Supporting information for

Reverse Water-Gas Shift Reaction Catalyzed by Diatomic Rhodium Anions

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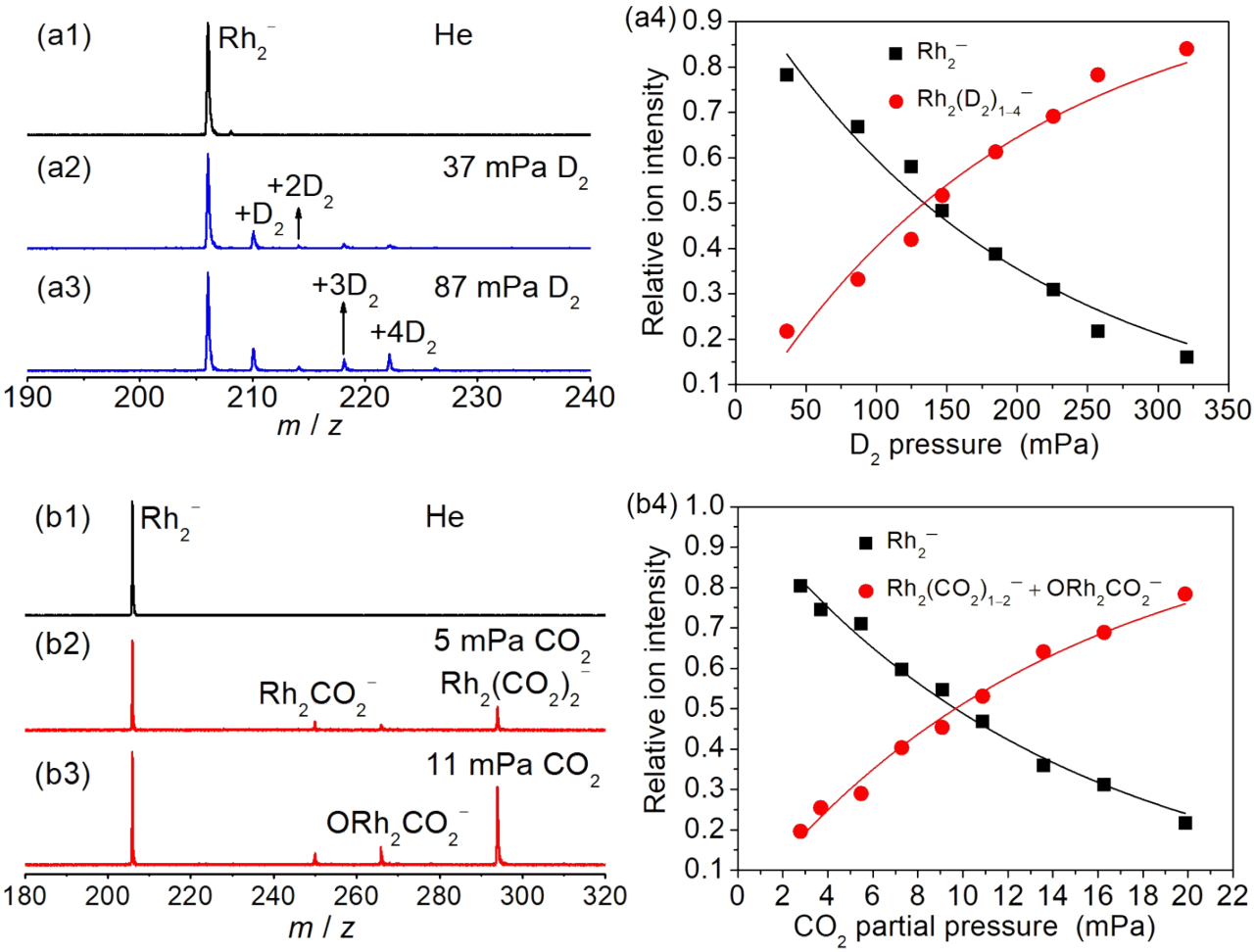

Fig. S1 The time-of-flight (TOF) mass spectra for the reactions of mass-selected Rh_2^- anions with D_2 (a1-a3) and CO_2 (b1-b3) are shown and reactant pressures are given in mPa (= 10^{-3} Pa). Variations of ion intensities with respect to the reactant pressures on the reactions of Rh_2^- with D_2 and CO_2 are presented in a4 and b4, respectively. The solid lines are fitted to the experimental data points by the least-square procedure. The determined rate constants are given in Table S1.

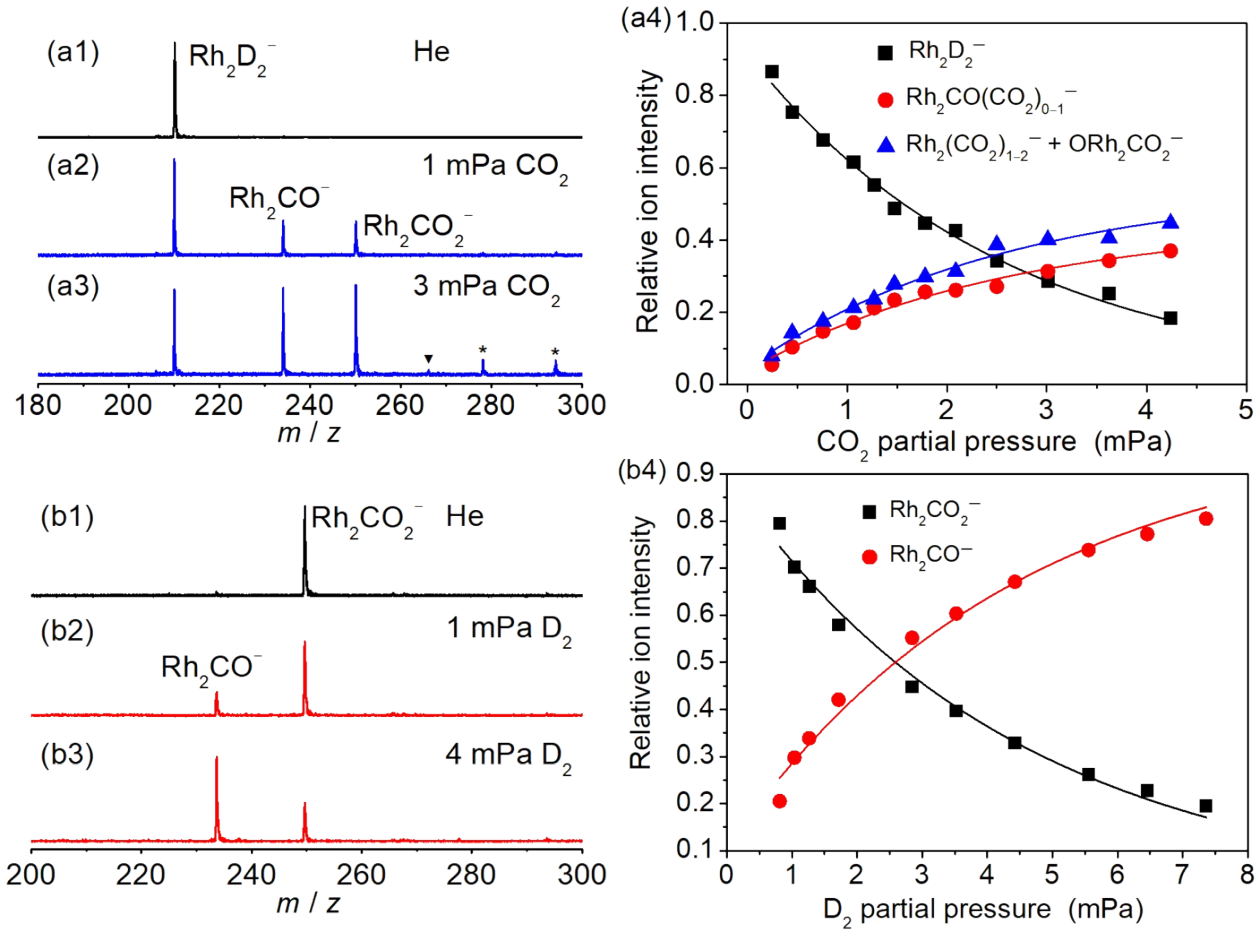

Fig. S2 The TOF mass spectra for the reactions of mass-selected products $Rh_2D_2^-$ and $Rh_2CO_2^-$ generated in LIT1 with CO_2 (a1-a3) and D_2 (b1-b3) in LIT2, respectively. The reactant pressures are shown in mPa (= 10^{-3} Pa). The weak signal marked with a triangle in panel a3 is $ORh_2CO_2^-$ due to the reduction of CO_2 by $Rh_2CO_2^-$ ($Rh_2CO_2^- + CO_2 \rightarrow ORh_2CO_2^- + CO$). The signals marked with asterisks are $Rh_2CO(CO_2)^-$ and $Rh_2(CO_2)_2^-$, respectively, corresponding with the adsorption of CO_2 on Rh_2CO^- and $Rh_2CO_2^-$. Variations of ion intensities with respect to the reactant pressures on the reactions of $Rh_2D_2^-$ with CO_2 and $Rh_2CO_2^-$ with D_2 are presented in a4 and b4, respectively. The solid lines are fitted to the experimental data points by the least-square procedure. The determined rate constants are given in Table S1.

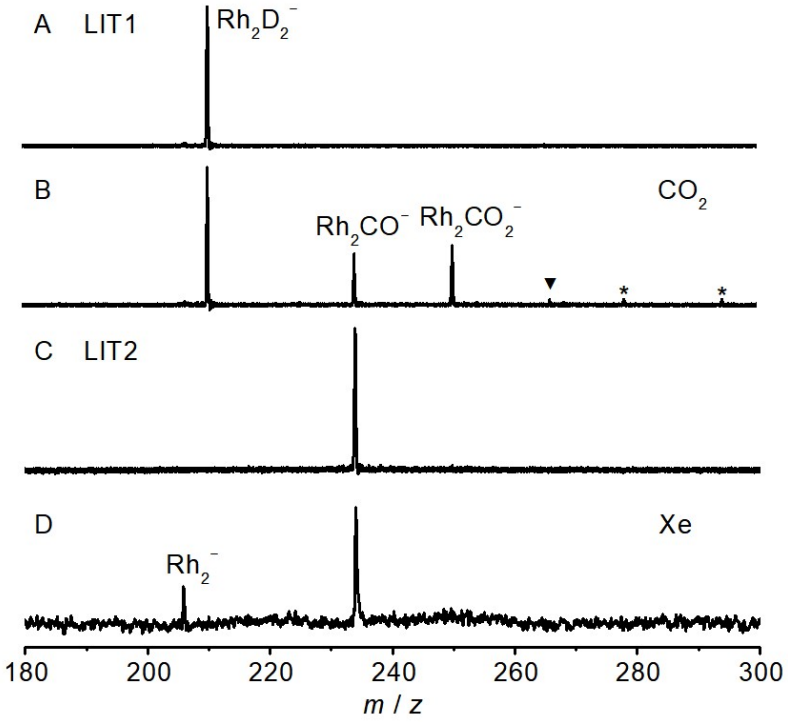

Fig. S3 The TOF mass spectra for the reactions of mass-selected $Rh_2D_2^-$ (A) anions with CO_2 (B) in LIT1. Collision-induced dissociation spectra of mass-selected Rh_2CO^- with 50 mPa Xe in the collision cell (LIT2). The center-of-mass collision energy E_c is roughly estimated to be about 5.38 eV.

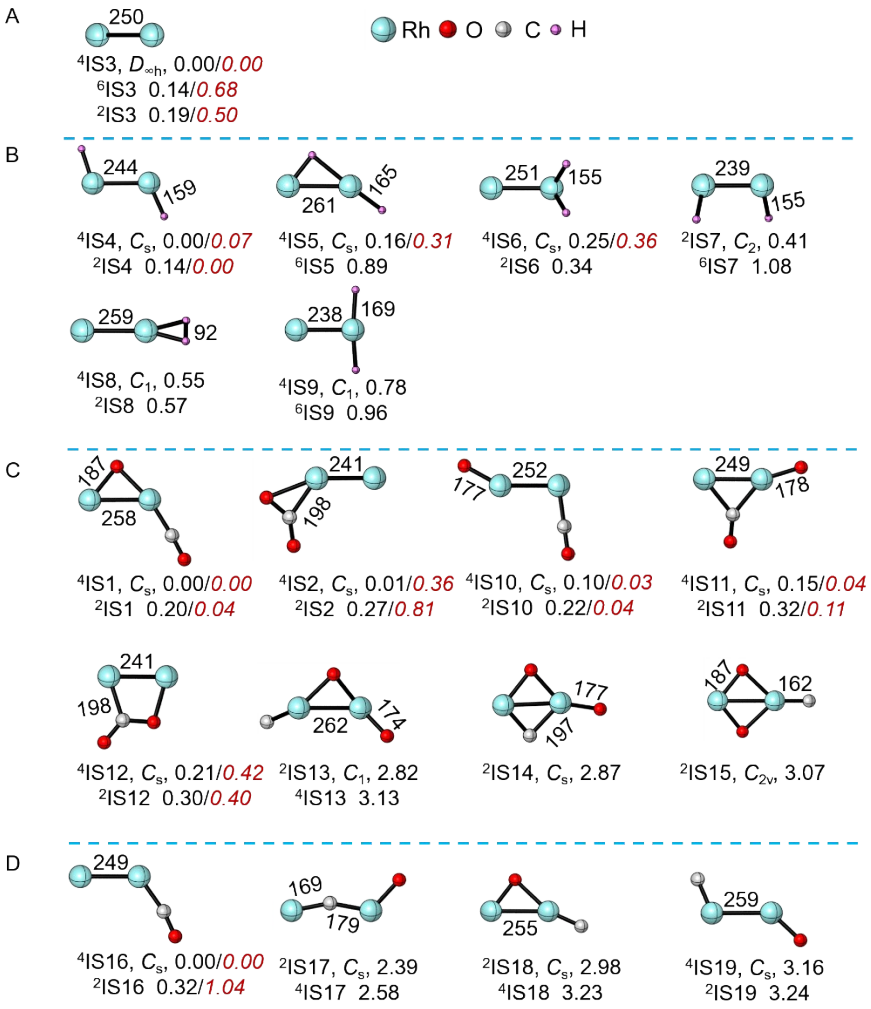

Fig. S4 The calculated low-lying isomers of Rh_2^- (A), $Rh_2H_2^-$ (B), $Rh_2CO_2^-$ (C), and Rh_2CO^- (D). The relative energies (ΔH_0, in eV) with respect to the lowest-lying isomer are given at the B3LYP and the RCCSD(T) (the red values in italic) levels of theory.

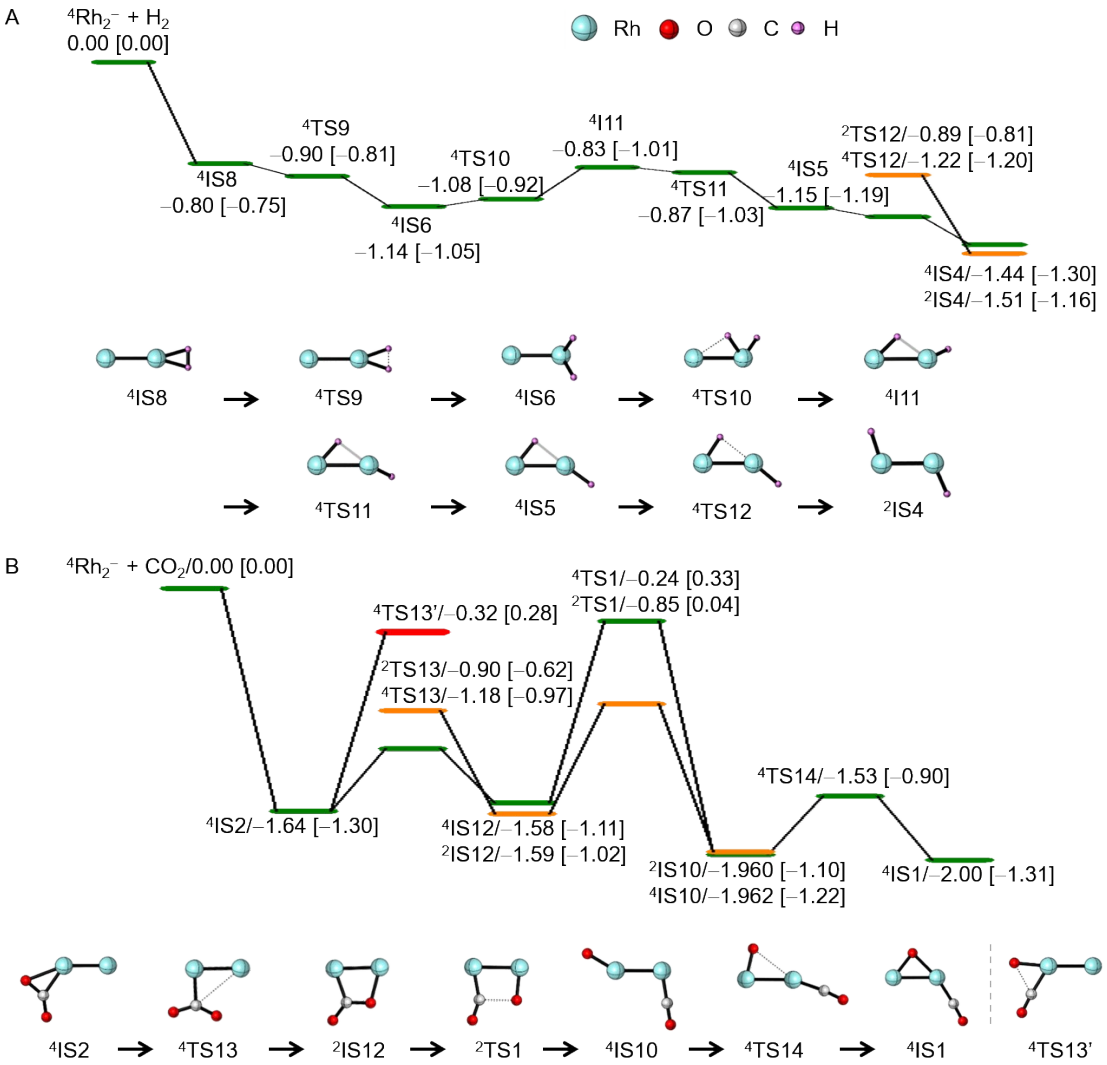

Fig. S5 The potential energy profiles for the reaction of Rh_2^- with H_2 (A) and CO_2 (B). The zero-point vibration corrected energies (ΔH_0, in eV) with respect to the separated reactants are given at the RCCSD(T) and the B3LYP (in square brackets) levels of theory. The superscripts represent the spin multiplicities.

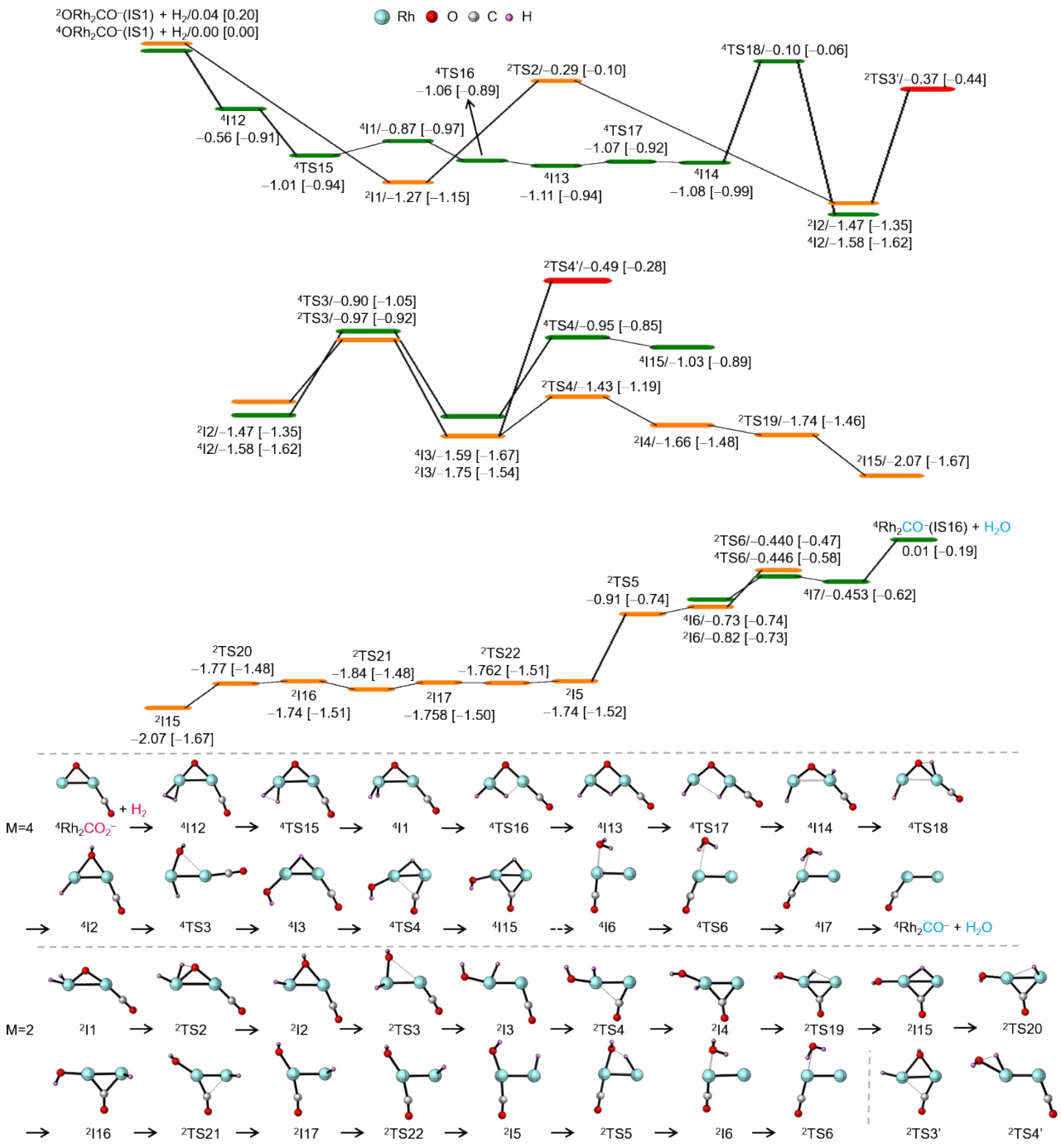

Fig. S6 The potential energy profiles for the reaction of ORh_2CO^- with H_2. The zero-point vibration corrected energies (ΔH_0, in eV) with respect to the separated reactants ($^4ORh_2CO^- + H_2$) are given at the RCCSD(T) and the B3LYP (in square brackets) levels of theory. The superscripts represent the spin multiplicities.

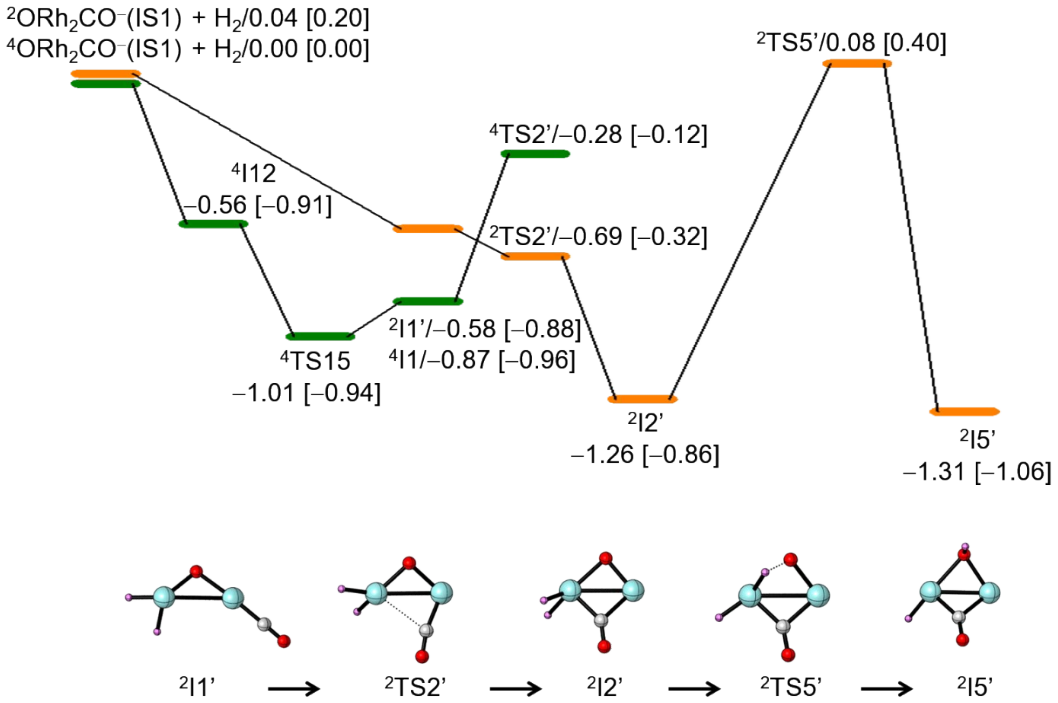

Fig. S7 The potential energy profile for the reaction of ORh_2CO^- with H_2. The zero-point vibration corrected energies (ΔH_0, in eV) with respect to the separated reactants ($^4ORh_2CO^- + H_2$) are given at the RCCSD(T) and the B3LYP (in square brackets) levels of theory. The superscripts represent the spin multiplicities.

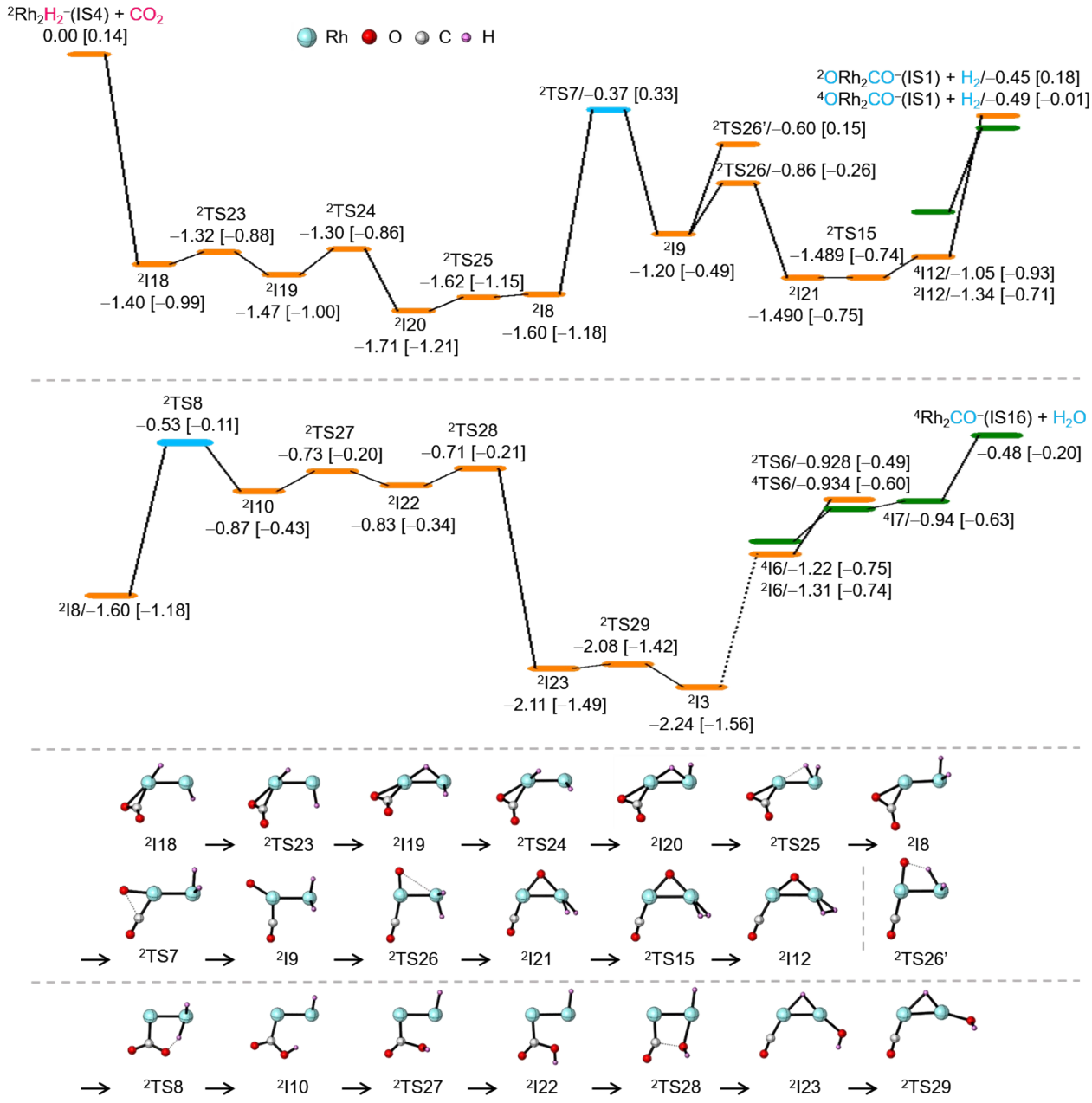

Fig. S8 The potential energy profiles for the reaction of $Rh_2H_2^-$ with CO_2. The zero-point vibration corrected energies (ΔH_0, in eV) with respect to the separated reactants ($^2Rh_2H_2^- + CO_2$) are given at the RCCSD(T) and the B3LYP (in square brackets) levels of theory. The superscripts represent the spin multiplicities.

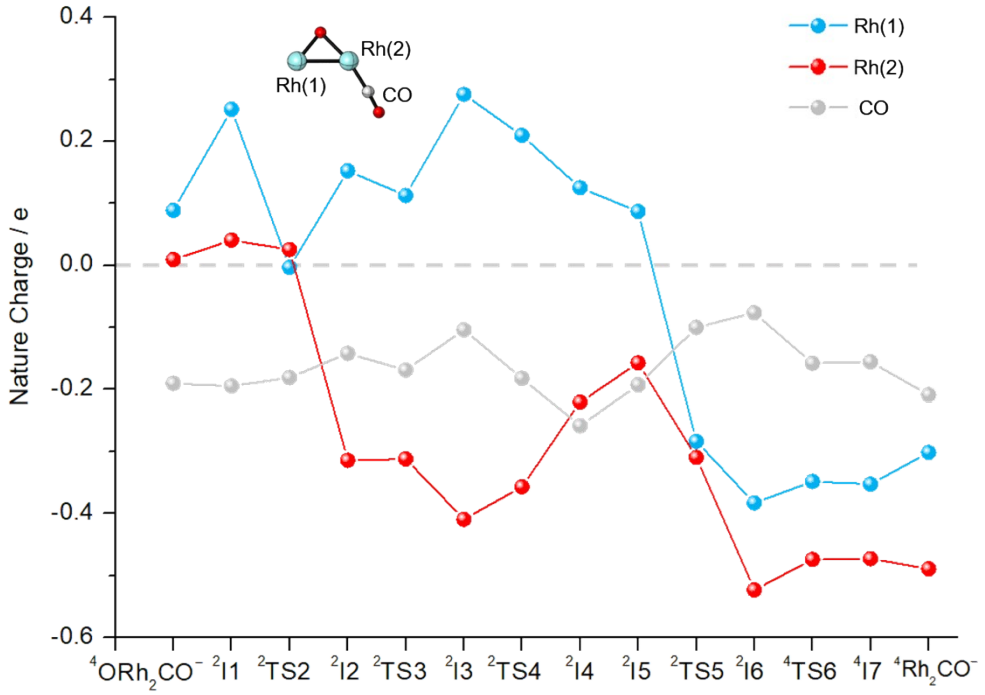

Fig. S9 Natural charges on the Rh(1) and Rh(2) atoms and the CO moiety along with the reaction coordinates of ORh_2CO^- (^{4}IS1) + H_2 (Fig. 3).

Table S1. DFT calculated and experimental bond dissociation enthalpies (in eV) of Rh–Rh, Rh–H, Rh–C, Rh–O, O–CO, C–O, H–H, O–H, and H–OH as well as vertical detachment energies (VDE in eV) of Rh_2^-.

	D (A–B)									VDE
	Rh–Rh	Rh–H	Rh–C	Rh–O	O–CO	C–O	H–H	O–H	H–OH	Rh_2^-
Exp[1,2]	2.406	2.420	5.973	4.159	5.477	11.120	4.478	4.417	5.113	1.65
M06L	2.931	3.001	6.060	4.354	5.774	10.928	4.215	4.191	4.749	1.092
BPW91	2.813	2.963	6.314	4.638	5.917	11.185	4.312	4.384	4.901	1.334
BLYP	2.919	3.007	6.175	4.664	5.723	11.119	4.469	4.440	4.905	1.260
BP86	3.012	3.146	6.487	4.808	6.014	11.367	4.563	4.583	5.077	1.517
TPSS	3.138	3.335	6.222	4.594	5.576	10.779	4.619	4.319	4.866	1.222
PBE	3.083	3.013	6.564	4.873	6.121	11.425	4.268	4.446	4.965	1.361
BPBE	2.829	2.961	6.339	4.653	5.935	11.195	4.288	4.376	4.898	1.323
B3LYP	**1.736**	**2.862**	**5.303**	**3.799**	**5.441**	**10.803**	**4.497**	**4.364**	**4.884**	**1.472**
B1LYP	1.559	2.756	4.932	3.466	5.229	10.558	4.442	4.260	4.779	1.164
X3LYP	1.727	2.846	5.251	3.755	5.437	10.794	4.473	4.353	4.879	1.430
B1B95	1.696	2.823	5.351	3.720	5.522	10.902	4.379	4.264	4.914	1.103
B3P86	1.812	2.992	5.613	3.967	5.745	11.061	4.575	4.506	5.054	1.986
B3PW91	1.651	2.822	5.401	3.760	5.576	10.819	4.371	4.307	4.873	1.240
PBE1PBE	1.630	2.752	5.291	3.634	5.590	10.810	4.247	4.255	4.828	1.425
M062X	1.605	2.742	5.076	3.435	5.317	10.969	4.405	4.300	4.860	1.064

Table S2. Total rate constants (k_1, in unit of 10^{-10} cm^3 molecule^{-1} s^{-1}), and reaction efficiency (Φ) for the reactions $Rh_2^- + D_2$, $Rh_2D_2^- + CO_2$, $Rh_2^- + CO_2$, and $Rh_2CO_2^- + D_2$.

reactions	products	k_1	Φ^a (%)
$Rh_2^- + D_2$	$Rh_2D_2^-$	0.013 ± 0.003	0.07 ± 0.01
$Rh_2D_2^- + CO_2$	$Rh_2CO^- + D_2O$	8.1 ± 1.7	77 ± 16
	$Rh_2CO_2^- + D_2$		
$Rh_2^- + CO_2$	$Rh_2CO_2^-$	0.33 ± 0.07	3.2 ± 0.7
$Rh_2CO_2^- + D_2$	$Rh_2CO^- + D_2O$	5.1 ± 1.1	25 ± 5.3

[a]Reaction efficiency defined as $\Phi = k_1/k_{calc}$, in which k_{calc} is the theoretical rate of collision that is calculated with the surface charge capture (SCC) theory.[3]

References

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