten   -- | 0.0182 | 0.0266 | 0.3486 |

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