

Table S1 CDA results of partial orbitals HRh(CO)(P-frame)<sub>3</sub> complexes (in electron)

configuration	fragment	orbital	d	b	d-b	r
HRh(CO)(P-frame) <sub>3</sub> -1(a)	(P-frame) <sub>3</sub> -1 and Rh <sup>-</sup>	HOMO-25	0.0176	0.0027	0.0148	0.0601
		HOMO-24	0.0415	0.0144	0.0271	0.1002
		HOMO-23	0.0371	0.0107	0.0264	0.0448
HRh(CO)(P-frame) <sub>3</sub> -1(b)	CO and Rh <sup>-</sup>	HOMO-22	0.0435	-0.0023	0.0459	-0.2141
		HOMO-24	0.0308	0.0039	0.0269	0.0929
	(P-frame) <sub>3</sub> -1 and Rh <sup>-</sup>	HOMO-23	0.0508	0.0074	0.0434	0.0836
		HOMO-22	0.0387	-0.0012	0.0399	-0.0923
HRh(CO)(P-frame) <sub>3</sub> -2(a)	CO and Rh <sup>-</sup>	HOMO-91	0.0276	-0.0005	0.0280	0.0420
		HOMO-27	0.0313	0.0022	0.0291	0.0245
	(P-frame) <sub>3</sub> -2 and Rh <sup>-</sup>	HOMO-25	0.0447	0.0116	0.0331	0.0592
		HOMO-23	0.0382	0.0113	0.0269	0.0529
HRh(CO)(P-frame) <sub>3</sub> -2(b)	CO 和 Rh <sup>-</sup>	HOMO-96	0.0357	-0.0016	0.0373	0.0629
		HOMO-25	0.0555	0.0046	0.0509	0.0681
	(P-frame) <sub>3</sub> -2 and Rh <sup>-</sup>	HOMO-23	0.0332	0.0024	0.0307	0.0416
		HOMO-22	0.0386	-0.0011	0.0397	-0.1095
	CO and Rh <sup>-</sup>	HOMO-89	0.0164	0.0001	0.0163	0.0261

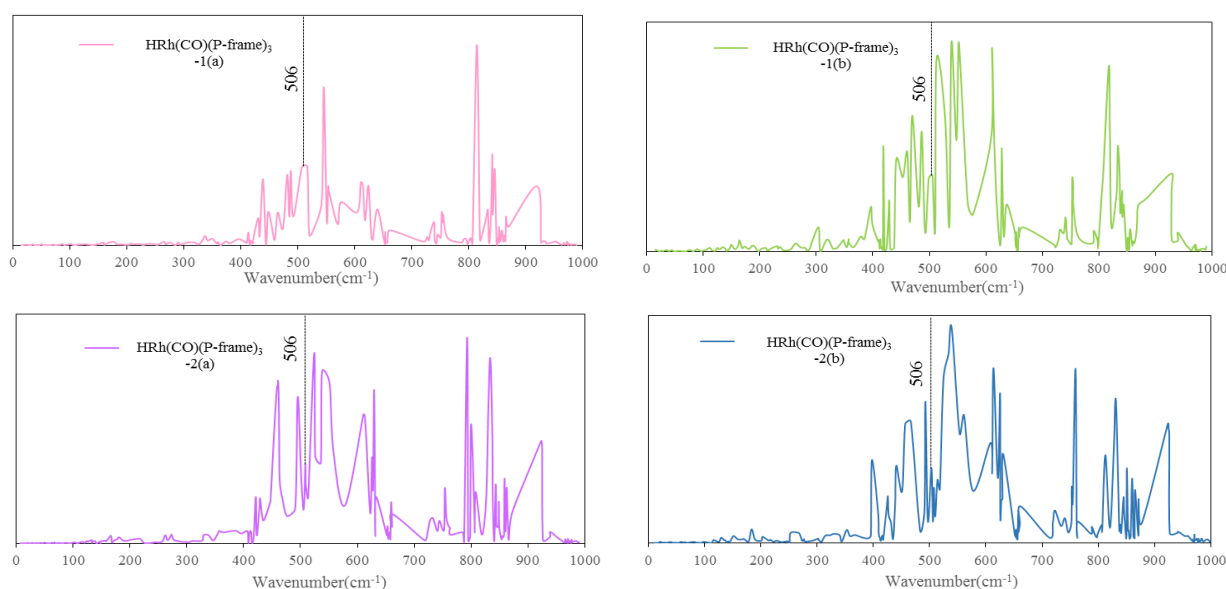


Fig. S1 FT-IR spectrum of four HRh(CO)(P-frame)<sub>3</sub> complexes

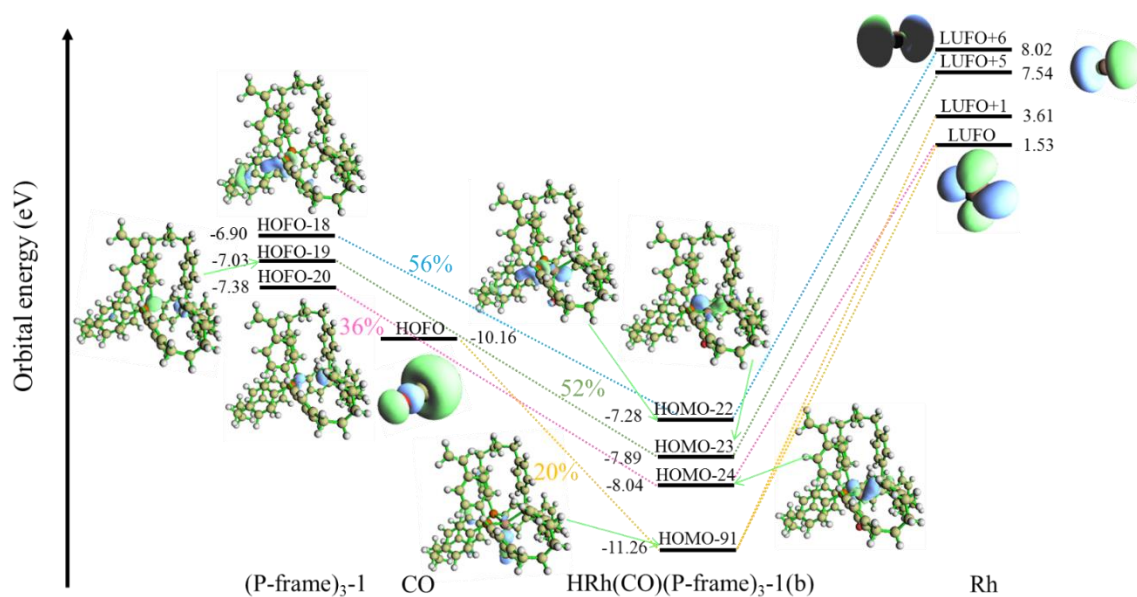


Fig. S2 The partial orbital interaction diagrams of HRh(CO)(P-frame)<sub>3</sub>-1(b) (Green and blue represents positive and negative orbital phases, respectively)

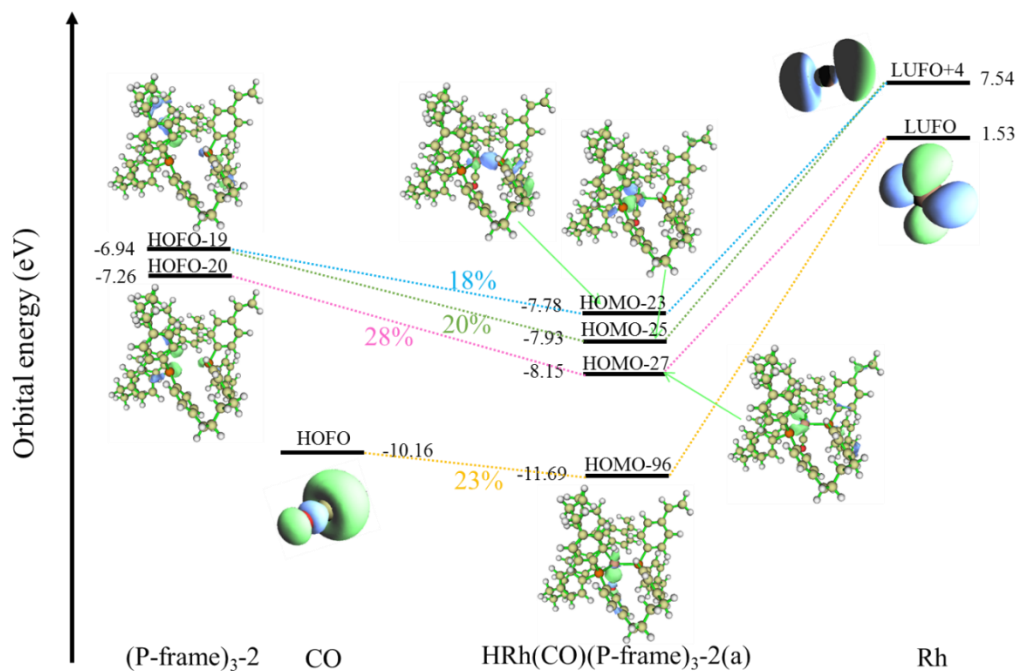


Fig. S3 The partial orbital interaction diagrams of HRh(CO)(P-frame)<sub>3</sub>-2(a) (Green and blue represents positive and negative orbital phases, respectively)

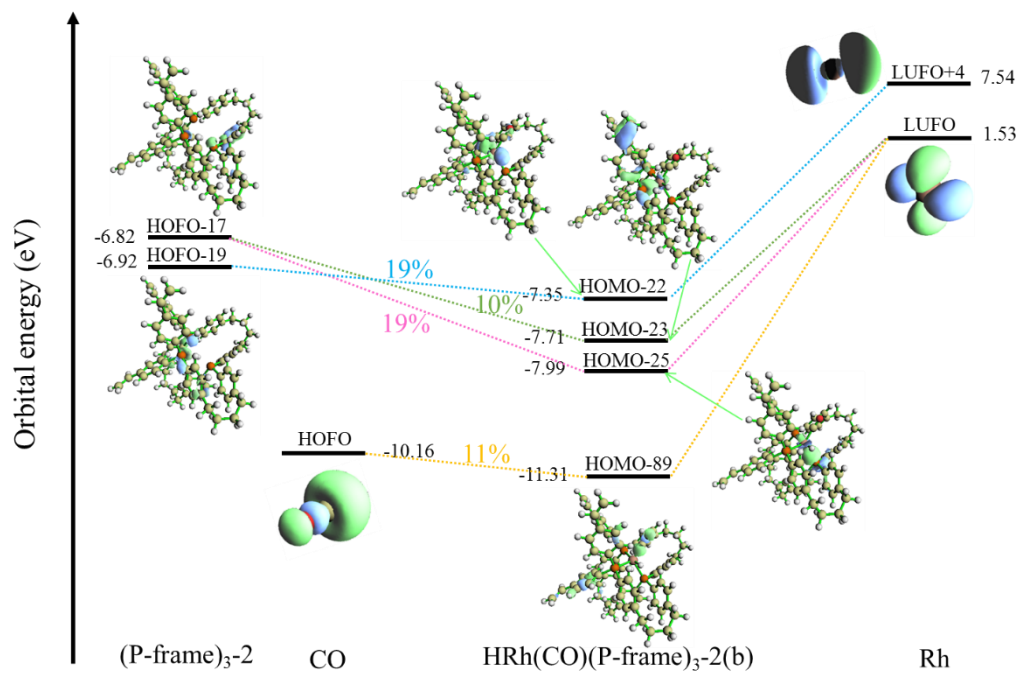


Fig. S4 The partial orbital interaction diagrams of  $HRh(CO)(P\text{-frame})_3\text{-}2(b)$  (Green and blue represents positive and negative orbital phases, respectively)