Supporting Information

Propylene hydroformylation catalyzed by rhodium-based catalysts with phosphine-sulfur ligands: a combined theoretical and experimental study

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Catalyst Preparation

The Rh_1/POPs catalyst was prepared as our previous work[1,2]. Firstly, the POPs were synthesized via solvothermal polymerization. In a typical case, a tri-vinyl functionalized triphenylphosphine (3v-PPh_3) monomer was synthesized with the reaction between PCl_3 and (4-vinyl phenyl) magnesium bromide solution, and then a saturated NH_4Cl aqueous solution was added. The organic phase was extracted with ethyl acetate and then dried with $MgSO_4$. After being filtered and purified by silica gel chromatography, the monomer was obtained. POPs were synthesized from the polymerization of the 3V-PPh_3 monomer under solvothermal conditions. 1.0 g of monomer was dissolved in 10 ml of THF, followed by the addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 373 K for 24 h. After evaporation of THF under vacuum, the POPs support was obtained. Rhodium dicarbonyl-2,4-pentanedionate was dissolved in 30 ml THF in a three-necked round bottom flask under an argon atmosphere, followed by a 30 min stirring to obtain a homogeneous solution. Then the POPs support was added to the round bottom flask and the obtained Rh mixture was stirred under an argon atmosphere at room temperature for another 24 h. The Rh_1/POPs catalyst was obtained by filtrating, washing with THF (70 ml), and drying under vacuum at 338 K. The weight loading of Rh metal was 0.25wt%.

Catalyst Activity Evaluation of Environmental sulfides on single-Rh_1-site Rh_1/POPs catalyst

The effect of environmental sulfides on single-Rh_1-site Rh_1/POPs was carried out with propylene hydroformylation reaction. The hydroformylation of propylene was performed in a stainless-steel autoclave (50 mL) equipped with a magnetic bar. As a typical run, 5.0 g of toluene, 0.1g Rh_1/POPs was added into them autoclave. For the propylene hydroformylation, syngas (C_3H_6:CO:H_2=1:1:1) was pressed to 2.0 MPa after sealing and purging with same syngas. Then, the autoclave was heated to 353 K within 60 min at a stirring speed of 600 r/min. After reaction, the autoclave was cooled in an ice bath and released the pressure, the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890B gas chromatography with an HP-5 column, using an FID detector.

The catalytic activity (Conversion, Selectivity, and Turnover frequency (TOF) of Rh_1/POPs) was calculated with the moles of product aldehydes and byproducts alkanes. For example, the conversion of propylene, the selectivity of aldehydes were calculated based on the moles of aldehydes (include including orthoaldehydes and isomeraldehydes), isobutane, n-butane in the products. The turnover frequency (TOF) was calculated based on the CO mole conversed per mole metal atoms of the Rh_1/POPs per hour.

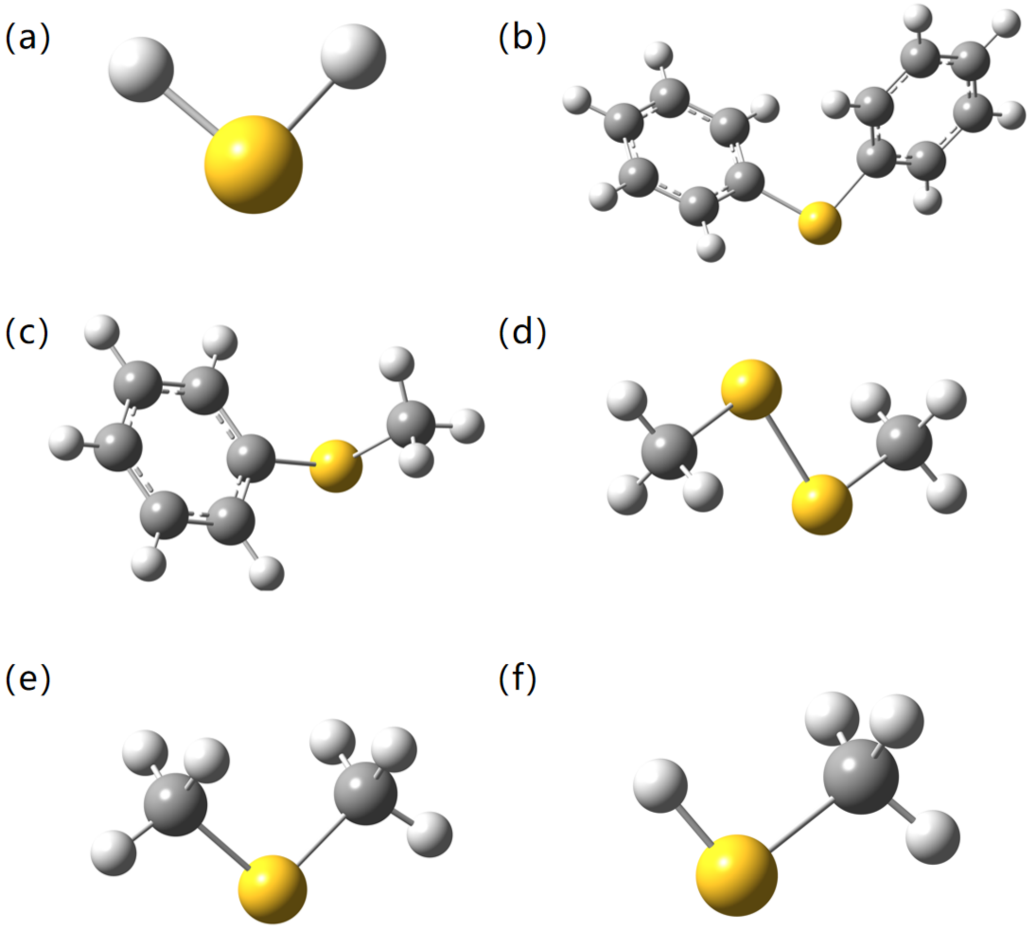

Fig. S1 Sulfides used in catalytic cycle calculations for propylene hydroformylation. (a) hydrogen sulfide, (b) phenyl sulfide, (c) thioanisole, (d) dimethyl disulfide, (e) dimethyl sulfide, (f) methyl mercaptan. White: H atoms, grey: C atoms, yellow: S atoms.

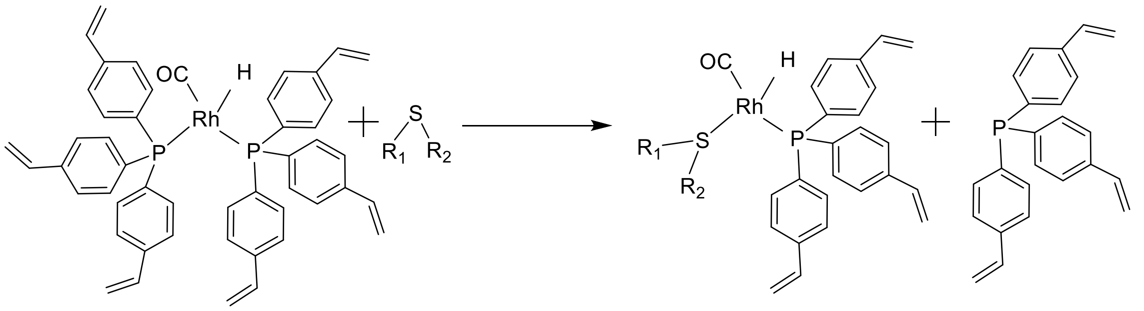

Fig. S2 Substitution reaction after introduction of sulfide.

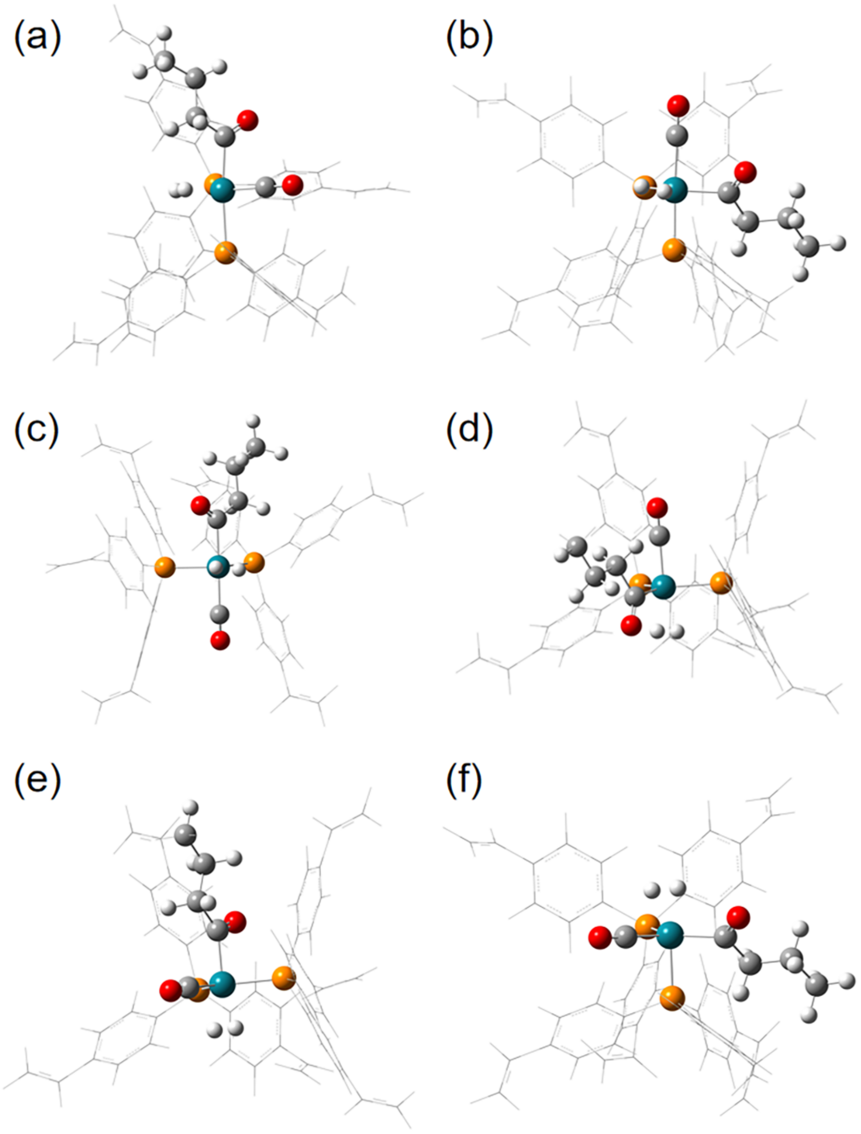

Fig. S3 All the six considered coordination modes (a-f) of structure 6 (see Scheme 1) in the catalytic cycle promoted by $HRh(CO)(PAr_3\text{-}Ar_3P)$. White: H atoms, grey: C atoms, red: O atoms, orange: P atoms, blue-green: Rh atoms.

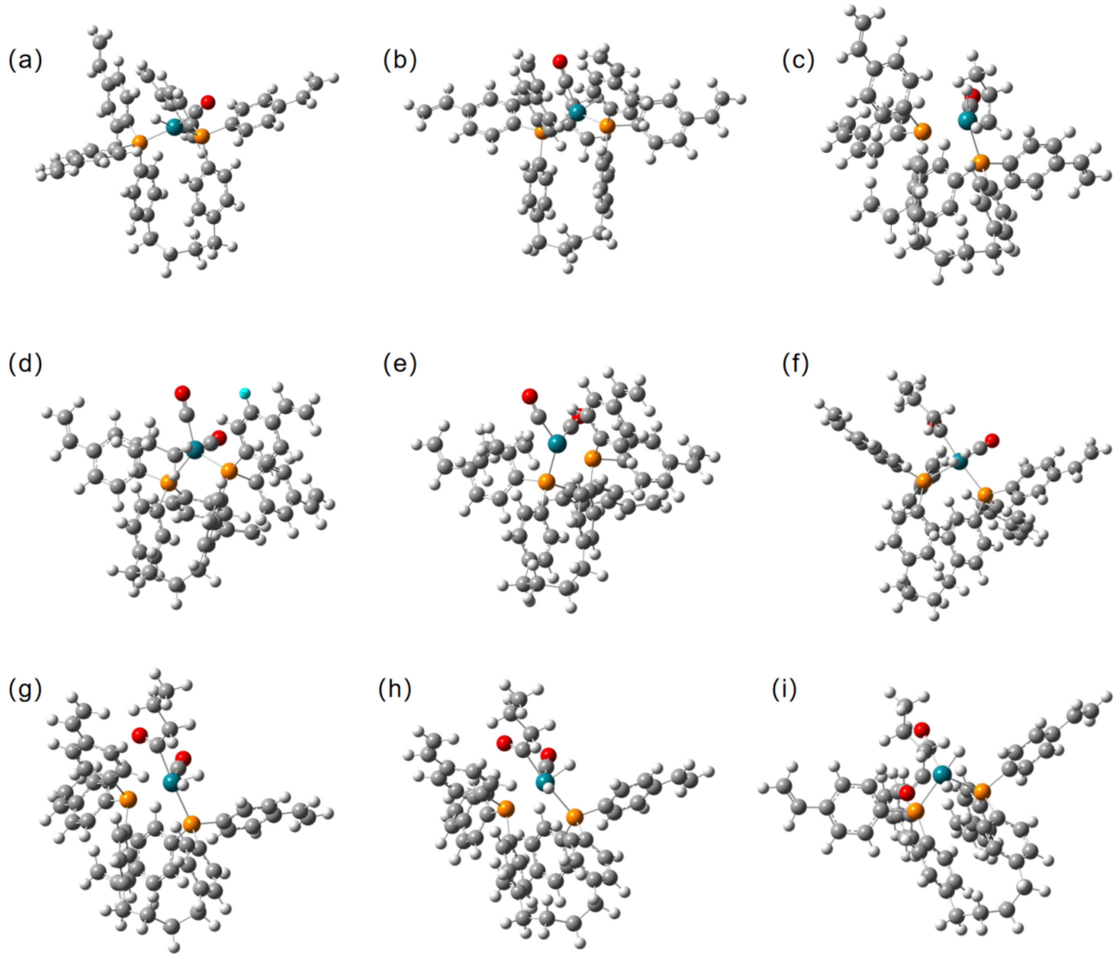

Fig. S4 Structures of individual states of the HRh(CO)(PAr$_3$-Ar$_3$P) catalyzed propylene hydroformylation reaction process. (a-i) correspond to states 1-9 in Scheme 1, respectively. In particular, the structure in (a) is the reactant, the structures in (c), (e), (g), and (i) correspond to the transition states, and those in (b), (d), (f) and (h) represent the reaction intermediates. White: H atoms, grey: C atoms, yellow: S atoms, red: O atoms, orange: P atoms, blue-green: Rh atoms.

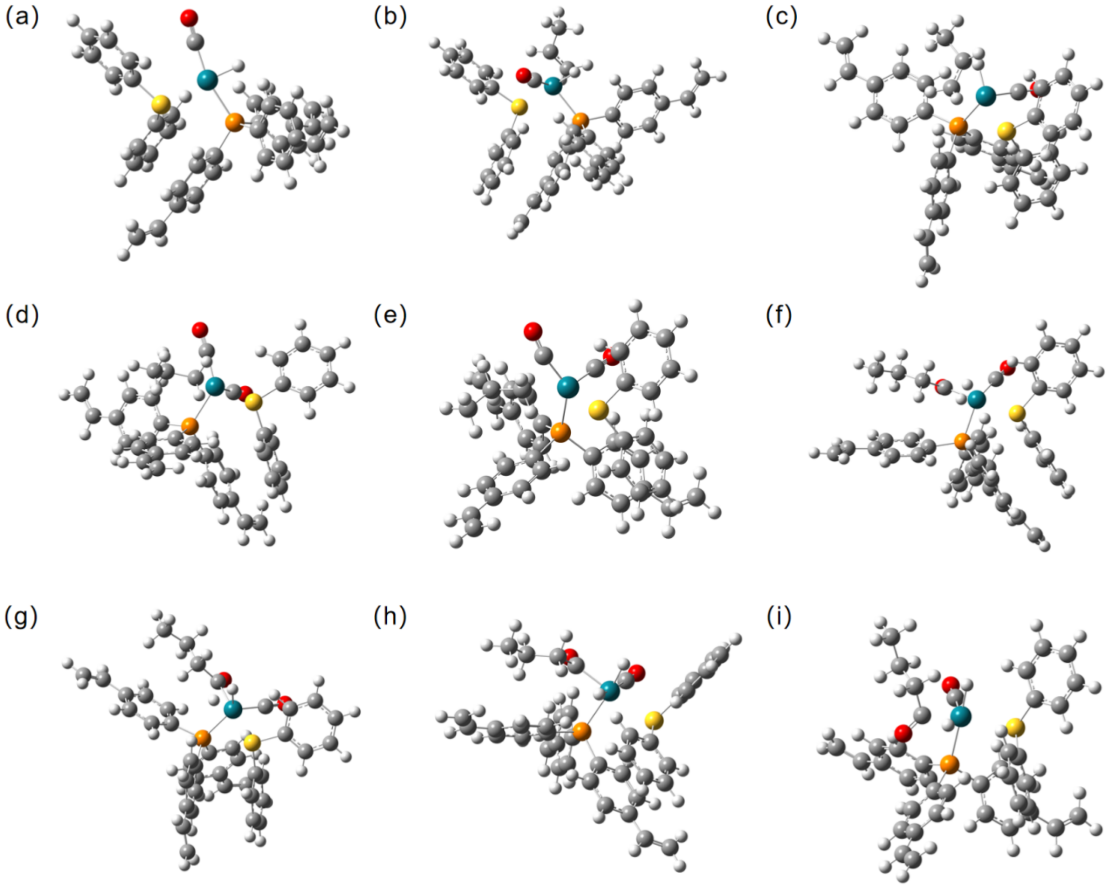

Fig. S5 Structures of individual states of the $HRh(CO)(PAr_3)(C_6H_5SC_6H_5)$ catalyzed propylene hydroformylation reaction process. (a-i) correspond to states 1-9 in Scheme 1, respectively.

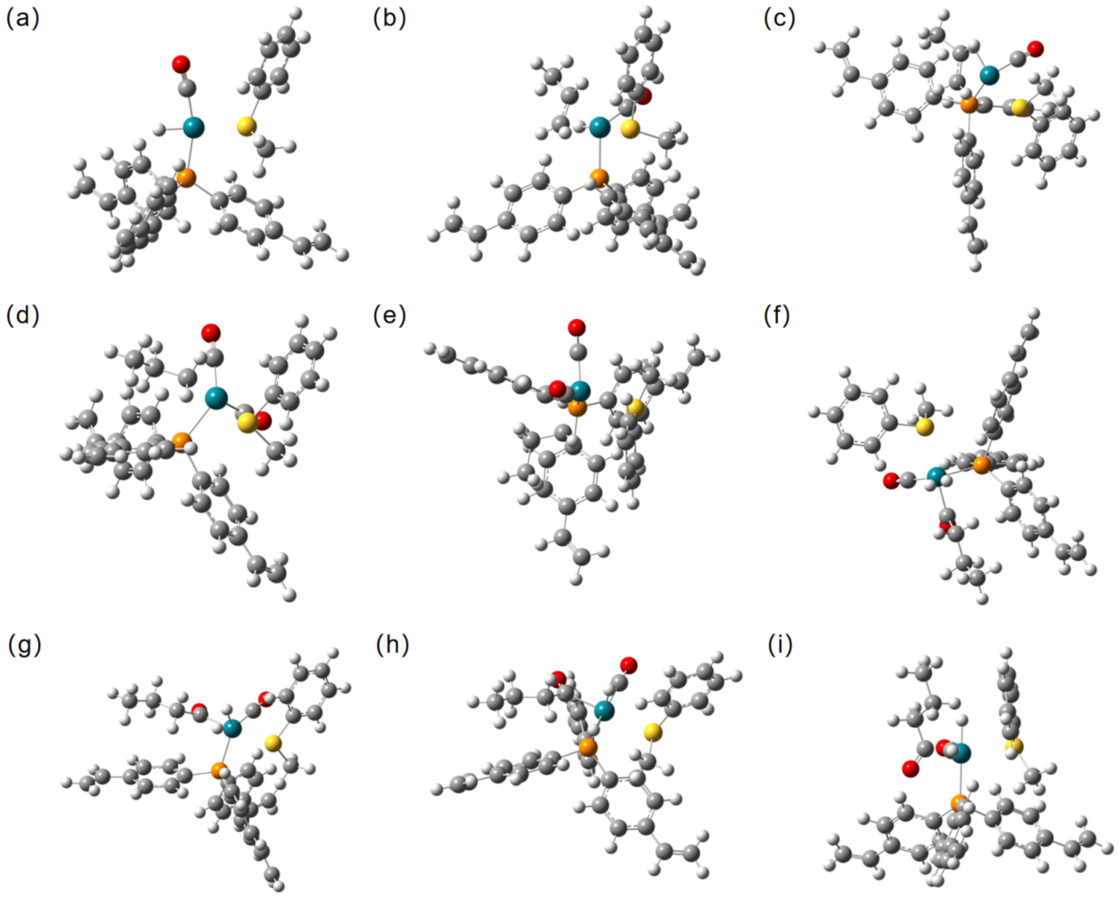

Fig. S6 Structures of individual states of the $HRh(CO)(PAr_3)(C_6H_5SCH_3)$ catalyzed propylene hydroformylation reaction process. (a-i) correspond to states 1-9 in Scheme 1, respectively.

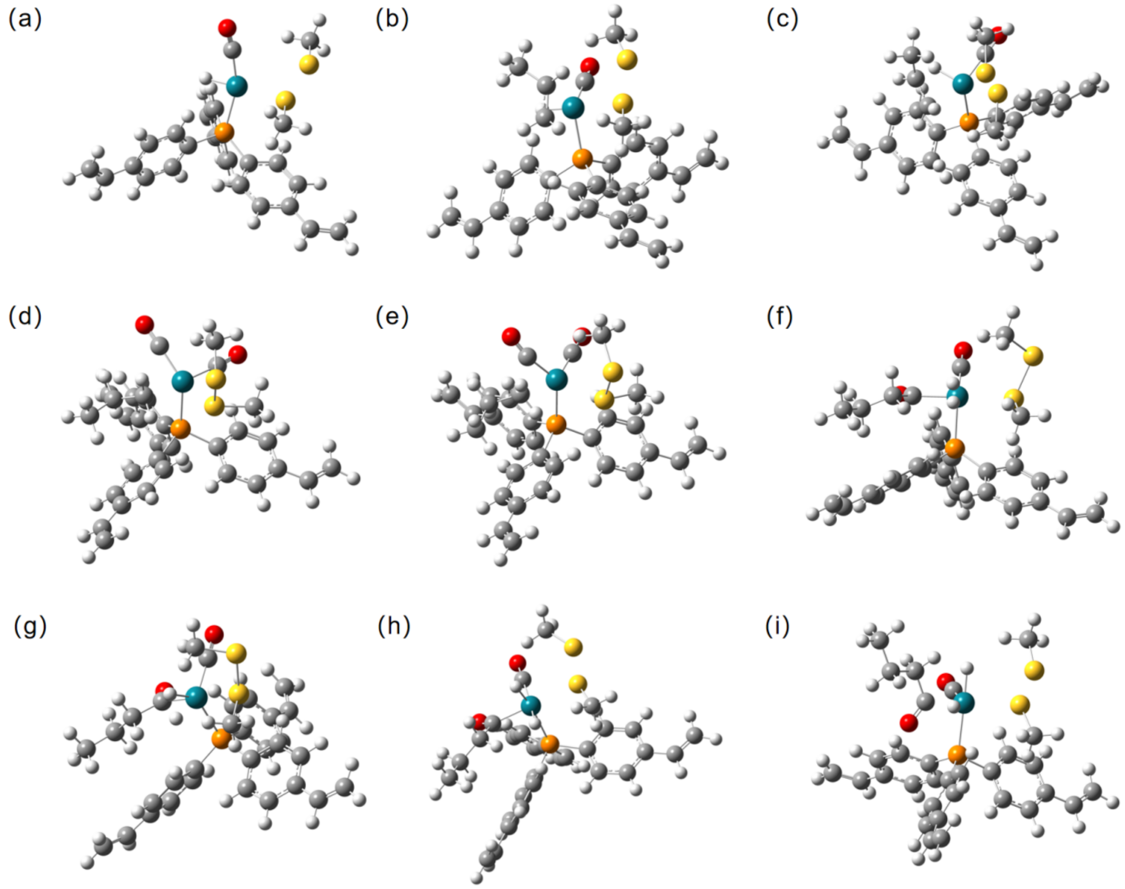

Fig. S7 Structures of individual states of the $HRh(CO)(PAr_3)(CH_3S_2CH_3)$ catalyzed propylene hydroformylation reaction process. (a-i) correspond to states 1-9 in Scheme 1, respectively.

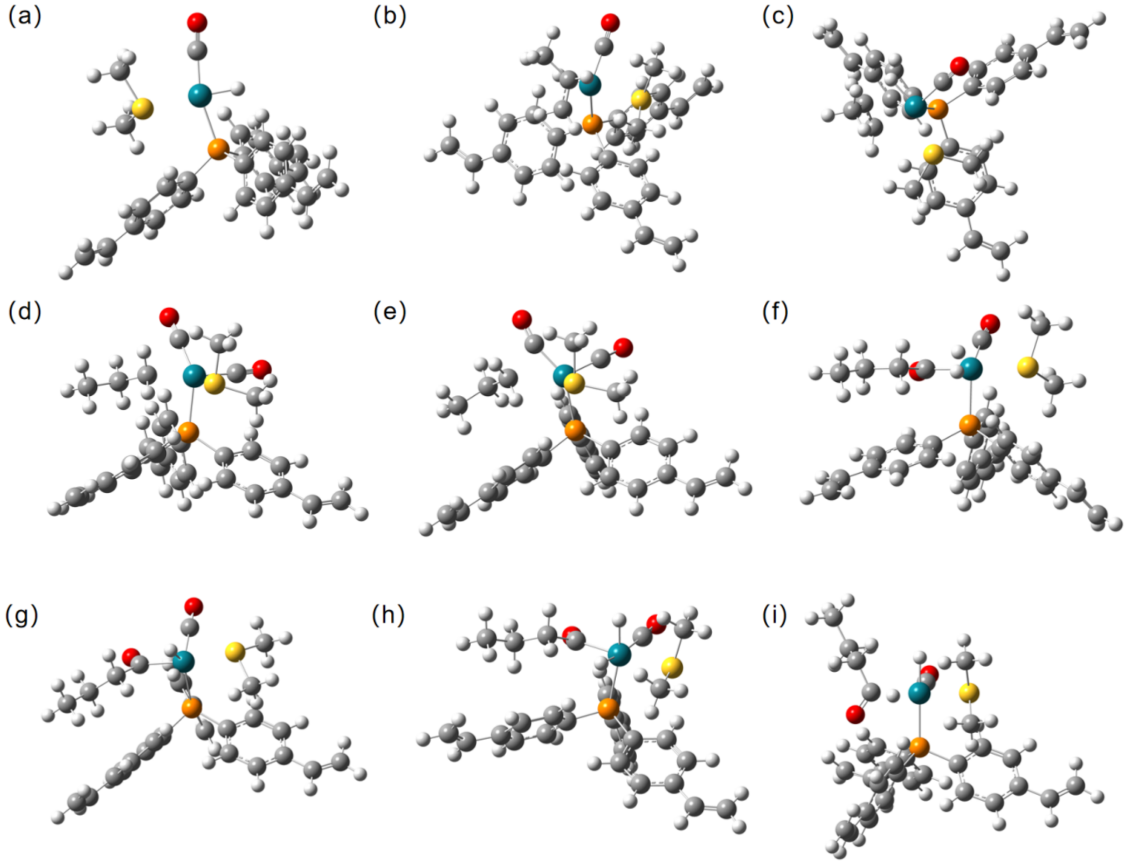

Fig. S8 Structures of individual states of the HRh(CO)(PAr$_3$)(CH$_3$SCH$_3$) catalyzed propylene hydroformylation reaction process. (a-i) correspond to states 1-9 in Scheme 1, respectively.

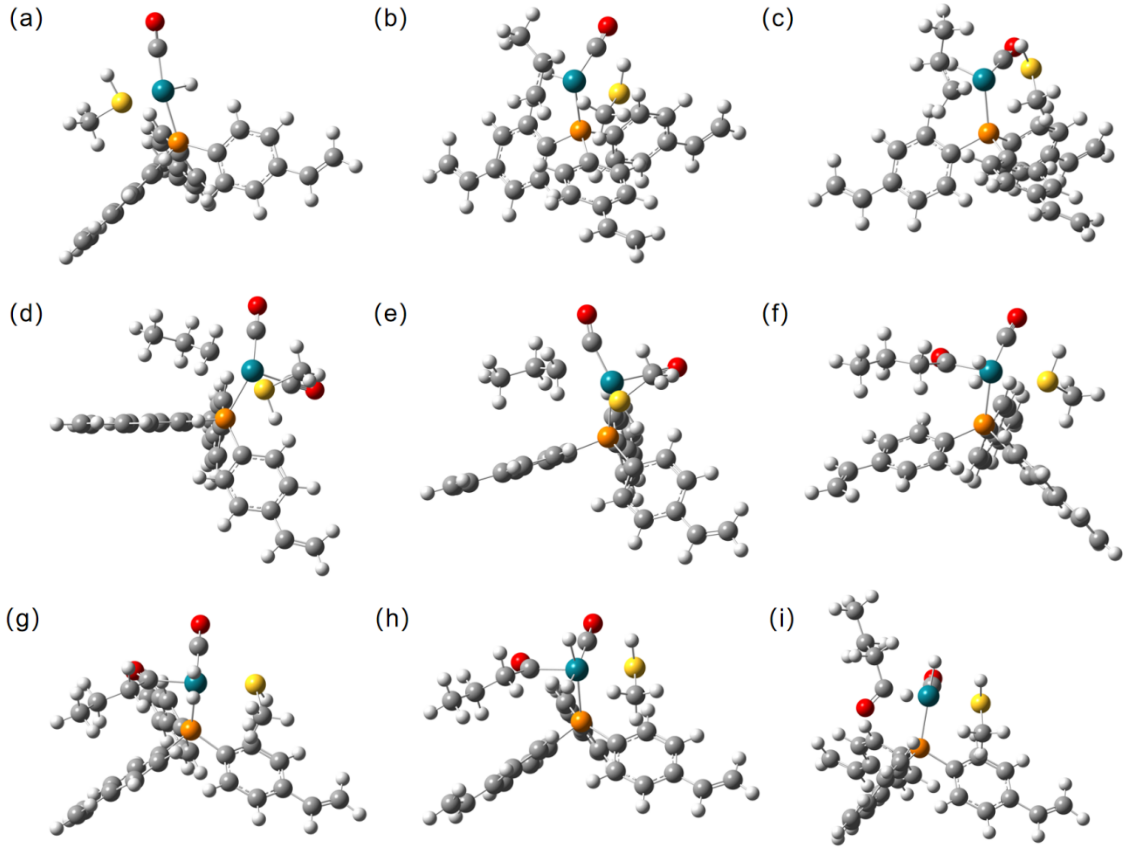

Fig. S9 Structures of individual states of the HRh(CO)(PAr$_3$)(CH$_3$SH) catalyzed propylene hydroformylation reaction process. (a-i) correspond to states 1-9 in Scheme 1, respectively.

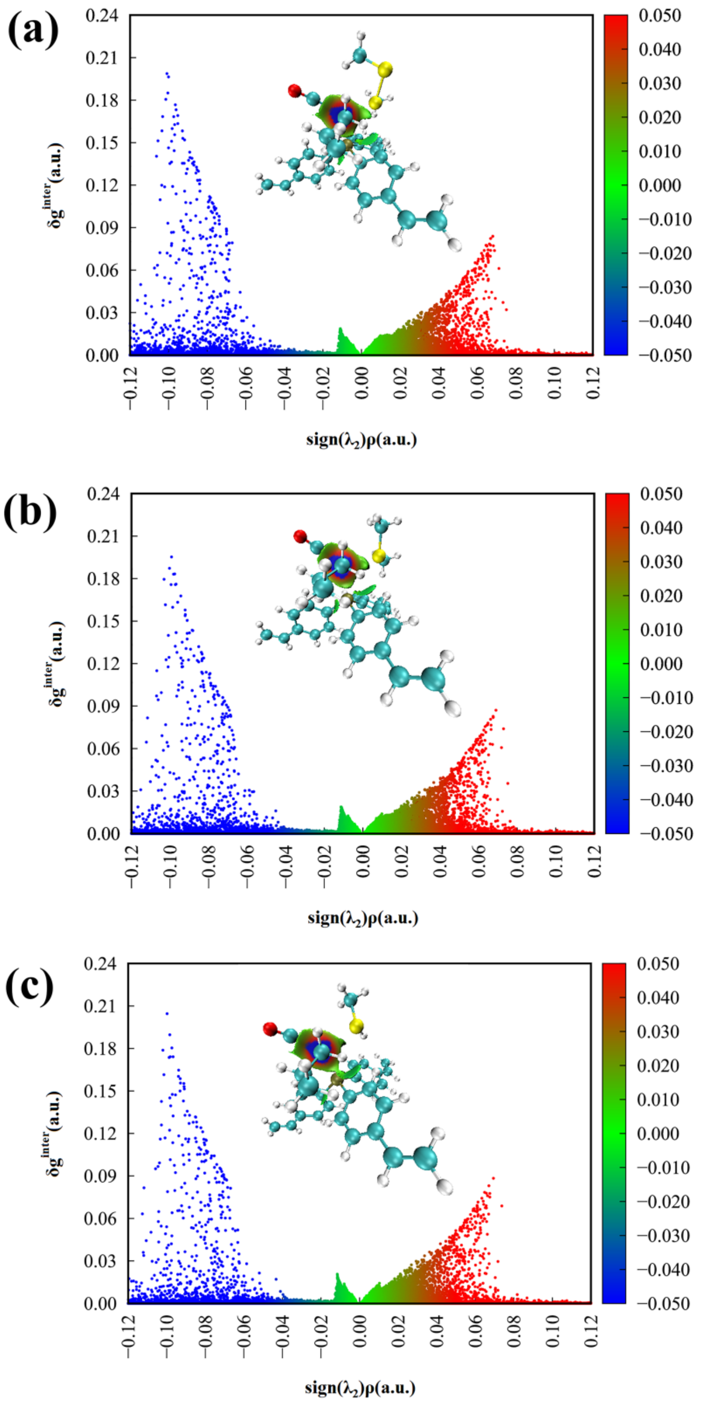

Fig. S10 The visualized weak interaction regions and the corresponding IGMH plots for structure 4 (see Scheme 1) in different catalytic systems. (a) HRh(CO)(PAr3)(CH3S2CH3), (b) HRh(CO)(PAr3)(CH3SCH3), (c) HRh(CO)(PAr3)(CH3SH).

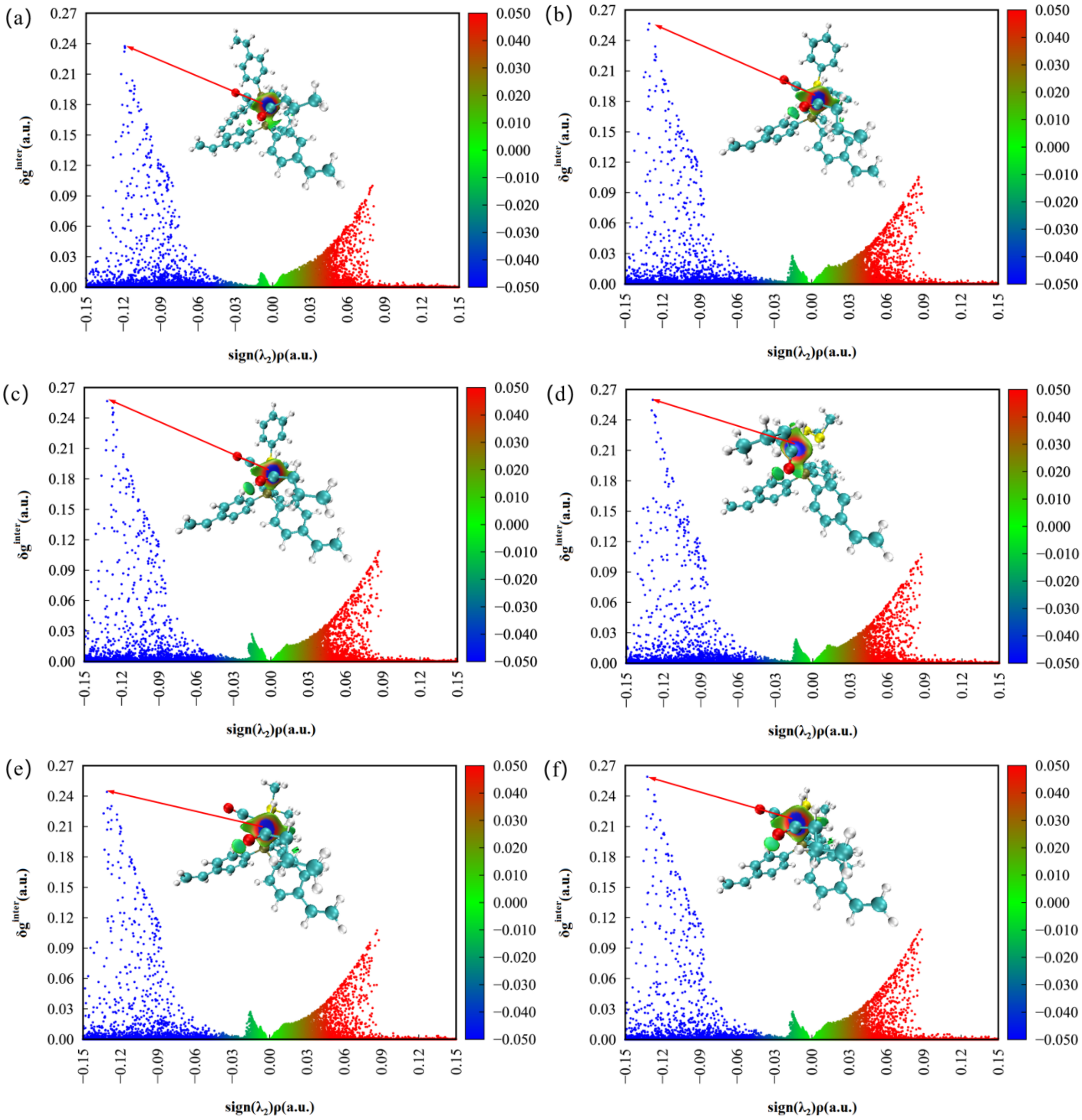

Fig. S11 The visualized weak interaction regions and the corresponding IGMH scatter map for structure 8 (see Scheme 1) in different catalytic systems. (a) HRh(CO)(PAr_3-Ar_3P), (b) HRh(CO)(PAr_3)($C_6H_5SC_6H_5$), (c) HRh(CO)(PAr_3)($C_6H_5SCH_3$), (d) HRh(CO)(PAr_3)($CH_3S_2CH_3$), (e) HRh(CO)(PAr_3)(CH_3SCH_3), (f) HRh(CO)(PAr_3)(CH_3SH).

Table S1 Calculated energies required for sulfide substitution.

Sulfides	Energies (kcal/mol)
H_2S	358.1
$C_6H_5SC_6H_5$	13.5
$C_6H_5SCH_3$	16.1
$CH_3S_2CH_3$	12.0
CH_3SCH_3	14.8
CH_3SH	17.5

Table S2 Calculated Bader charges for structure 2 (see Scheme 1) in different catalytic systems.

	Bader charge (|**e**|)	
catalyst	2-Rh-Bader	2-H-Bader
$HRh(CO)(PAr_3\text{-}Ar_3P)$	0.196	-0.125
$HRh(CO)(PAr_3)(C_6H_5SC_6H_5)$	0.210	-0.077
$HRh(CO)(PAr_3)(C_6H_5SCH_3)$	0.226	-0.088
$HRh(CO)(PAr_3)(CH_3S_2CH_3)$	0.228	-0.063
$HRh(CO)(PAr_3)(CH_3SCH_3)$	0.216	-0.070
$HRh(CO)(PAr_3)(CH_3SH)$	0.208	-0.064

Table S3 Experimental data and reaction conditions.

	Conv. %	Sel. %	TOF/h^{-1}	n/i
Rh1/POPs	57.7	98.4	1260.6	4.6
Rh1/POPs+H_2S	2.5	2.5	263.8	-
Rh1/POPs+PhSPh	69.0	97.7	1523.5	5.8
Rh1/POPs+PhSMe	77.9	98.3	1760.9	6.4
Rh1/POPs+MeSSMe	63.7	97.3	1460.6	8.6
Rh1/POPs+MeSMe	71.7	99.8	1578.7	6.0
Rh1/POPs+MeSH	51.9	98.3	1062.8	8.9

Conditions: Rh1/POPs 0.25wt%, 0.1 g, $CO/H_2/C_3H_6$=1:1:1, 80 ℃, 2.0 MPa, 50 ml autoclave, reaction 1.0 h.

References

1 M. Jiang, L. Yan, Y. Ding, Q. Sun, J. Liu, H. Zhu, R. Lin, F. Xiao, Z. Jiang and J. Liu, *Journal of Molecular Catalysis A: Chemical*, 2015, 404-405, 211-217.

2 S. Feng, M. Jiang, X. Song, P. Qiao, L. Yan, Y. Cai, B. Li, C. Li, L. Ning, S. Liu, W. Zhang, G. Wu, J. Yang, W. Dong, X. Yang, Z. Jiang and Y. Ding, *Angewandte Chemie International Edition*, 2023, 62, e202304282.