Supporting Information for

Filtration of the preferred catalyst for reverse water-gas shift among the Rh_n^- (n = 3–11) clusters by mass spectrometry under variable temperatures

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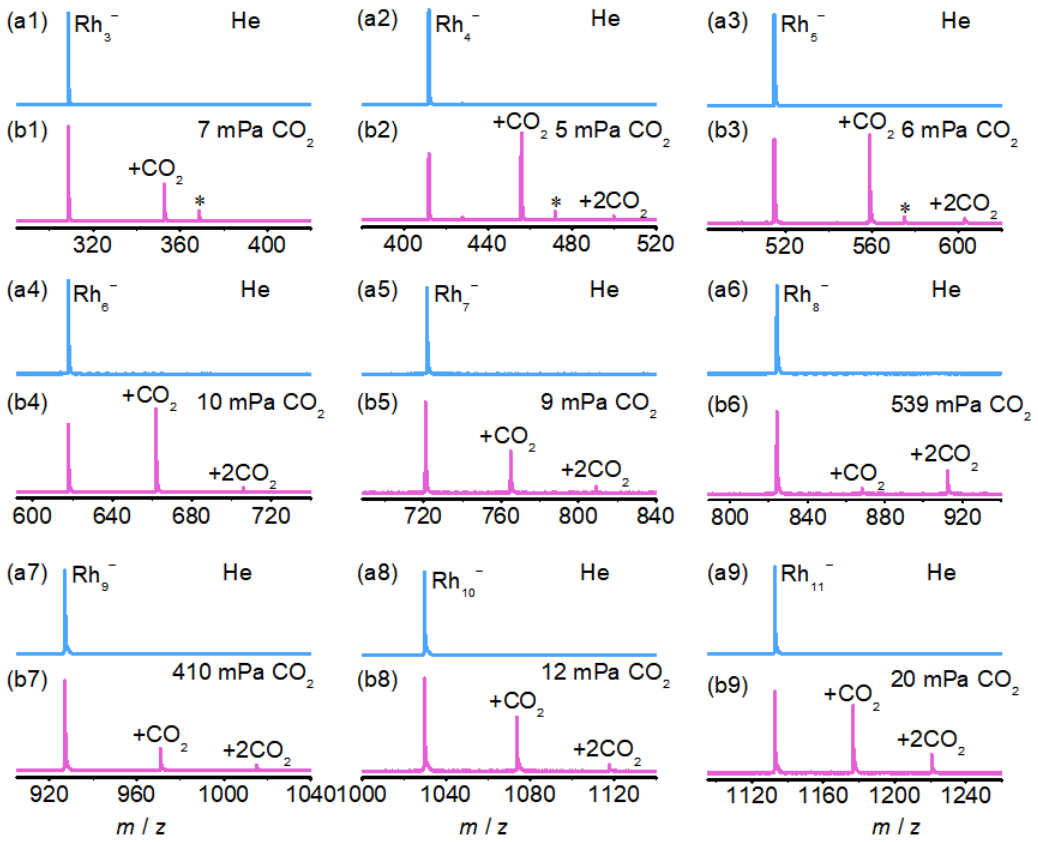

Fig. S1 The time-of-flight (TOF) mass spectra for the reactions of mass-selected Rh_n^- (n = 3–11) clusters (a) with CO_2 (b) at 298 K. The reactant pressures are given in mPa (= 10^{-3} Pa). The reaction times are 1.8 ms for Rh_n^- (n = 3–7, 9–11) + CO_2 and 3.8 ms for Rh_8^- + CO_2. The Rh_nX^- (X = CO_2 and $2CO_2$) species are labeled as +X. The signals marked with asterisks are $ORh_nCO_2^-$ (n = 3–5) ($Rh_nCO_2^-$ + CO_2 → $ORh_nCO_2^-$ + CO).

Note that in the temperature-variable experiments, molecule density of reactants (CO_2 and H_2) was used, while for the reactions performed under the same temperature, reactant pressure (in Pa or mPa) was used in this paper.

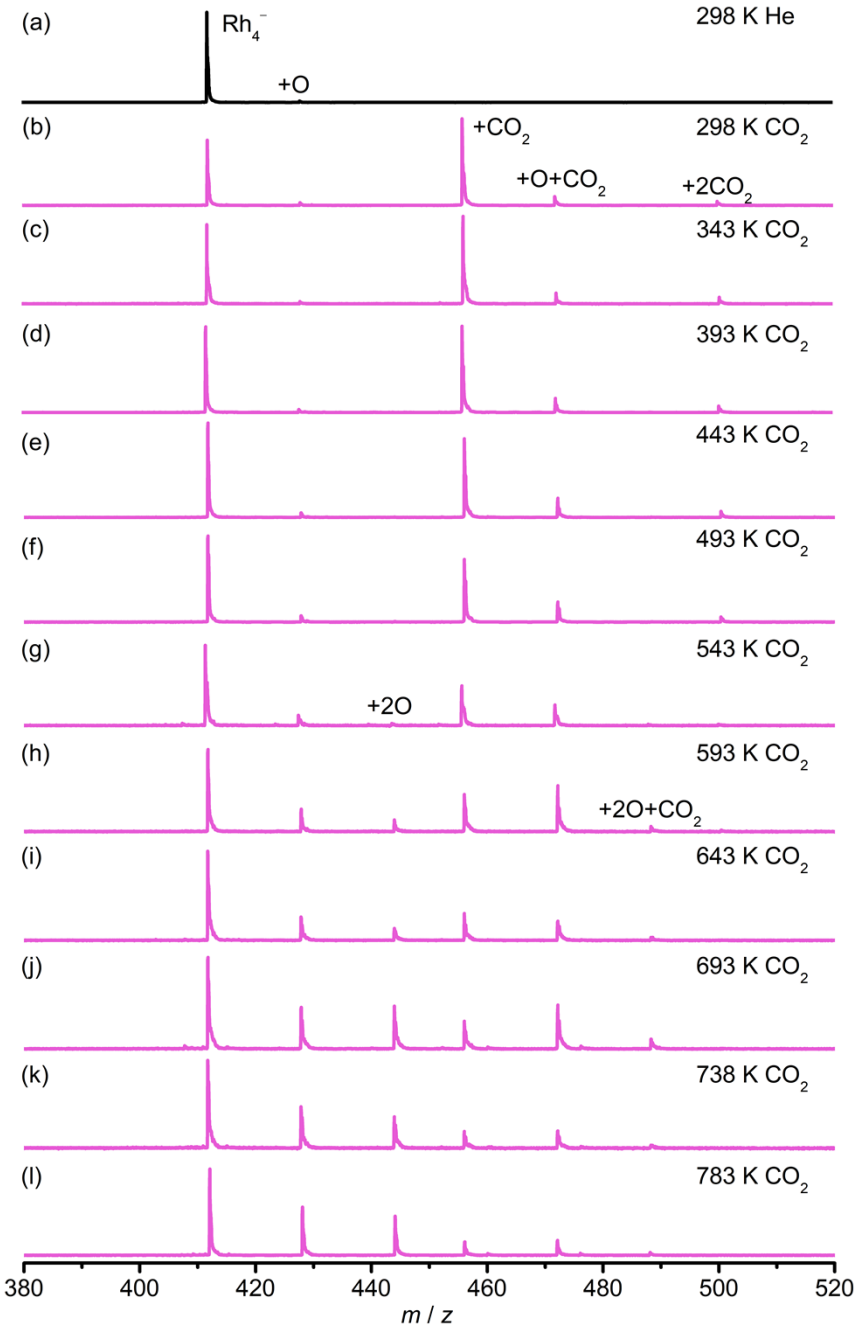

Fig. S2 The TOF mass spectra for the reactions of mass-selected Rh_4^- clusters with He at 298 K (a) and CO_2 at 298 K (b), 343 K (c), 393 K (d), 443 K (e), 493 K (f), 543 K (g), 593 K (h), 643 K (i), 693 K (j), 738 K (k), and 783 K (l). The maximum molecule density of CO_2 is about 1.8×10^{12} (b), 1.4×10^{12} (c), 1.9×10^{12} (d), 2.4×10^{12} (e), 3.5×10^{12} (f), 8.7×10^{12} (g), 16×10^{12} (h), 15×10^{12} (i), 23×10^{12} (j), 22×10^{12} (k), and 50×10^{12} molecules cm^{-3} (l). The Rh_4X^- (X = O, CO_2, etc) species are labeled as +X.

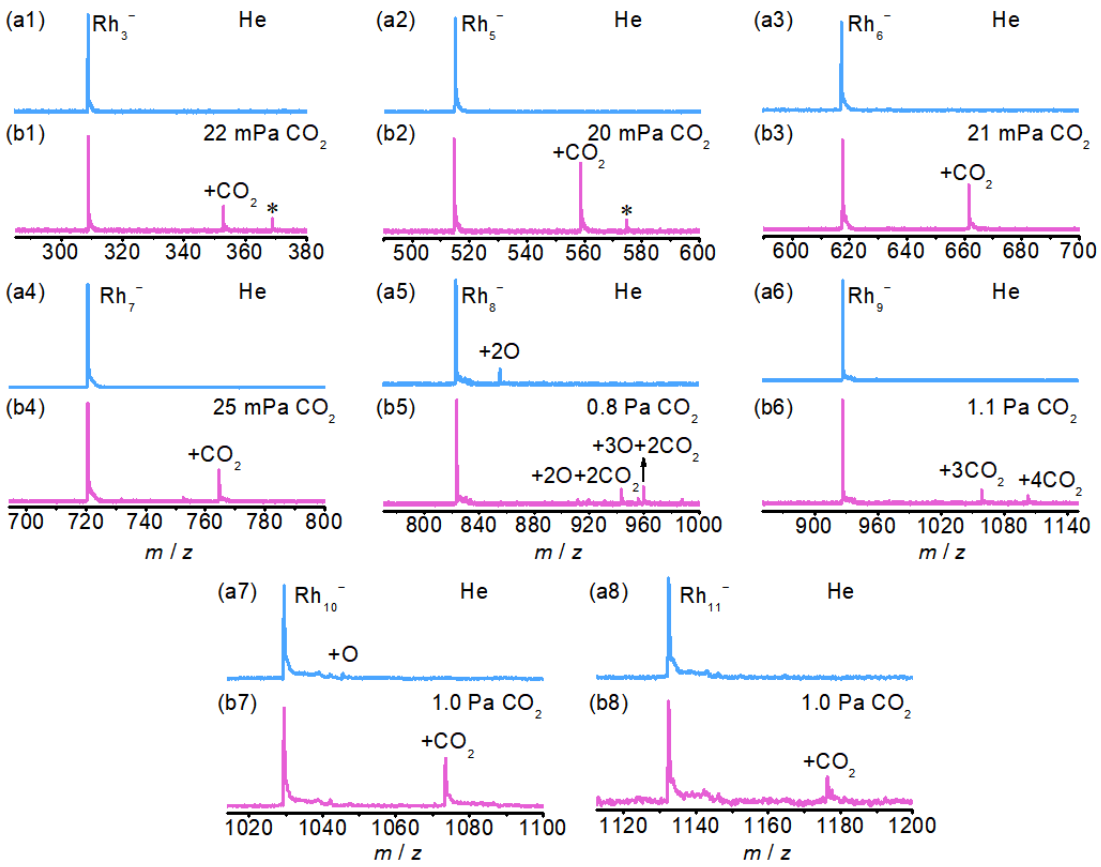

Fig. S3 The TOF mass spectra for the reactions of mass-selected Rh_n^- (n = 3, 5–11) clusters with He (a) and CO_2 (b) at 443 K. The reactant pressures are given in mPa (= 10^{-3} Pa) or Pa. The Rh_nX^- (X = O, CO_2, etc) species are labeled as +X. The signals marked with asterisks are $ORh_nCO_2^-$ (n = 3, 5) ($Rh_nCO_2^- + CO_2 \rightarrow ORh_nCO_2^- + CO$).

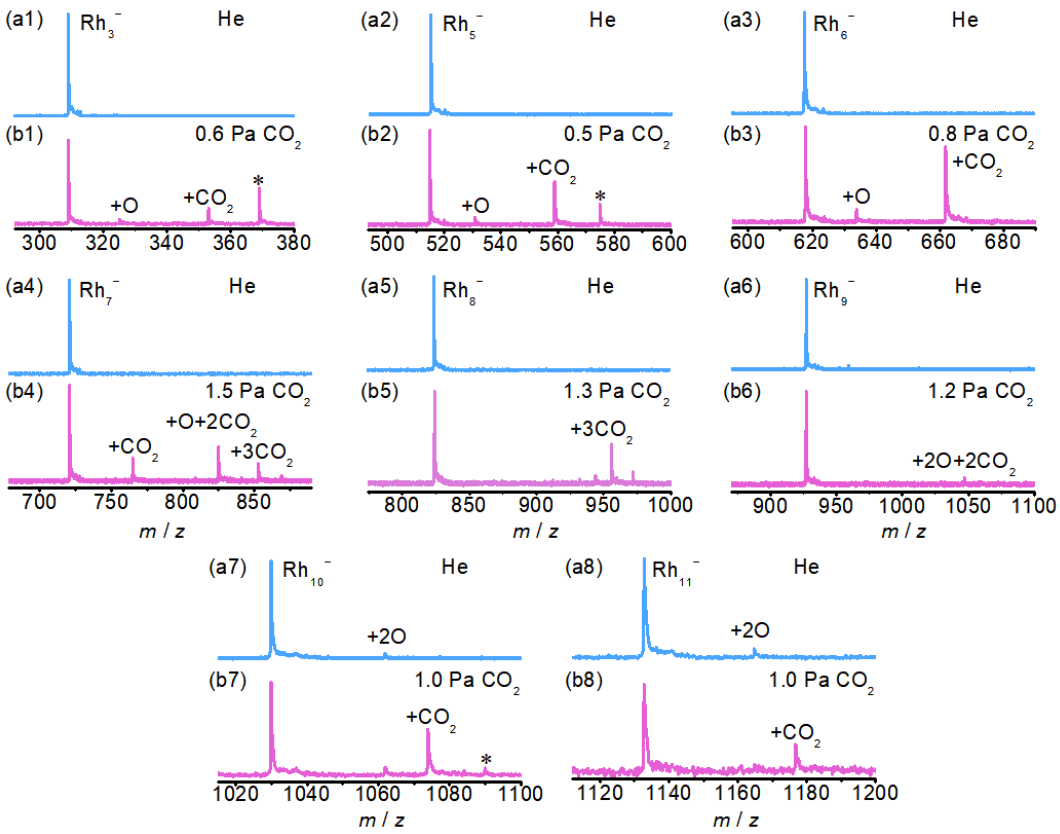

Fig. S4 The TOF mass spectra for the reactions of mass-selected Rh_n^- (n = 3, 5–11) clusters with He (a) and CO_2 (b) at 593 K. The reactant pressures are given in Pa. The Rh_nX^- (X = O, CO_2, etc) species are labeled as +X. The signals marked with asterisks are $ORh_nCO_2^-$ (n = 3, 5, and 10) ($Rh_nCO_2^-$ + $CO_2 \rightarrow ORh_nCO_2^-$ + CO).

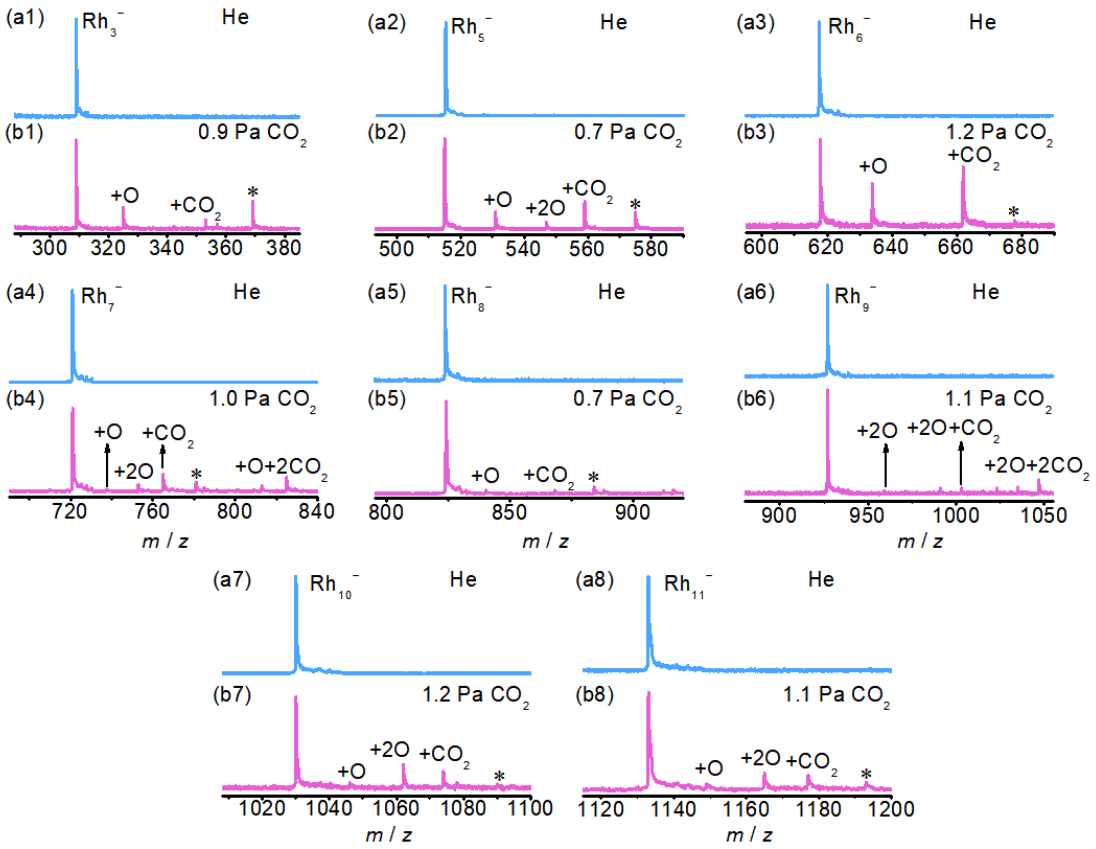

Fig. S5 The TOF mass spectra for the reactions of mass-selected Rh_n^- (n = 3, 5–11) clusters with He (a) and CO_2 (b) at 693 K. The reactant pressures are given in Pa. The Rh_nX^- (X = O, CO_2, etc) species are labeled as +X. The signals marked with asterisks are $ORh_nCO_2^-$ (n = 3, 5–8, 10–11) ($Rh_nCO_2^-$ + $CO_2 \rightarrow ORh_nCO_2^-$ + CO).

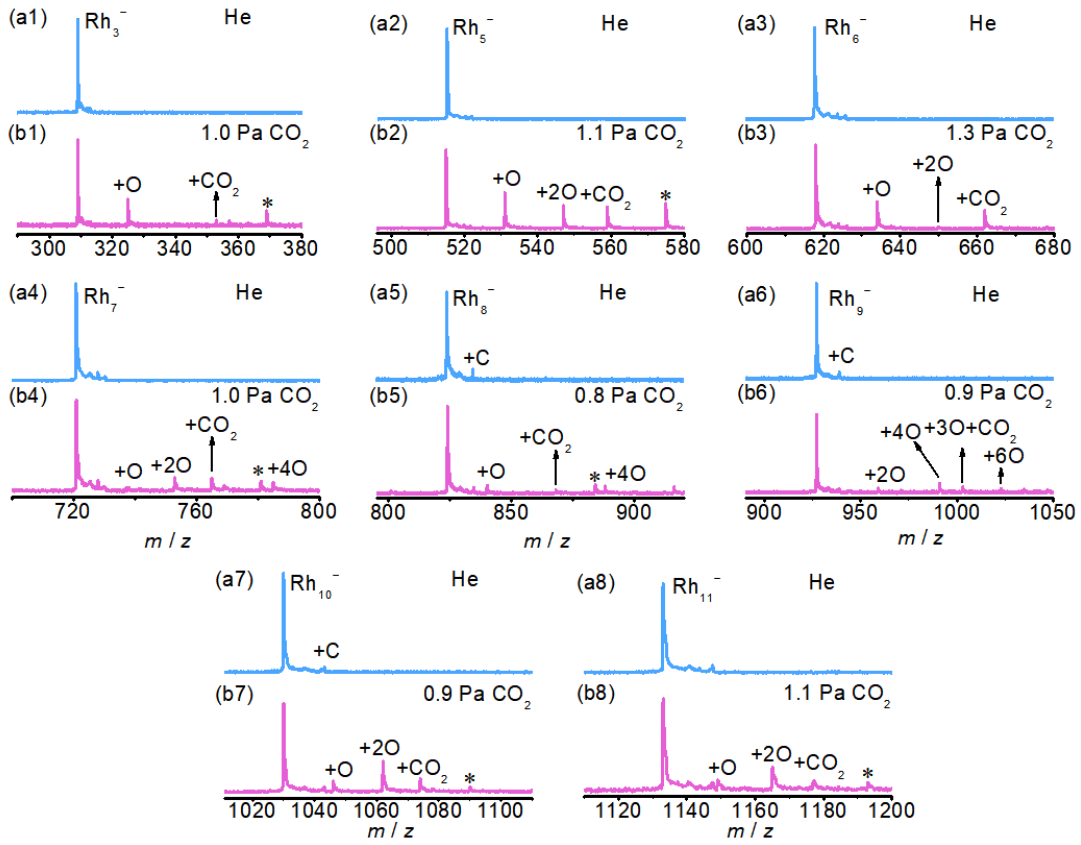

Fig. S6 The TOF mass spectra for the reactions of mass-selected Rh_n^- (n = 3, 5–11) clusters with He (a) and CO_2 (b) at 738 K. The reactant pressures are given in Pa. The Rh_nX^- (X = O, CO_2, etc) species are labeled as +X. The signals marked with asterisks are $ORh_nCO_2^-$ (n = 3, 5, 7–8, 10–11) ($Rh_nCO_2^-$ + CO_2 → $ORh_nCO_2^-$ + CO).

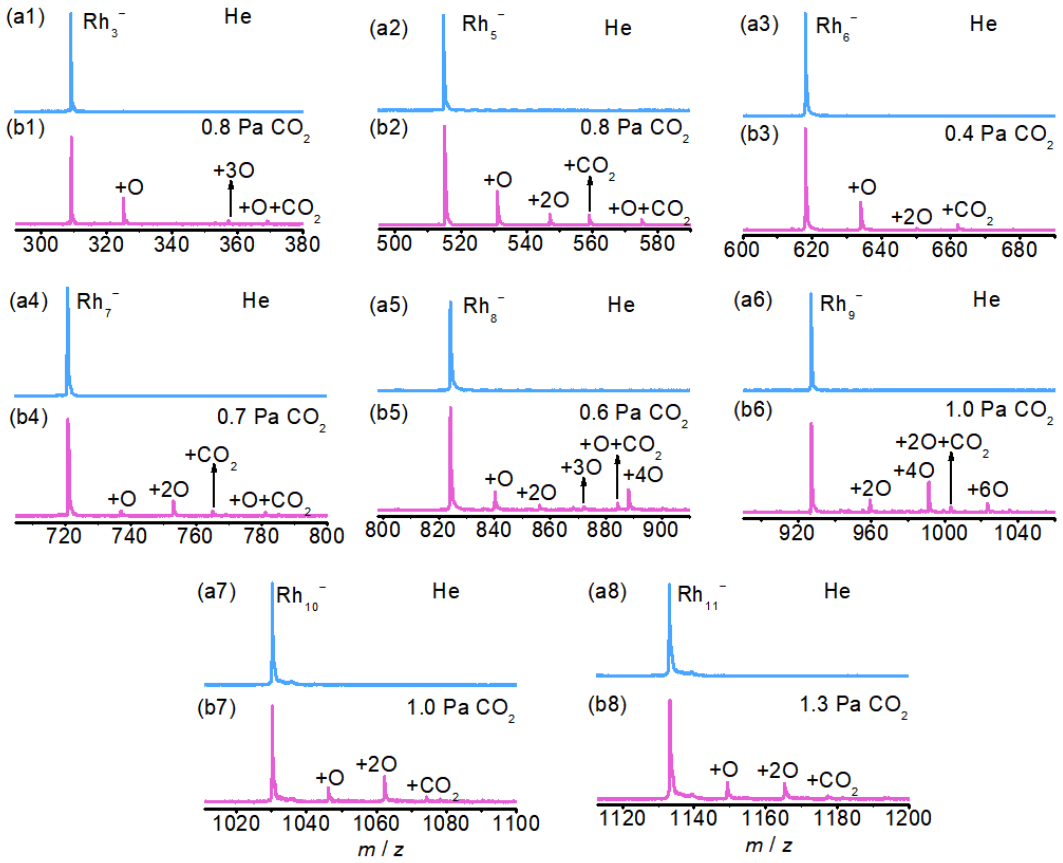

Fig. S7 The TOF mass spectra for the reactions of mass-selected Rh_n^- (n = 3, 5–11) clusters with He (a) and CO_2 (b) at 783 K. The reactant pressures are given in Pa. The Rh_nX^- (X = O, CO_2, etc) species are labeled as +X.

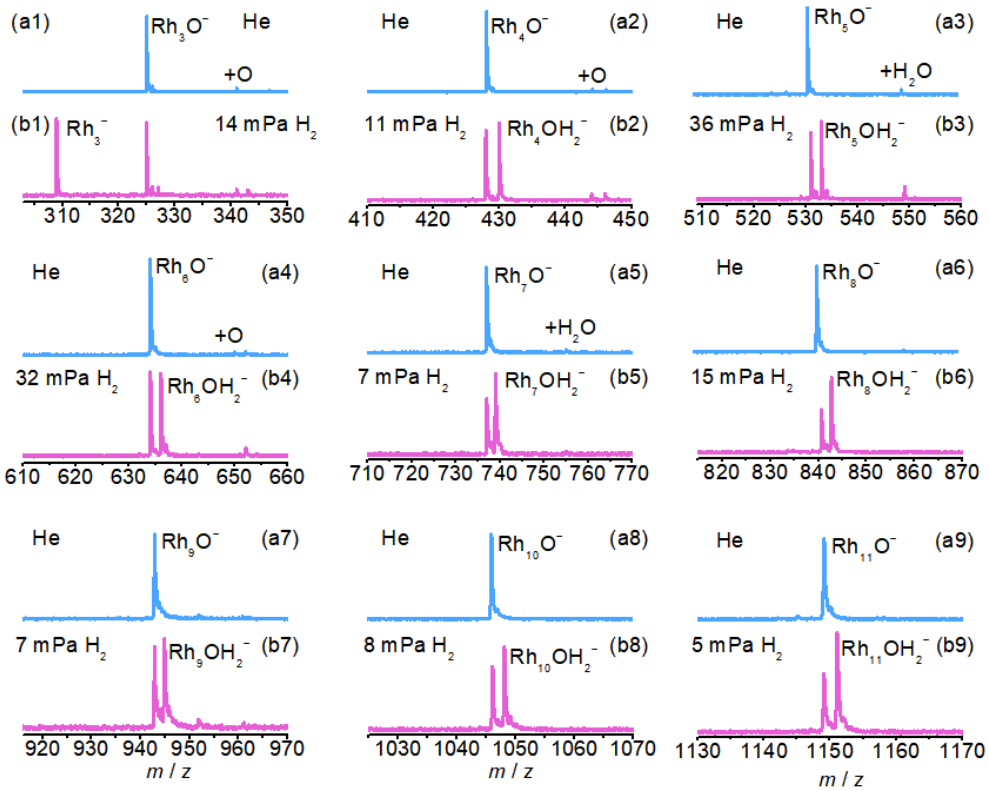

Fig. S8 The TOF mass spectra for the reactions of mass-selected Rh_nO^- (n = 3–11) clusters with He (a) and H_2 (b) at 298 K. The reactant pressures are given in mPa (= 10^{-3} Pa). The Rh_nOX^- (X = O and H_2O) species are labeled as +X.

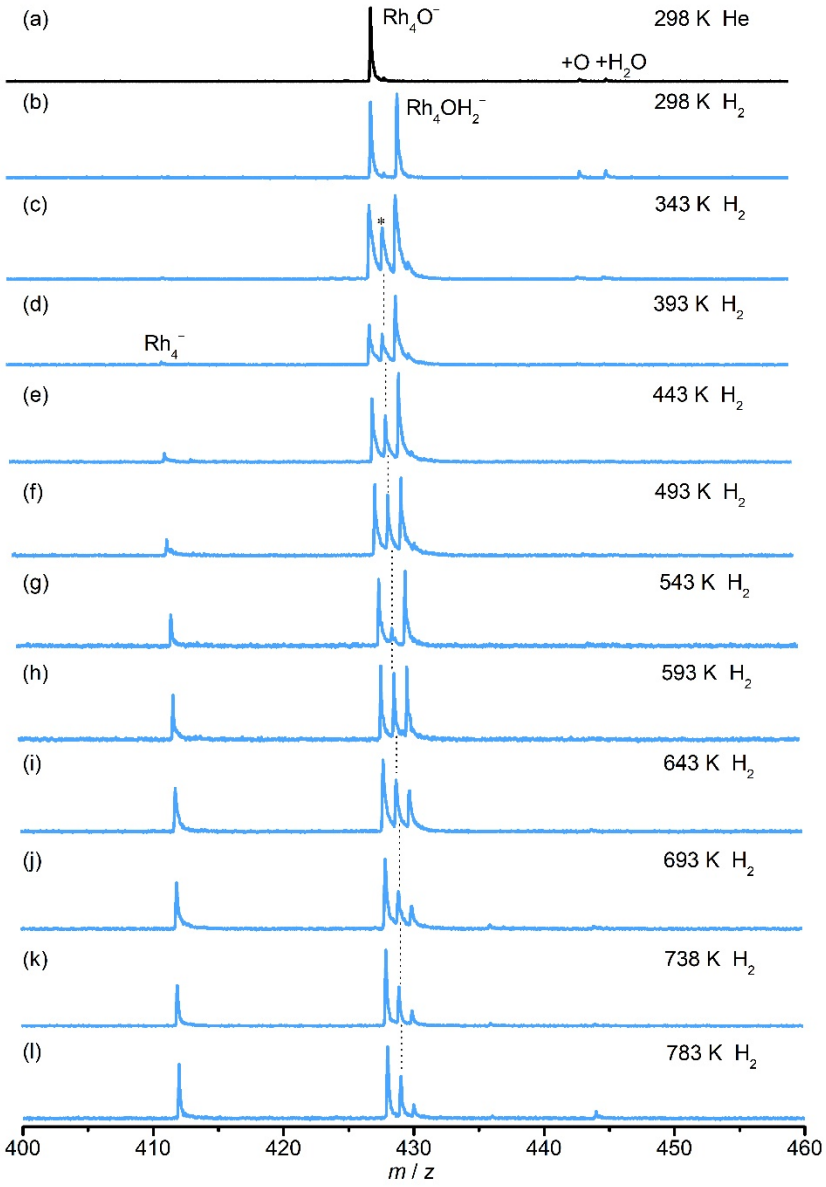

Fig. S9 The TOF mass spectra for the reactions of mass-selected Rh_4O^- with He at 298 K (a), H_2 at 298 K (b), 343 K (c), 393 K (d), 443 K (e), 493 K (f), 543 K (g), 593 K (h), 643 K (i), 693 K (j), 738 K (k), and 783 K (l). The maximum molecule density of H_2 is about 3.5×10^{12} (b), 3.8×10^{12} (c), 8.5×10^{12} (d), 10×10^{12} (e), 11×10^{12} (f), 18×10^{12} (g), 19×10^{12} (h), 17×10^{12} (i), 23×10^{12} (j), 19×10^{12} (k), and 30×10^{12} molecules cm^{-3} (l). Peaks marked with asterisk is Rh_4OH^-. The Rh_4OX^- (X = O and H_2O) species are labeled as +X.

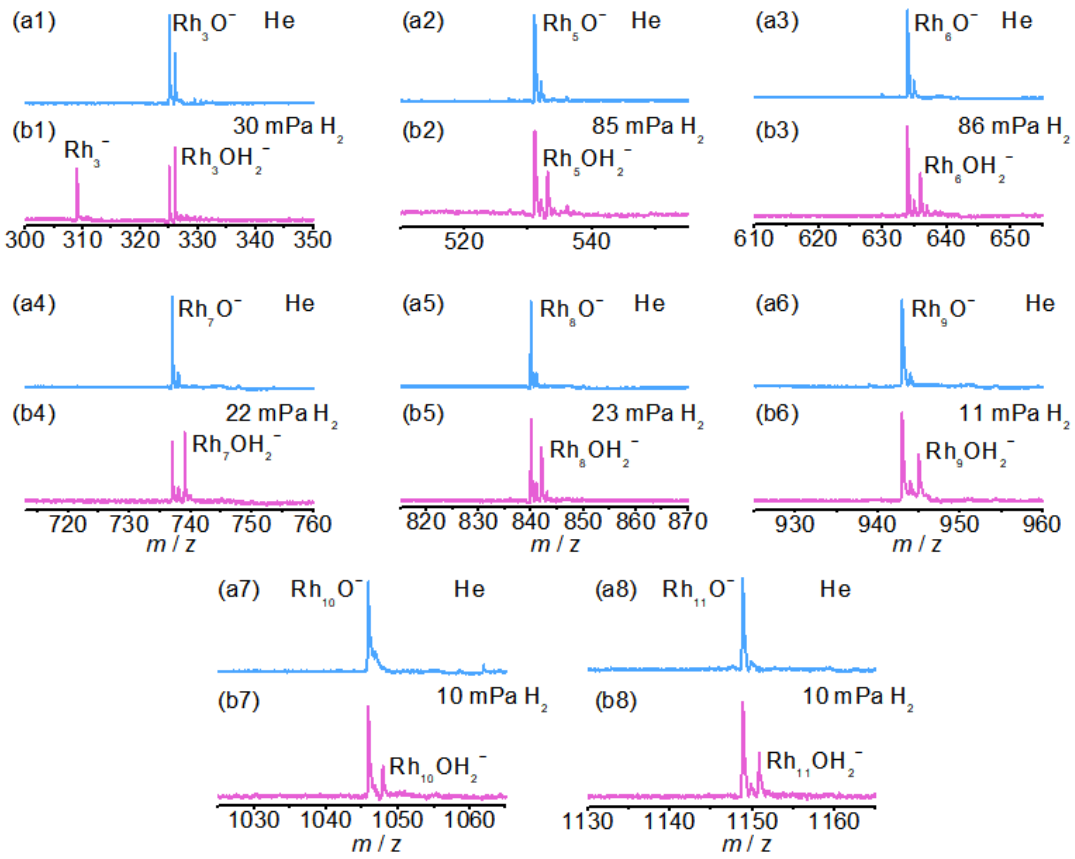

Fig. S10 The TOF mass spectra for the reactions of mass-selected Rh_nO^- (n = 3, 5–11) clusters with He (a) and H_2 (b) at 443 K. The reactant pressures are given in mPa (= 10^{-3} Pa).

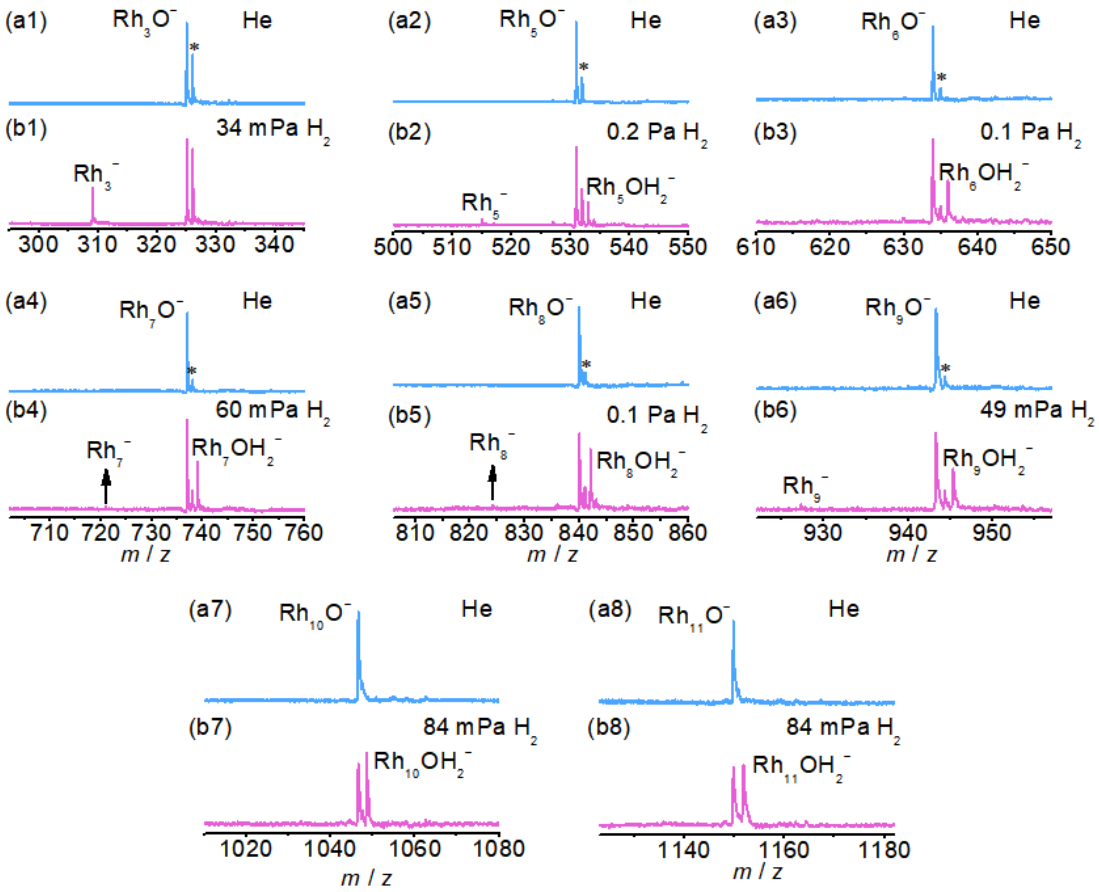

Fig. S11 The TOF mass spectra for the reactions of mass-selected Rh_nO^- (n = 3, 5–11) clusters with He (a) and H_2 (b) at 543 K. The reactant pressures are given in mPa (= 10^{-3} Pa) or Pa. Peaks marked with asterisks are Rh_nOH^-.

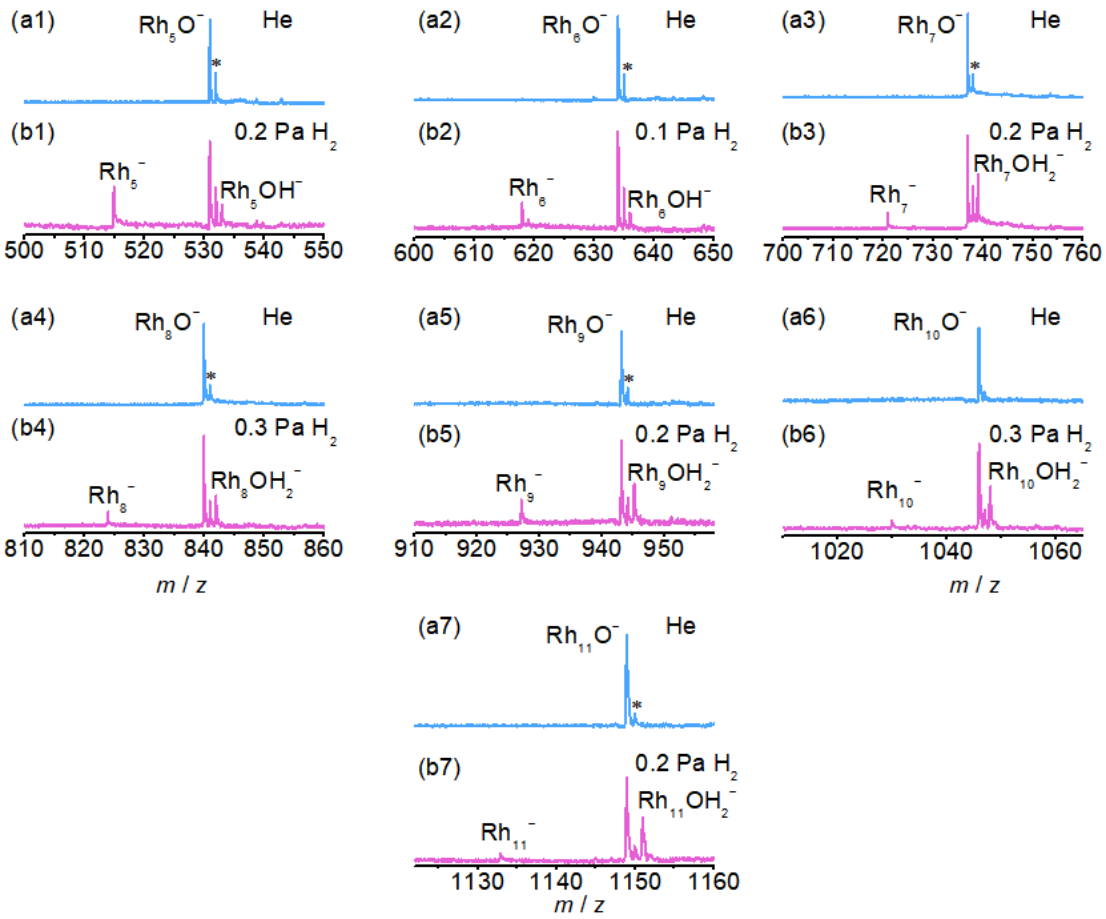

Fig. S12 The TOF mass spectra for the reactions of mass-selected Rh_nO^- (n = 5–11) clusters with He (a) and H_2 (b) at 643 K. The reactant pressures are given in Pa. Peaks marked with asterisks are Rh_nOH^-.

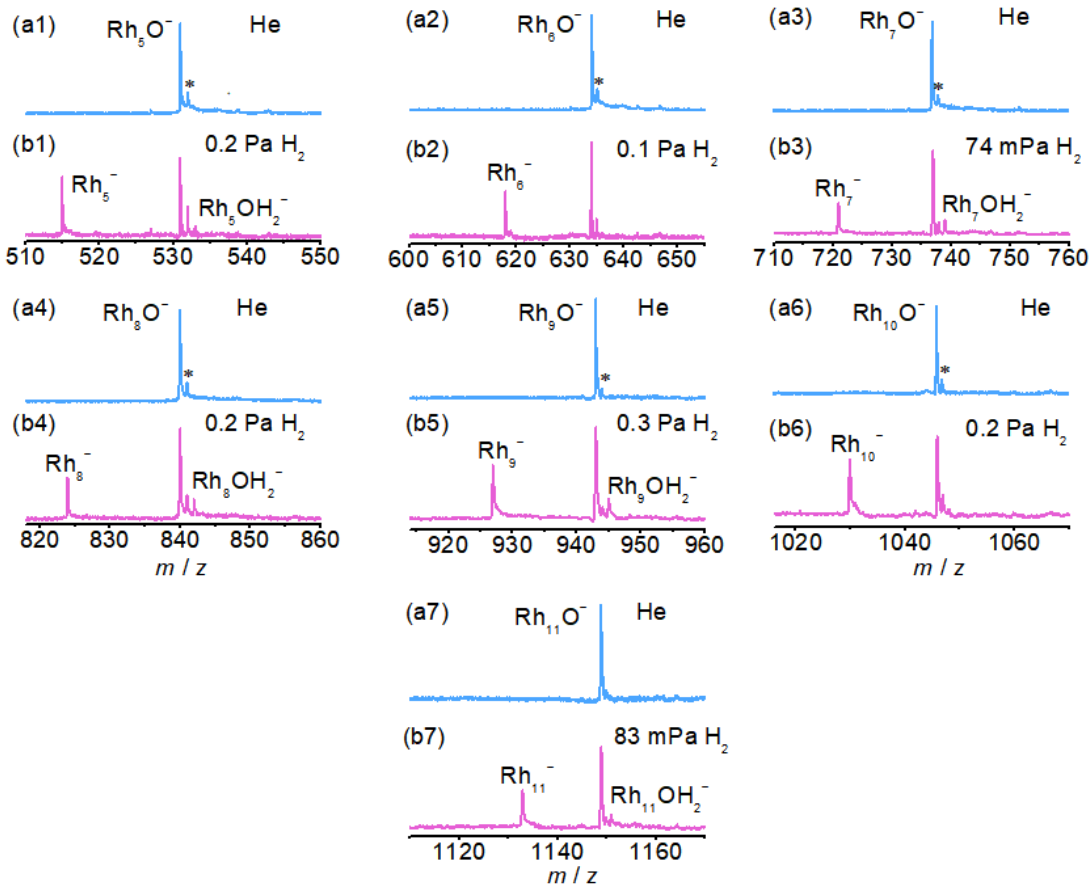

Fig. S13 The TOF mass spectra for the reactions of mass-selected Rh_nO^- (n = 5–11) clusters with He (a) and H_2 (b) at 693 K. The reactant pressures are given in mPa (= 10^{-3} Pa) or Pa. Peaks marked with asterisks are Rh_nOH^-.

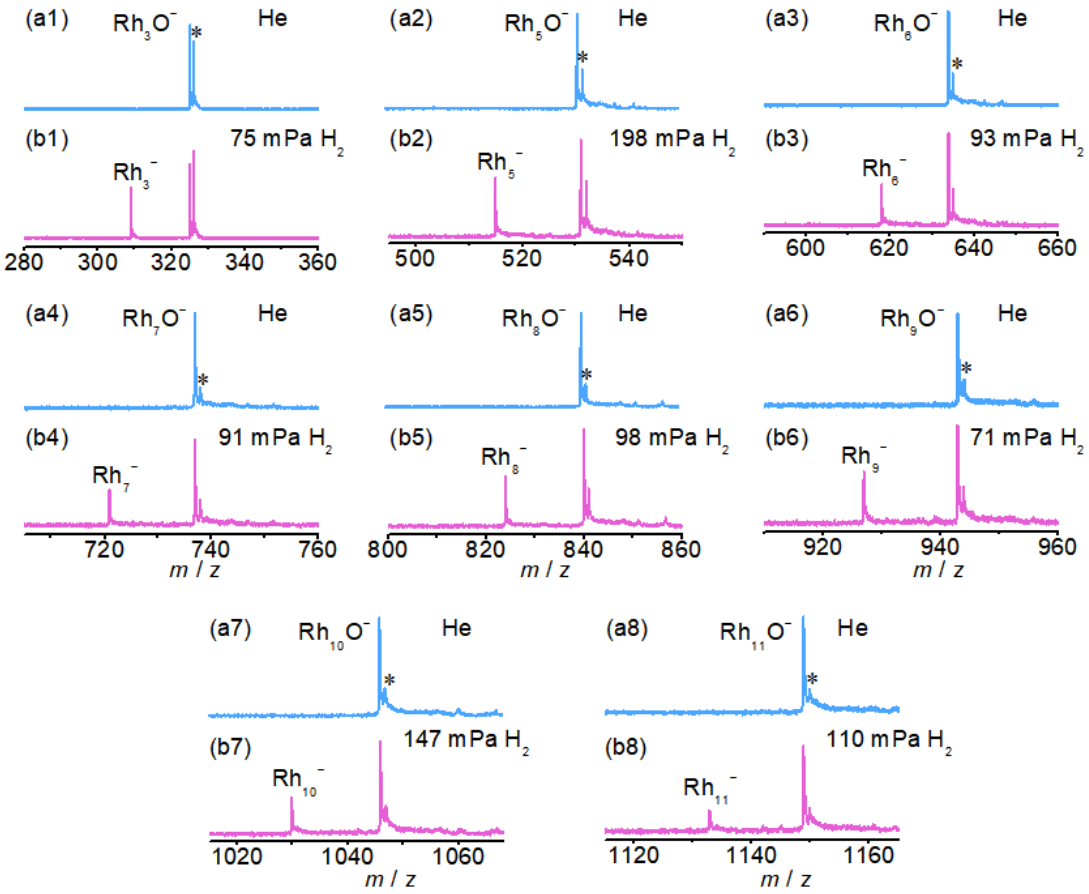

Fig. S14 The TOF mass spectra for the reactions of mass-selected Rh_nO^- (n = 3, 5–11) clusters with He (a) and H_2 (b) at 783 K. The reactant pressures are given in mPa (= 10^{-3} Pa). Peaks marked with asterisks are Rh_nOH^-.

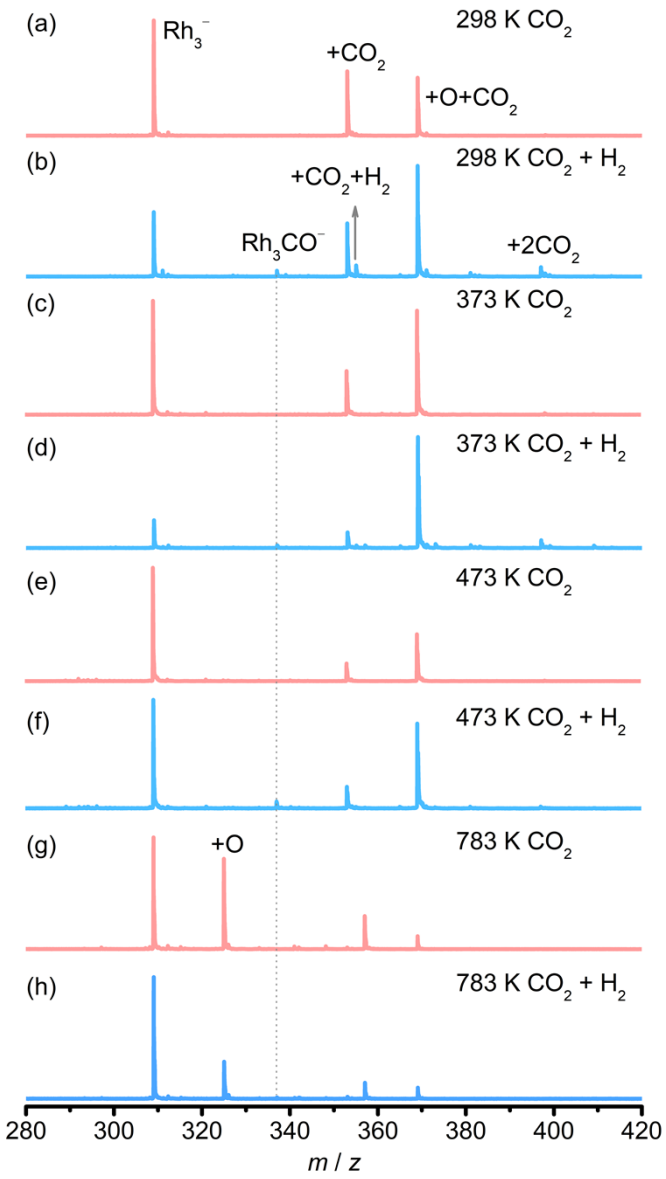

Fig. S15 The TOF mass spectra for the reactions of mass-selected Rh_3^- clusters with CO_2 at 298 K (a), 373 K (c), 473 K (e) and 783 K (g), with CO_2 + H_2 at 298 K (b), 373 K (d), 473 K (f) and 783 K (h) in the single ion trap experiment in which CO_2 and H_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 3.0×10^{12} (a), 1.9×10^{12} (c), 3.1×10^{12} (e), 13×10^{12} (g) for CO_2 and 104×10^{12} (b), 70×10^{12} (d), 78×10^{12} (f), 6.7×10^{12} molecules cm^{-3} (h) for H_2. The Rh_3X^- (X = O, CO_2, etc) species are labeled as +X.

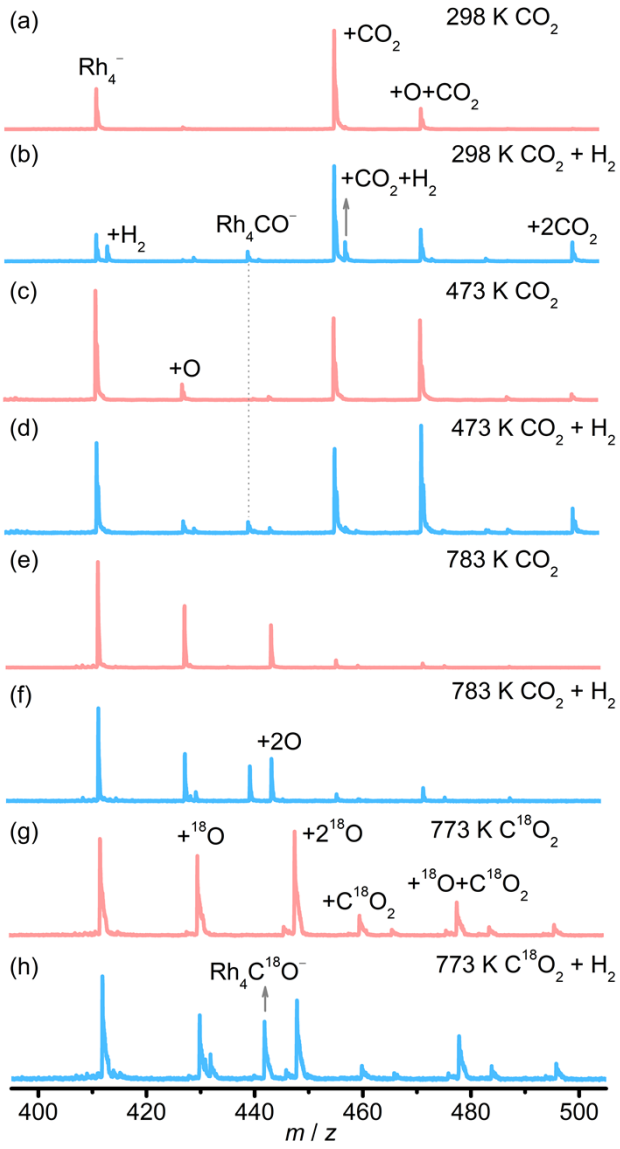

Fig. S16 The TOF mass spectra for the reactions of mass-selected Rh_4^- clusters with CO_2 at 298 K (a), 473 K (c), 783 K (e) and with $C^{18}O_2$ at 773 K (g), with $CO_2 + H_2$ at 298 K (b), 473 K (d), 783 K (f), and with $C^{18}O_2 + H_2$ at 773 K (h) in the single ion trap experiment in which CO_2 and H_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 1.4×10^{12} (a), 1.5×10^{12} (c), 1.7×10^{12} (e) for CO_2, 19×10^{12} (g) for $C^{18}O_2$, and 45×10^{12} (b), 14×10^{12} (d), 17×10^{12} (f), 36×10^{12} molecules cm^{-3} (h) for H_2. The Rh_4X^- (X = O, CO_2, etc) species are labeled as +X.

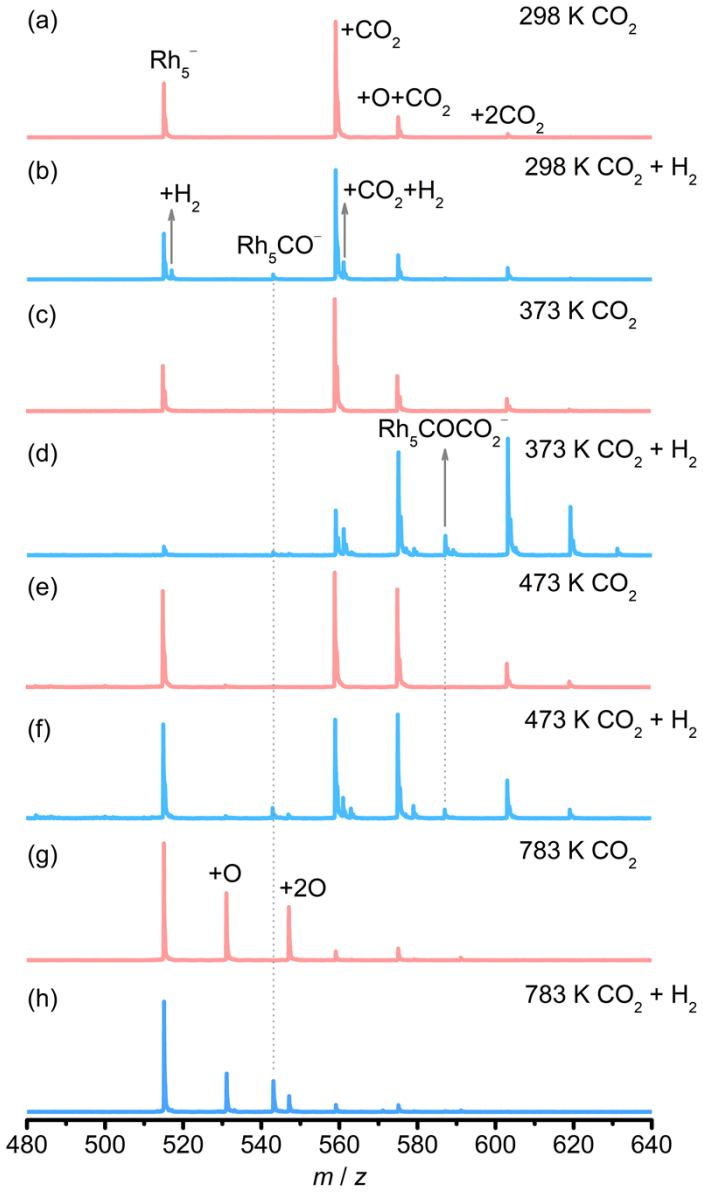

Fig. S17 The TOF mass spectra for the reactions of mass-selected Rh_5^- clusters with CO_2 at 298 K (a), 373 K (c), 473 K (e) and 783 K (g), with CO_2 + H_2 at 298 K (b), 373 K (d), 473 K (f) and 783 K (h) in the single ion trap experiment in which CO_2 and H_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 2.0×10^{12} (a), 2.4×10^{12} (c), 2.4×10^{12} (e), 12×10^{12} (g) for CO_2 and 21×10^{12} (b), 9.5×10^{12} (d), 12×10^{12} (f), 55×10^{12} molecules cm^{-3} (h) for H_2. The Rh_5X^- (X = O, CO_2, etc) species are labeled as +X.

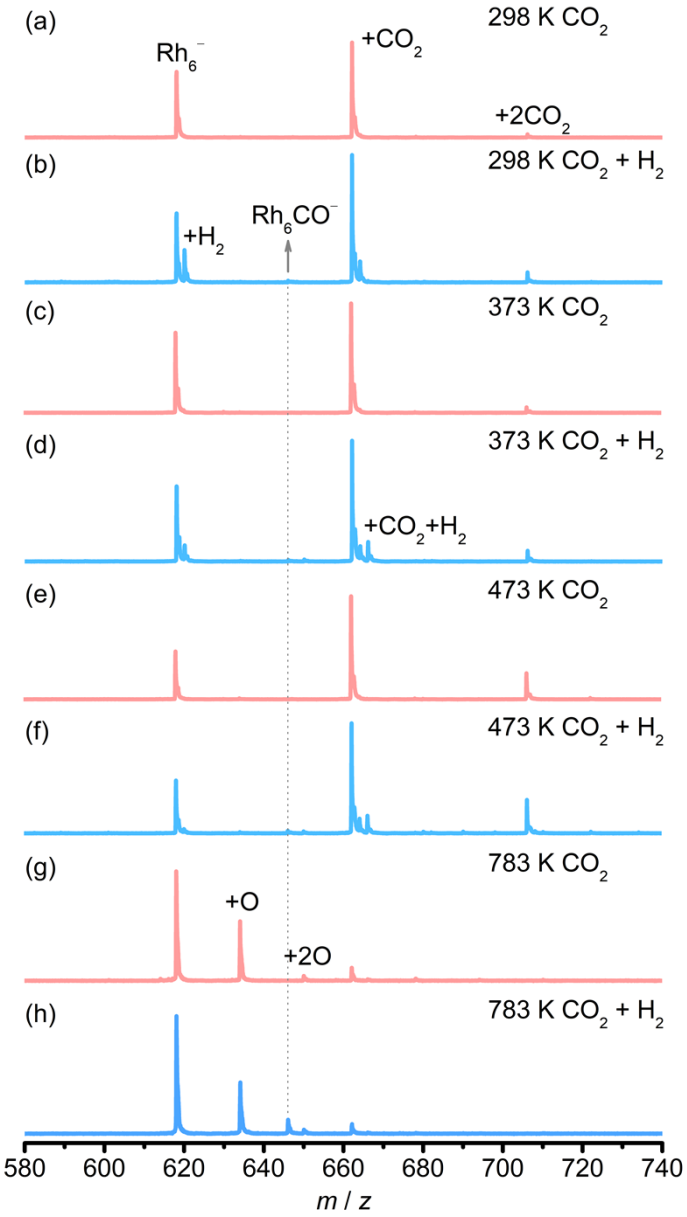

Fig. S18 The TOF mass spectra for the reactions of mass-selected Rh_6^- clusters with CO_2 at 298 K (a), 373 K (c), 473 K (e) and 783 K (g), with CO_2 + H_2 at 298 K (b), 373 K (d), 473 K (f) and 783 K (h) in the single ion trap experiment in which CO_2 and H_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 2.0×10^{12} (a), 2.3×10^{12} (c), 3.3×10^{12} (e), 35×10^{12} (g) for CO_2 and 28×10^{12} (b), 27×10^{12} (d), 12×10^{12} (f), 77×10^{12} molecules cm^{-3} (h) for H_2. The Rh_6X^- (X = O, CO_2, etc) species are labeled as +X.

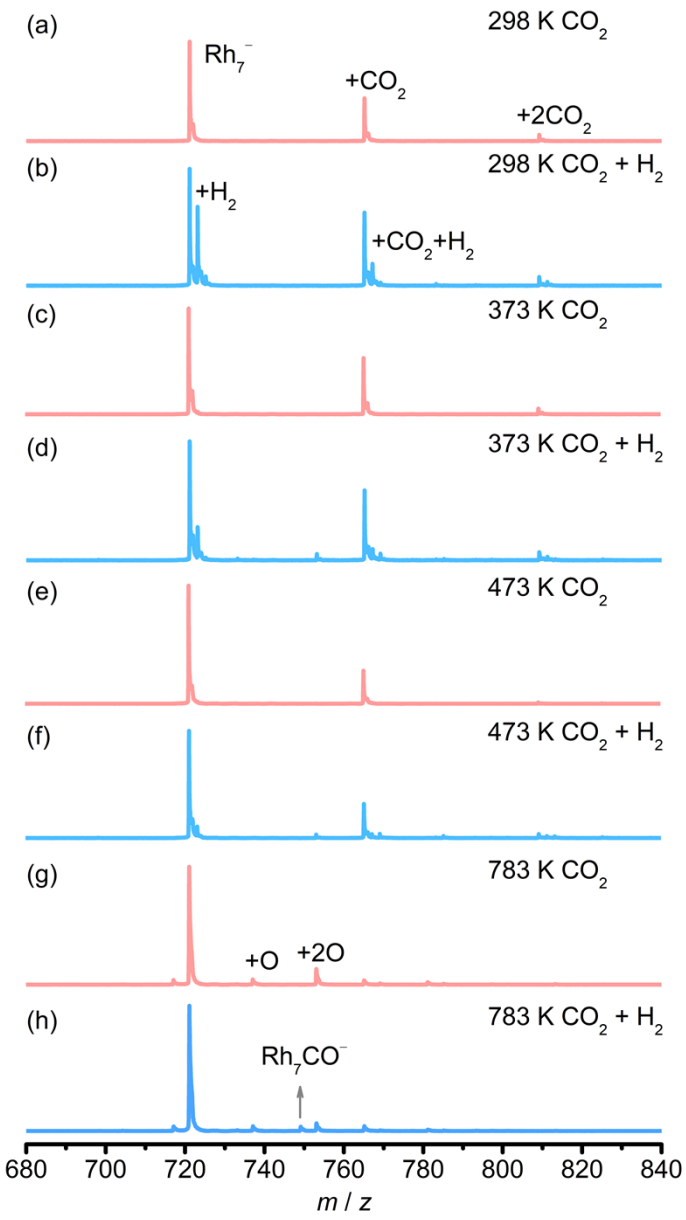

Fig. S19 The TOF mass spectra for the reactions of mass-selected Rh_7^- clusters with CO_2 at 298 K (a), 373 K (c), 473 K (e) and 783 K (g), with CO_2 + H_2 at 298 K (b), 373 K (d), 473 K (f) and 783 K (h) in the single ion trap experiment in which CO_2 and H_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 3.7×10^{12} (a), 5.3×10^{12} (c), 5.5×10^{12} (e), 49×10^{12} (g) for CO_2 and 14×10^{12} (b), 127×10^{12} (d), 9.4×10^{12} (f), 66×10^{12} molecules cm^{-3} (h) for H_2. The Rh_7X^- (X = O, CO_2, etc) species are labeled as +X.

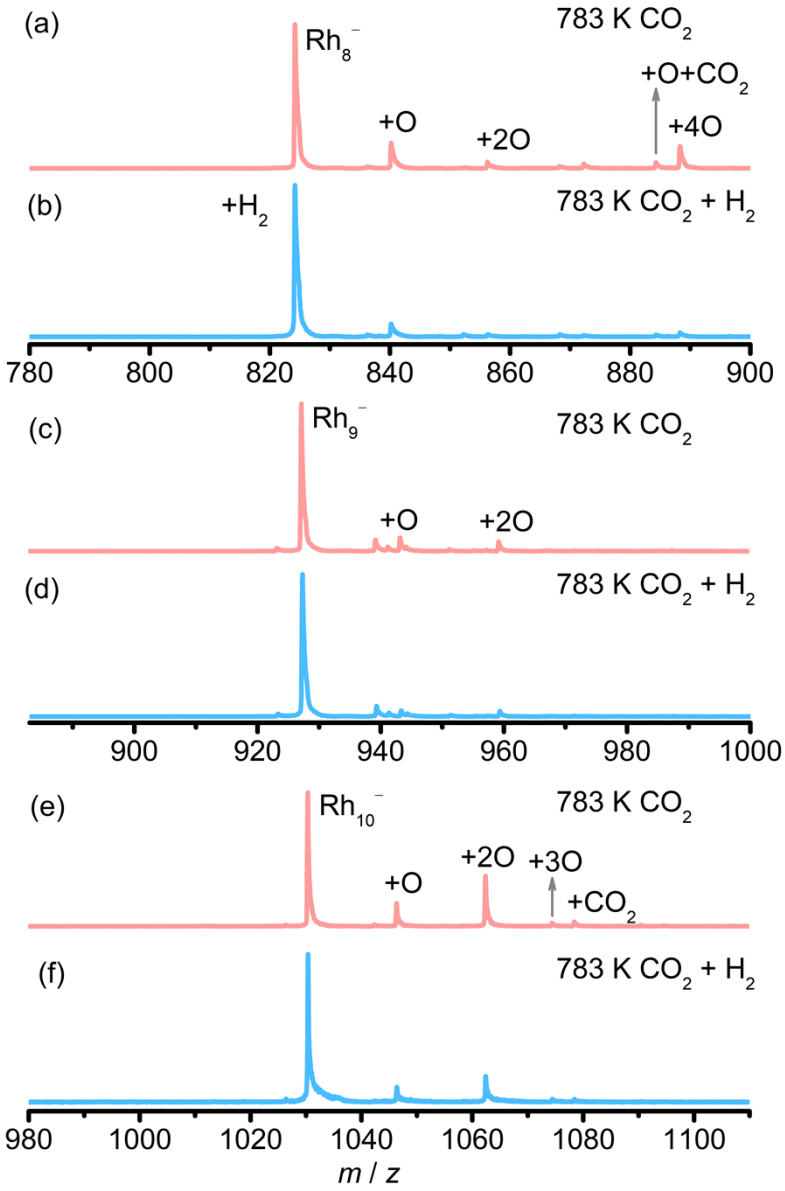

Fig. S20 The TOF mass spectra for the reactions of mass-selected Rh_8^- clusters with CO_2 at 783 K (a), with CO_2 + H_2 at 783 K (b), Rh_9^- clusters with CO_2 at 783 K (c), with CO_2 + H_2 at 783 K (d), and Rh_{10}^- clusters with CO_2 at 783 K (e), with CO_2 + H_2 at 783 K (f) in the single ion trap experiment in which CO_2 and H_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 50 × 10^{12} (a), 9.7 × 10^{12} (c), 49 × 10^{12} (e) for CO_2 and 71 × 10^{12} (b), 49 × 10^{12} (d), 82 × 10^{12} molecules cm^{-3} (f) for H_2. The Rh_nX^- (X = O, CO_2, etc) species are labeled as +X.

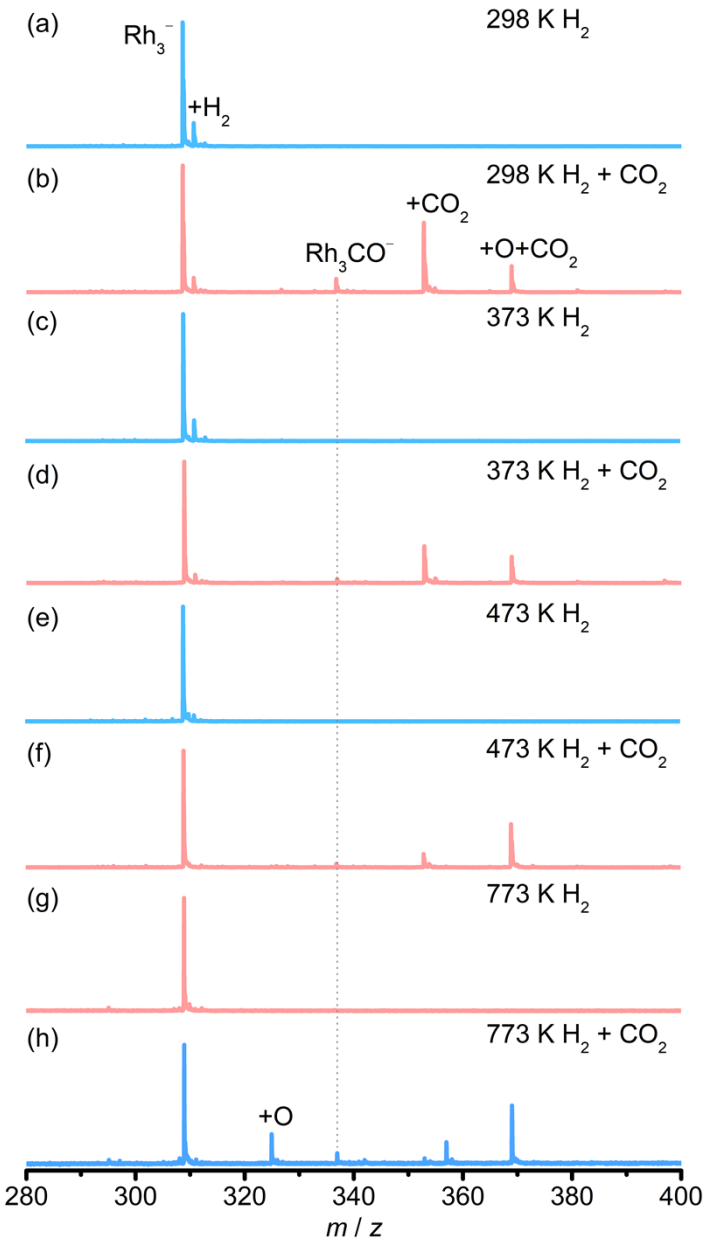

Fig. S21 The TOF mass spectra for the reactions of mass-selected Rh_3^- clusters with H_2 at 298 K (a), 373 K (c), 473 K (e) and 773 K (g), with H_2 + CO_2 at 298 K (b), 373 K (d), 473 K (f) and 773 K (h) in the single ion trap experiment in which H_2 and CO_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 16 × 10^{12} (a), 74 × 10^{12} (c), 65 × 10^{12} (e), 26 × 10^{12} (g) for H_2 and 2.5 × 10^{12} (b), 0.7 × 10^{12} (d), 0.9 × 10^{12} (f), 29 × 10^{12} molecules cm^{-3} (h) for CO_2. The Rh_3X^- (X = H_2, CO_2, etc) species are labeled as +X.

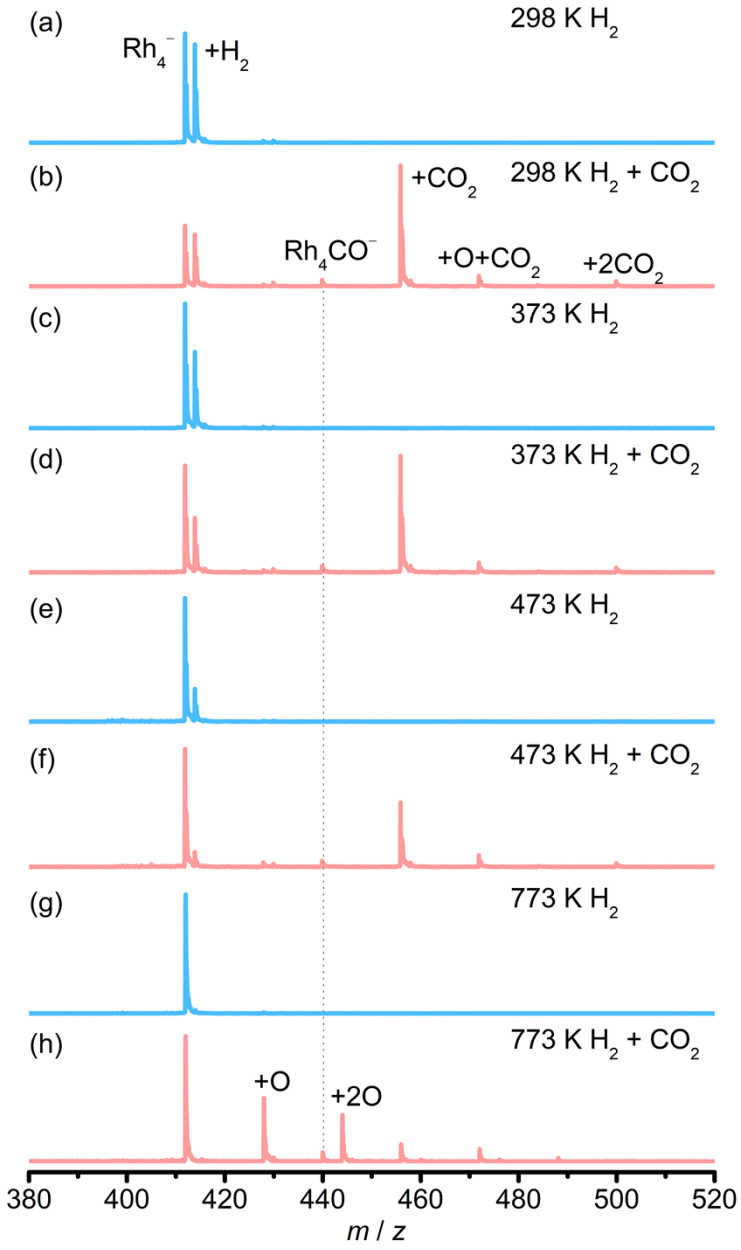

Fig. S22 The TOF mass spectra for the reactions of mass-selected Rh_4^- clusters with H_2 at 298 K (a), 373 K (c), 473 K (e) and 773 K (g), with H_2 + CO_2 at 298 K (b), 373 K (d), 473 K (f) and 773 K (h) in the single ion trap experiment in which H_2 and CO_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 28 × 10^{12} (a), 33 × 10^{12} (c), 39 × 10^{12} (e), 10 × 10^{12} (g) for H_2 and 1.2 × 10^{12} (b), 1.1 × 10^{12} (d), 0.7 × 10^{12} (f), 20 × 10^{12} molecules cm^{-3} (h) for CO_2. The Rh_4X^- (X = H_2, CO_2, etc) species are labeled as +X.

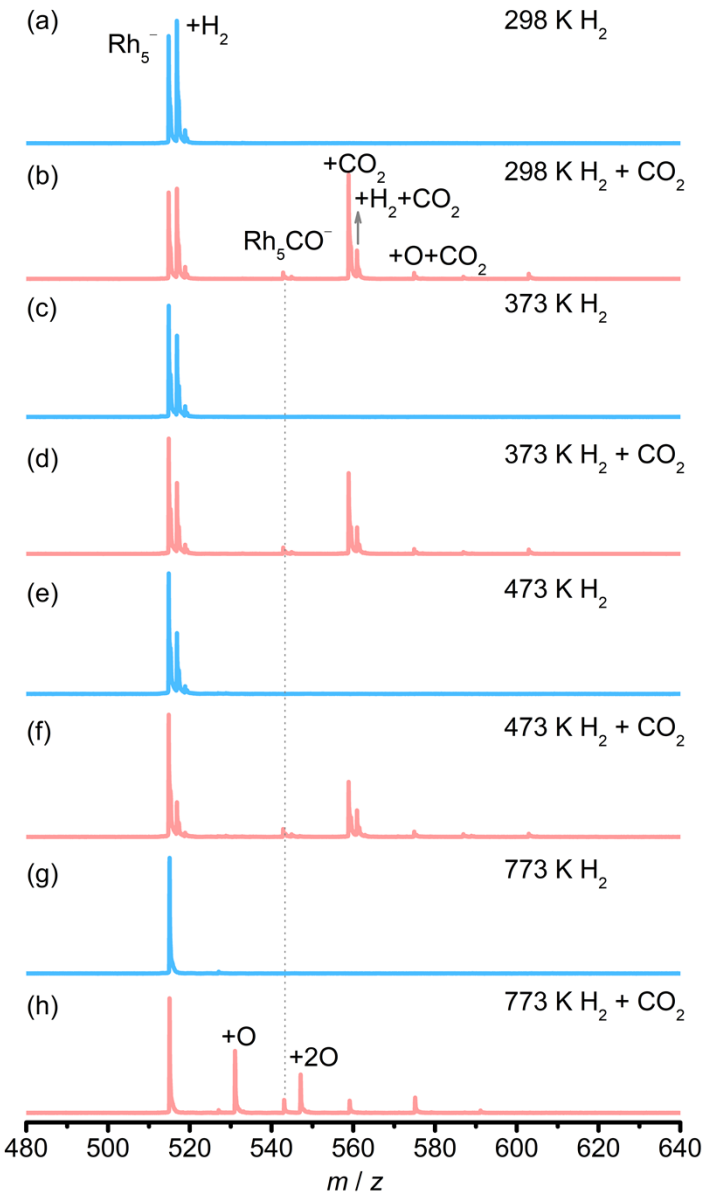

Fig. S23 The TOF mass spectra for the reactions of mass-selected Rh_5^- clusters with H_2 at 298 K (a), 373 K (c), 473 K (e) and 773 K (g), with H_2 + CO_2 at 298 K (b), 373 K (d), 473 K (f) and 773 K (h) in the single ion trap experiment in which H_2 and CO_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 24 × 10^{12} (a), 33 × 10^{12} (c), 68 × 10^{12} (e), 19 × 10^{12} (g) for H_2 and 0.2 × 10^{12} (b), 0.4 × 10^{12} (d), 0.7 × 10^{12} (f), 19 × 10^{12} molecules cm^{-3} (h) for CO_2. The Rh_5X^- (X = H_2, CO_2, etc) species are labeled as +X.

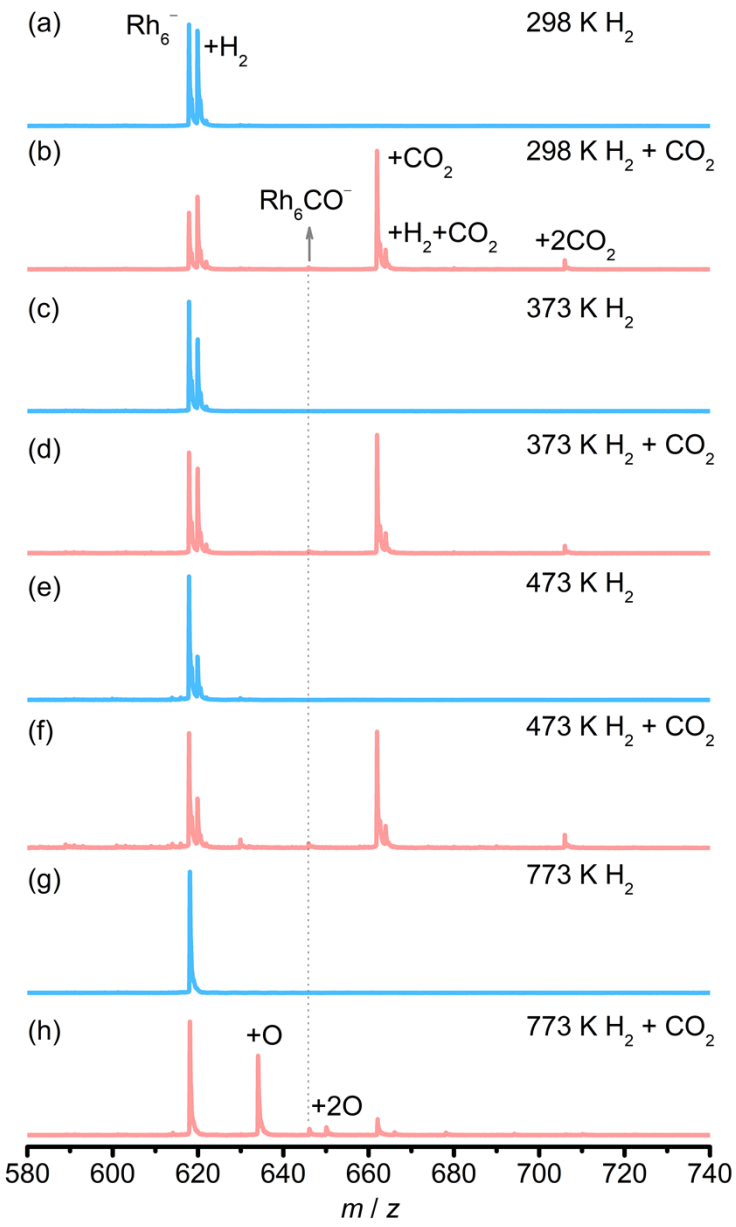

Fig. S24 The TOF mass spectra for the reactions of mass-selected Rh_6^- clusters with H_2 at 298 K (a), 373 K (c), 473 K (e) and 773 K (g), with H_2 + CO_2 at 298 K (b), 373 K (d), 473 K (f) and 773 K (h) in the single ion trap experiment in which H_2 and CO_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 16 × 10^{12} (a), 24 × 10^{12} (c), 44 × 10^{12} (e), 20 × 10^{12} (g) for H_2 and 0.8 × 10^{12} (b), 0.9 × 10^{12} (d), 2.2 × 10^{12} (f), 33 × 10^{12} molecules cm^{-3} (h) for CO_2. The Rh_6X^- (X = H_2, CO_2, etc) species are labeled as +X.

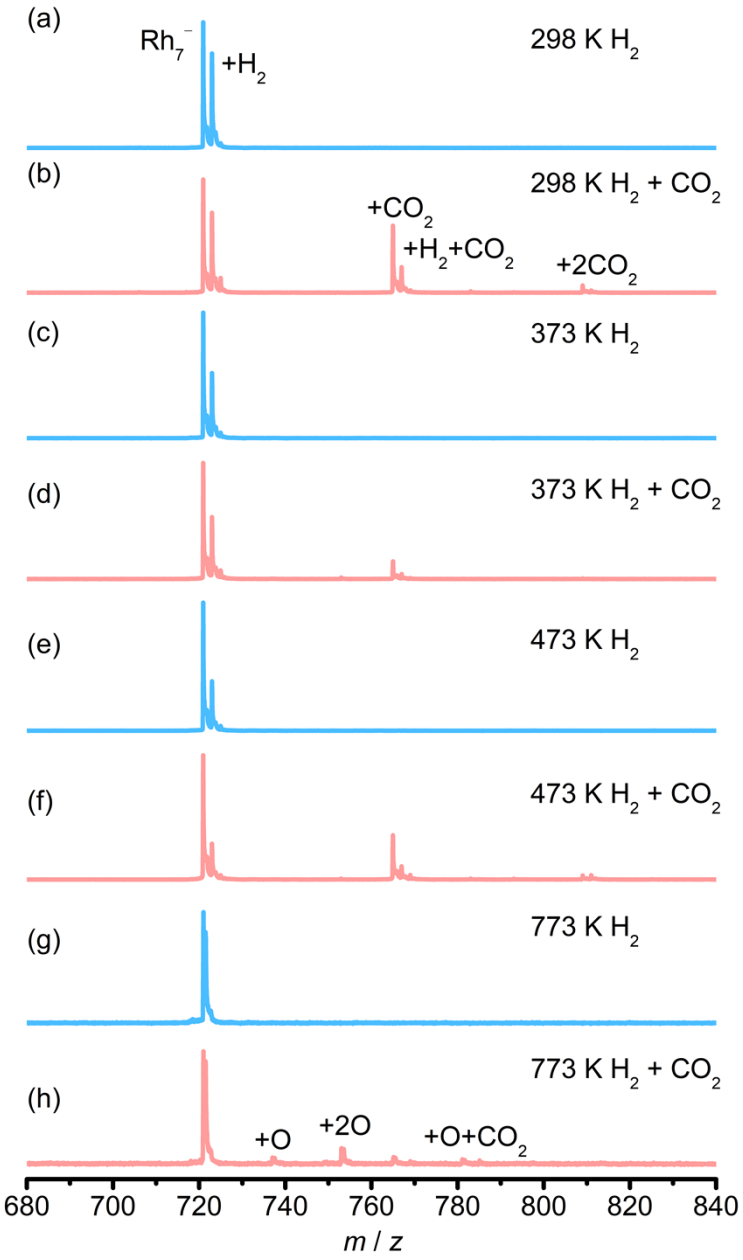

Fig. S25 The TOF mass spectra for the reactions of mass-selected Rh_7^- clusters with H_2 at 298 K (a), 373 K (c), 473 K (e) and 773 K (g), with H_2 + CO_2 at 298 K (b), 373 K (d), 473 K (f) and 773 K (h) in the single ion trap experiment in which H_2 and CO_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 16×10^{12} (a), 24×10^{12} (c), 36×10^{12} (e), 33×10^{12} (g) for H_2 and 1.3×10^{12} (b), 1.2×10^{12} (d), 5.6×10^{12} (f), 34×10^{12} molecules cm^{-3} (h) for CO_2. The Rh_7X^- (X = H_2, CO_2, etc) species are labeled as +X.

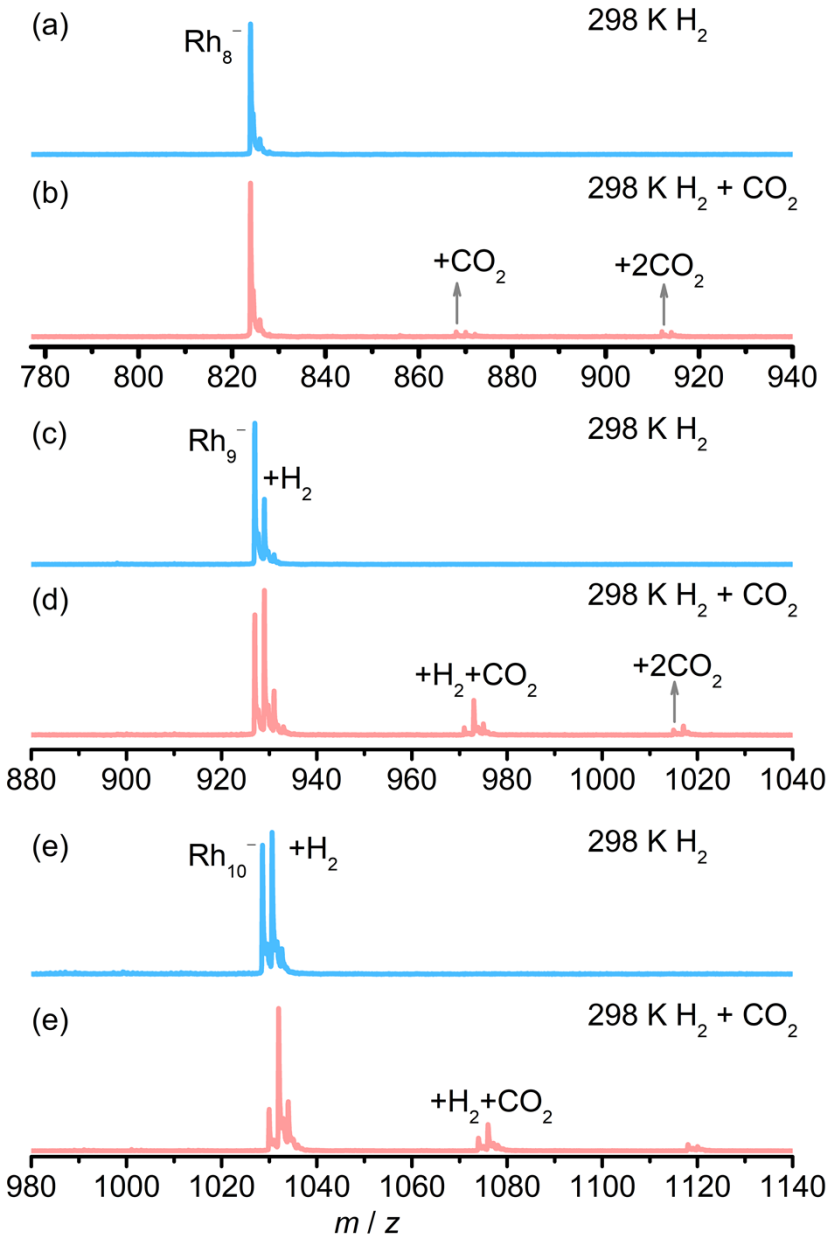

Fig. S26 The TOF mass spectra for the reactions of mass-selected Rh_8^- clusters with H_2 at 298 K (a), with H_2 + CO_2 at 298 K (b), Rh_9^- clusters with H_2 at 298 K (c), with H_2 + CO_2 at 298 K (d), Rh_{10}^- clusters with H_2 at 298 K (e), with H_2 + CO_2 at 298 K (f) in the single ion trap experiment in which H_2 and CO_2 are delivered into the same ion trap. The maximum molecule density of reactant gases is about 37 × 10^{12} (a), 26 × 10^{12} (c), 24 × 10^{12} (e) for H_2 and 19 × 10^{12} (b), 9.9 × 10^{12} (d), 4.3 × 10^{12} molecules cm^{-3} (f) for CO_2. The Rh_nX^- (X = H_2, CO_2, etc) species are labeled as +X.

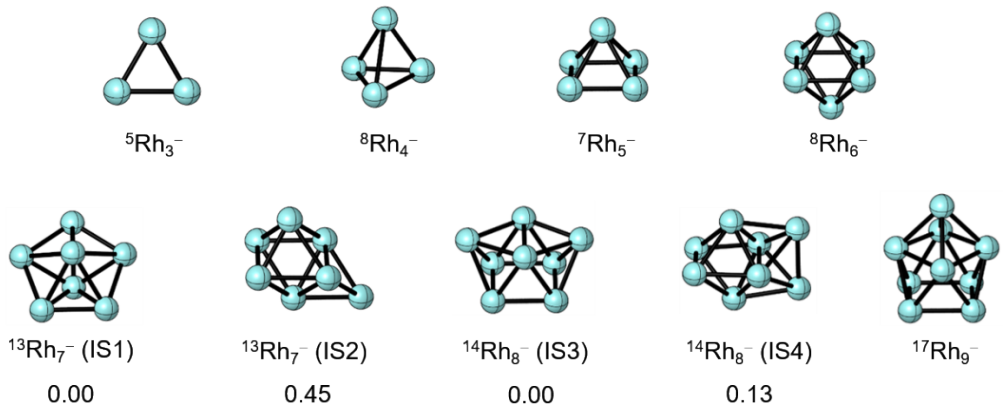

Fig. S27 The DFT-calculated lowest-lying isomers of Rh_n^- (n = 3–9) at the PBE level. The higher energy isomers of Rh_7^- and Rh_8^- could have also been produced in the experiment[1] and calculated, and their relative energies (in eV, zero-point vibrational corrected) are listed below each isomer.

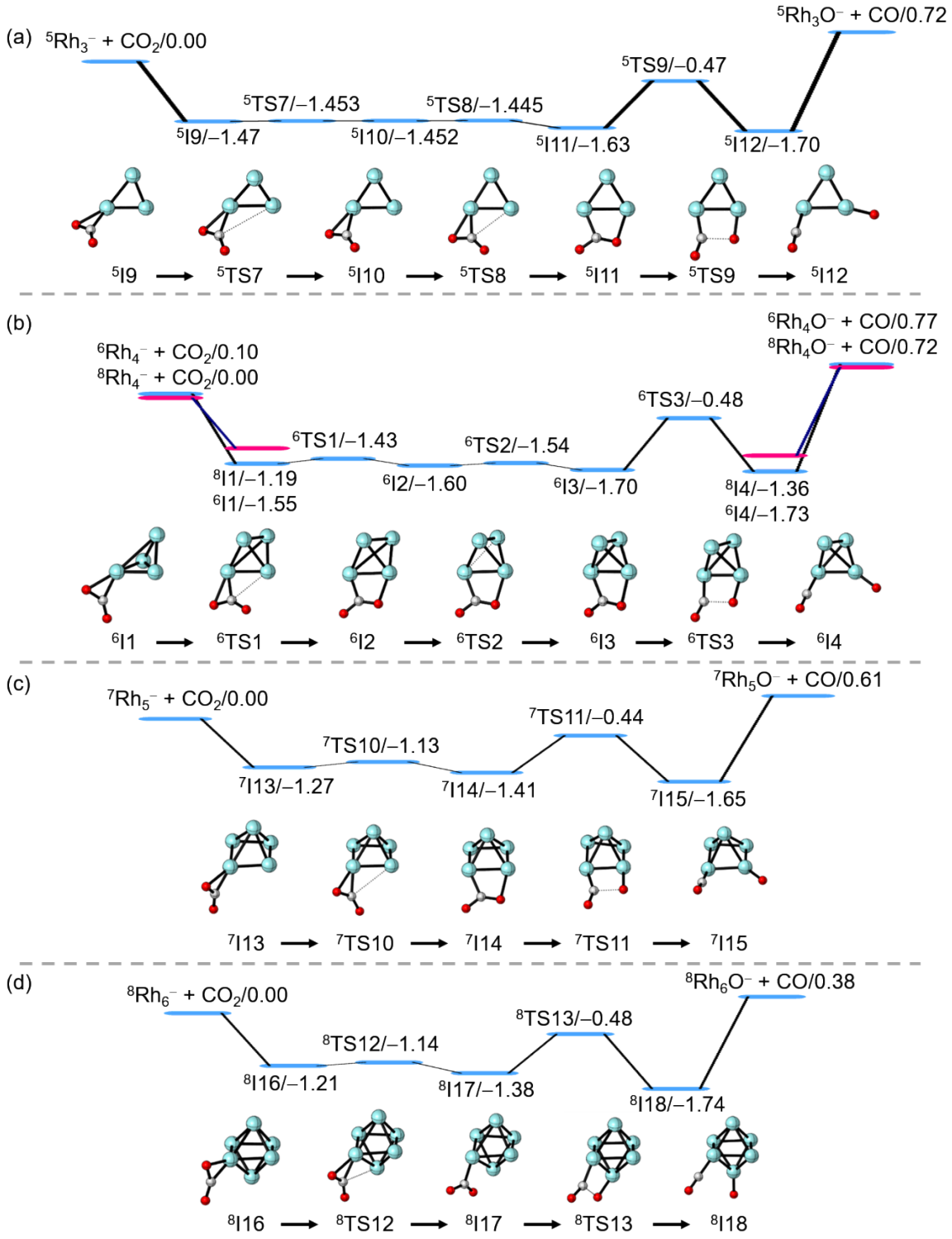

Fig. S28 The DFT calculated potential energy profiles for reactions $Rh_3^- + CO_2$ (a), $Rh_4^- + CO_2$ (b), $Rh_5^- + CO_2$ (c), and $Rh_6^- + CO_2$ (d). The zero-point vibration corrected energies (ΔH_0, eV) are given. The superscripts represent the spin multiplicities.

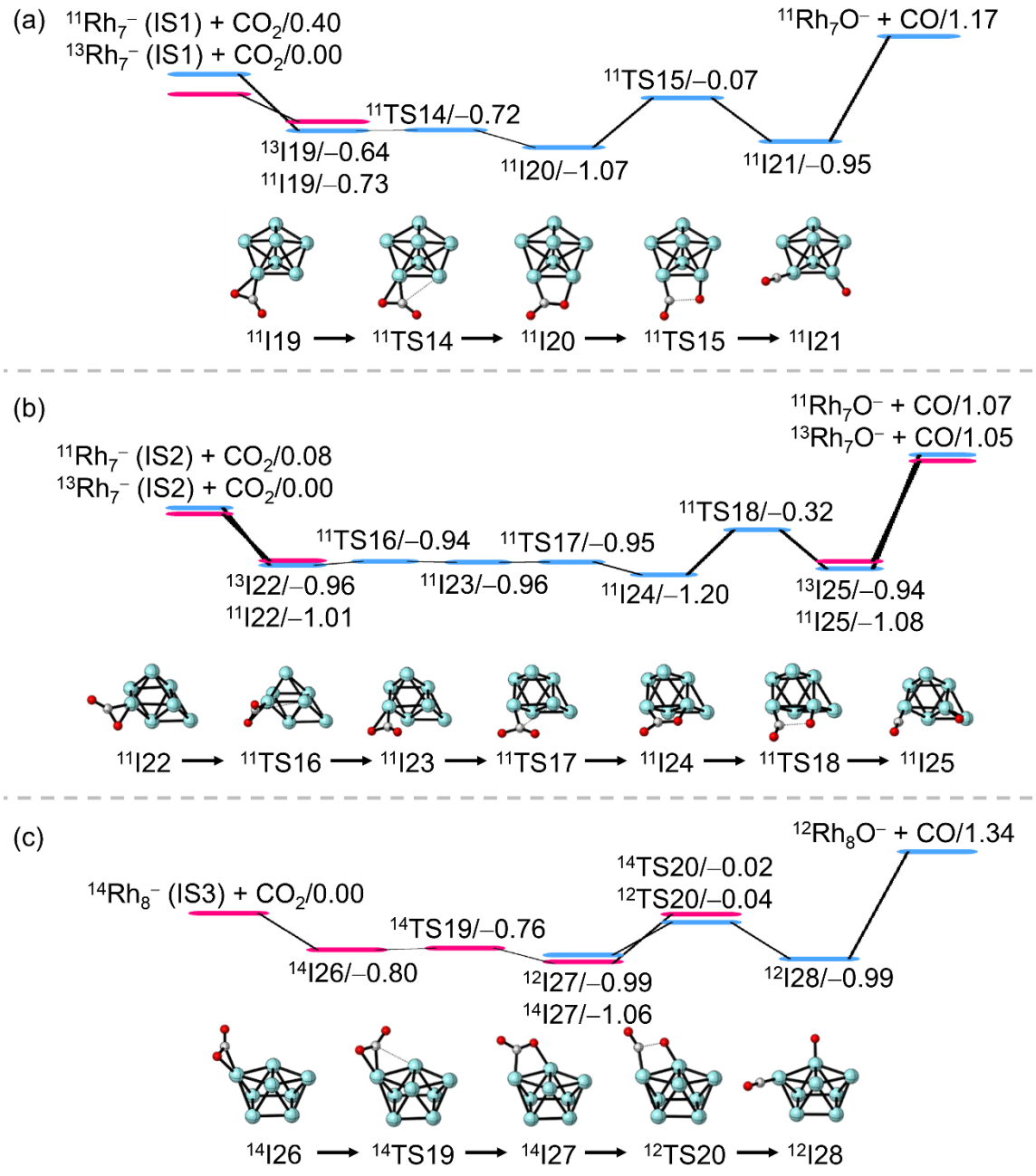

Fig. S29 The DFT calculated potential energy profiles for reactions Rh_7^- (IS1) + CO_2 (a), Rh_7^- (IS2) + CO_2 (b), and Rh_8^- (IS3) + CO_2 (c). The zero-point vibration corrected energies (ΔH_0, eV) are given. The superscripts represent the spin multiplicities.

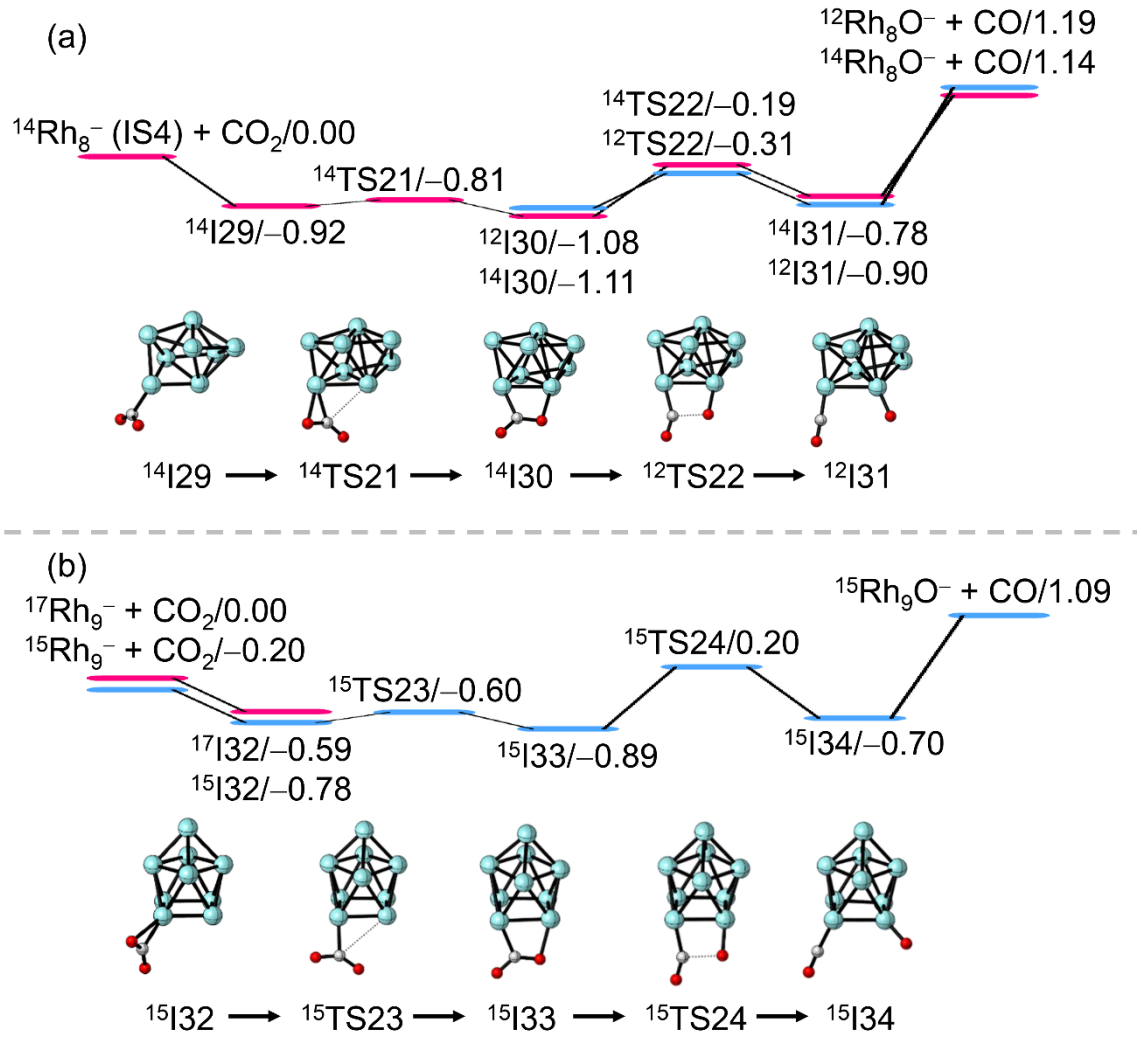

Fig. S30 The DFT calculated potential energy profiles for reactions Rh_8^- (IS4) + CO_2 (a) and Rh_9^- + CO_2 (b). The zero-point vibration corrected energies (ΔH_0, eV) are given. The superscripts represent the spin multiplicities.

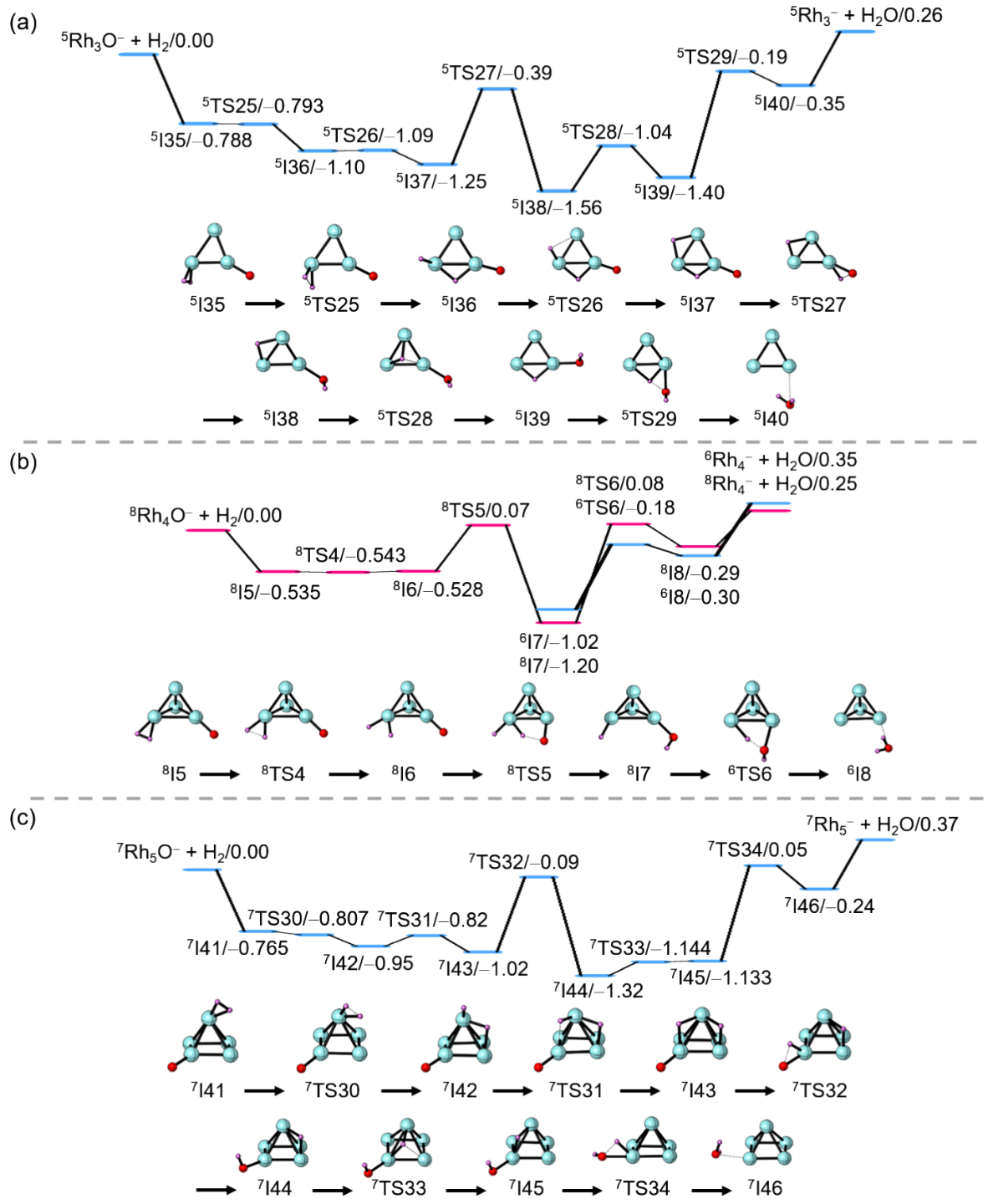

Fig. S31 The DFT calculated potential energy profiles for reactions $Rh_3O^- + H_2$ (a), $Rh_4O^- + H_2$ (b) and $Rh_5O^- + H_2$ (c). The zero-point vibration corrected energies (ΔH_0, eV) are given. The superscripts represent the spin multiplicities.

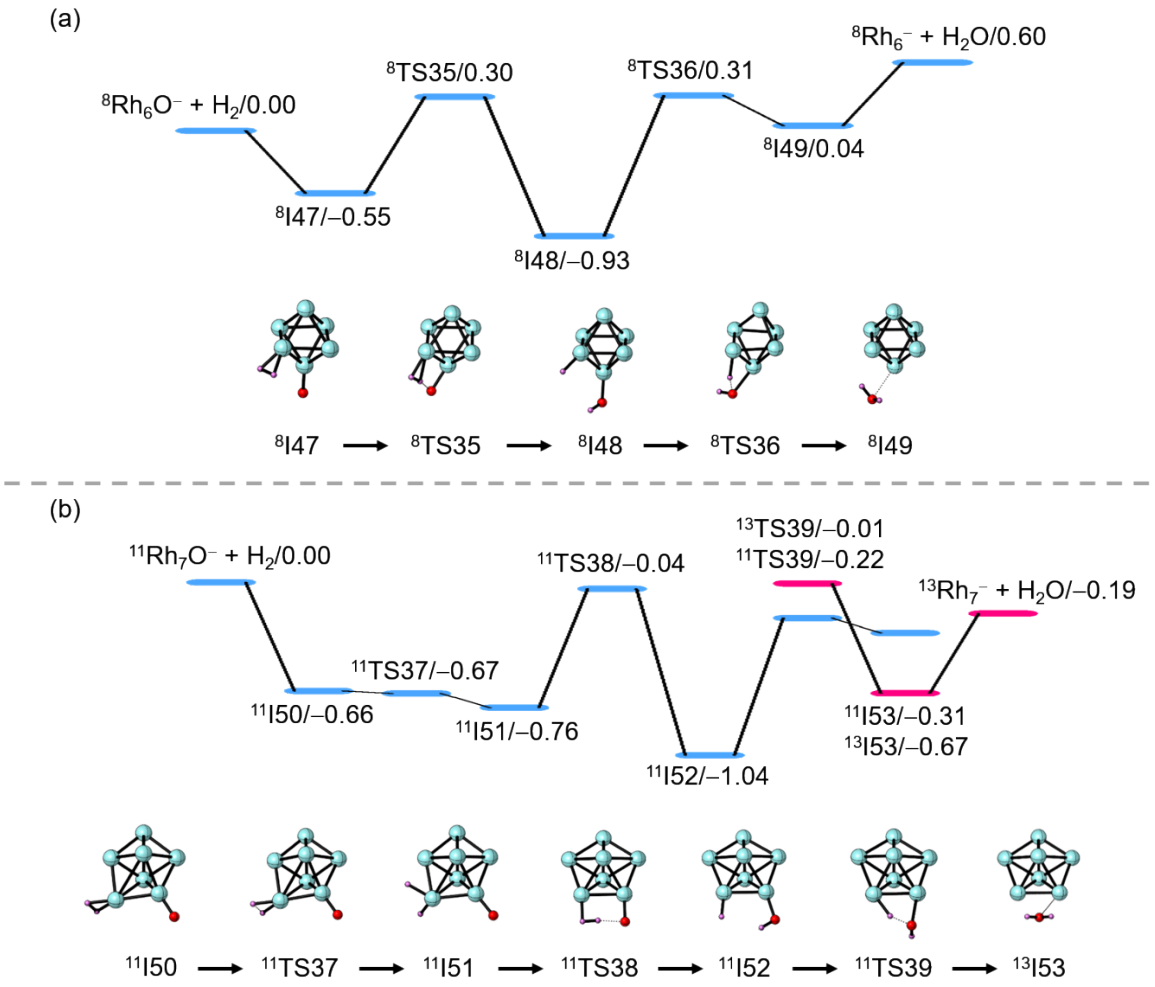

Fig. S32 The DFT calculated potential energy profiles for reactions $Rh_6O^- + H_2$ (a) and $Rh_7O^- + H_2$ (b). The zero-point vibration corrected energies (ΔH_0, eV) are given. The superscripts represent the spin multiplicities.

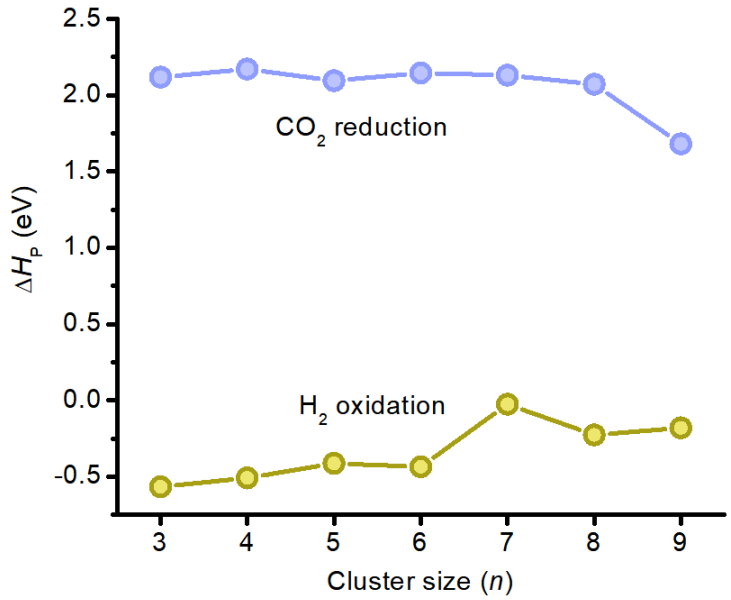

Fig. S33 The DFT calculated thermodynamics for reactions $Rh_nH_2^-$ (n = 3–9) + CO_2 → Rh_nCO^- + H_2O and $Rh_nH_2^-$ + CO_2 → Rh_n^- + CO + H_2O at 0 K.

References

1 M. R. Beltrán, F. Buendía Zamudio, V. Chauhan, P. Sen, H. Wang, Y. J. Ko and K. Bowen, *Eur. Phys. J. D*, 2013, **67**, 63.