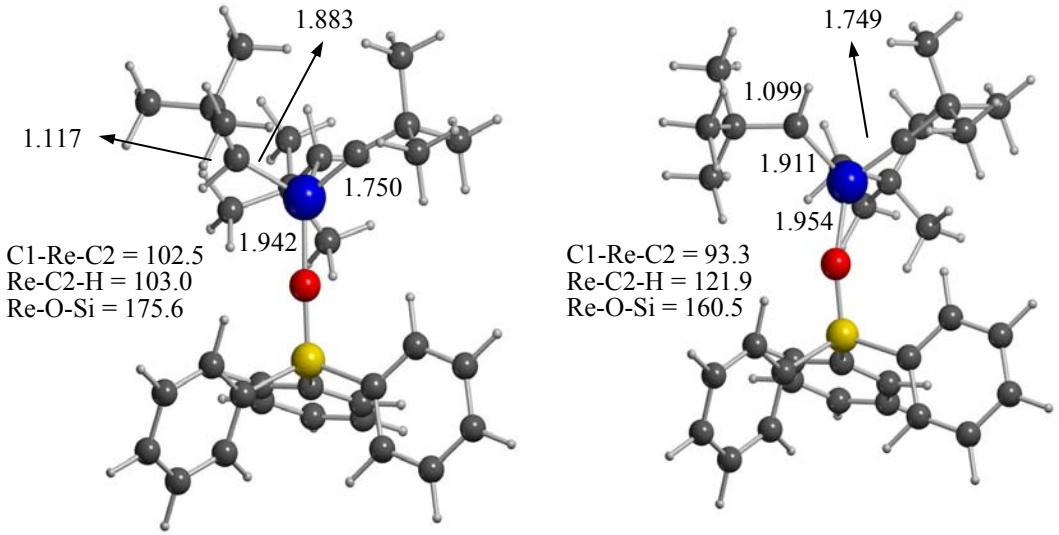
Table S1. Relative energies in kcal mol^{-1} and selected list of geometry parameters (distances in Å and angles in degrees) using different density functionals for $Re(\equiv CCH_3)(=CHCH_3)(CH_2CH_3)(OSiH_3)$ (**1M$_q$**) and $Re(\equiv CCH_3)(=CHCH_3)(CH_2CH_3)_2$ (**2M$_q$**) complexes.

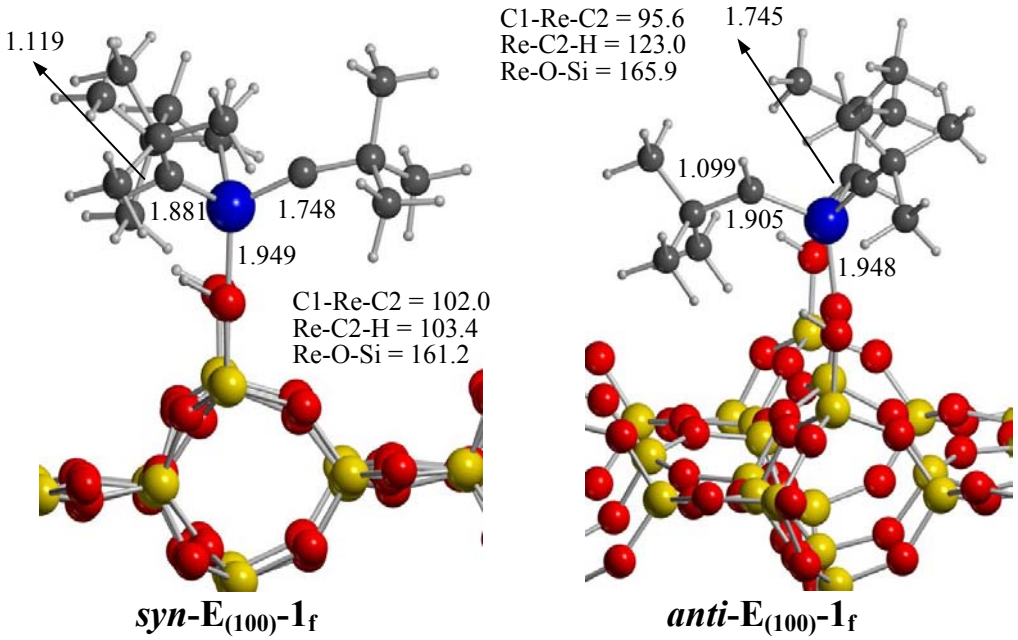
Functional	Structure	ΔE	Re-C1	Re-C2	Re-O	C2-H	C1-Re-C2	Re-C2-H	Re-O-Si
B3LYP	*syn*-**1M$_q$-G**[a]	0.0	1.728	1.873	1.928	1.110	99.3	107.2	146.6
B3LYP	*anti*-**1M$_q$-G**[a]	1.2	1.727	1.882	1.928	1.091	98.3	127.9	145.8
B3LYP	*syn*-**2M$_q$-G**[a]	0.0	1.726	1.861		1.112	101.4	104.2	
B3LYP	*anti*-**2M$_q$-G**[a]	2.2	1.725	1.872		1.090	99.7	128.5	
PBEPBE	*syn*-**1M$_q$-G**[a]	0.0	1.742	1.885	1.939	1.118	99.2	107.5	144.1
PBEPBE	*anti*-**1M$_q$-G**[a]	1.1	1.741	1.894	1.940	1.099	98.5	127.8	142.5
PBEPBE	*syn*-**2M$_q$-G**[a]	0.0	1.741	1.873		1.120	101.4	104.5	
PBEPBE	*anti*-**2M$_q$-G**[a]	2.1	1.740	1.884		1.098	100.0	128.3	

[a] Calculated as an isolated molecule with GAUSSIAN03 package.



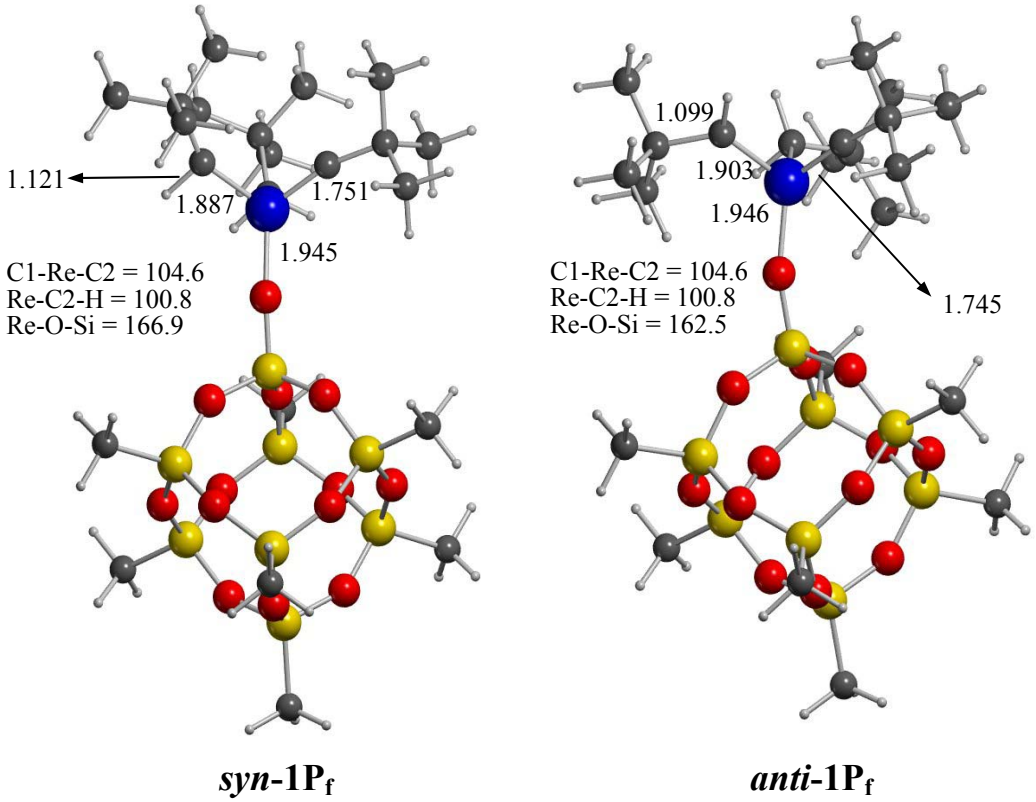
***syn*-1M$_f$** ***anti*-1M$_f$**

Figure S1. Optimized structures of Re(≡C*t*Bu)(=CH*t*Bu)(CH_2*t*Bu)($OSiPh_3$) (**1M$_f$**). Distances in Å and angles in degrees.



***syn*-E$_{(100)}$-1$_f$** ***anti*-E$_{(100)}$-1$_f$**

Figure S2. Optimized structures of [(≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH$_2$*t*Bu)] using Edingtonite as surface model (**E$_{(100)}$-1$_f$**). Distances in Å and angles in degrees.



***syn*-1P$_f$** ***anti*-1P$_f$**

Figure S3. Optimized structures of [(Me)$_7$Si$_7$O$_{12}$SiO-Re(≡C*t*Bu)(=CH*t*Bu)(CH$_2$*t*Bu)] (**1P$_f$**). Distances in Å and angles in degrees.

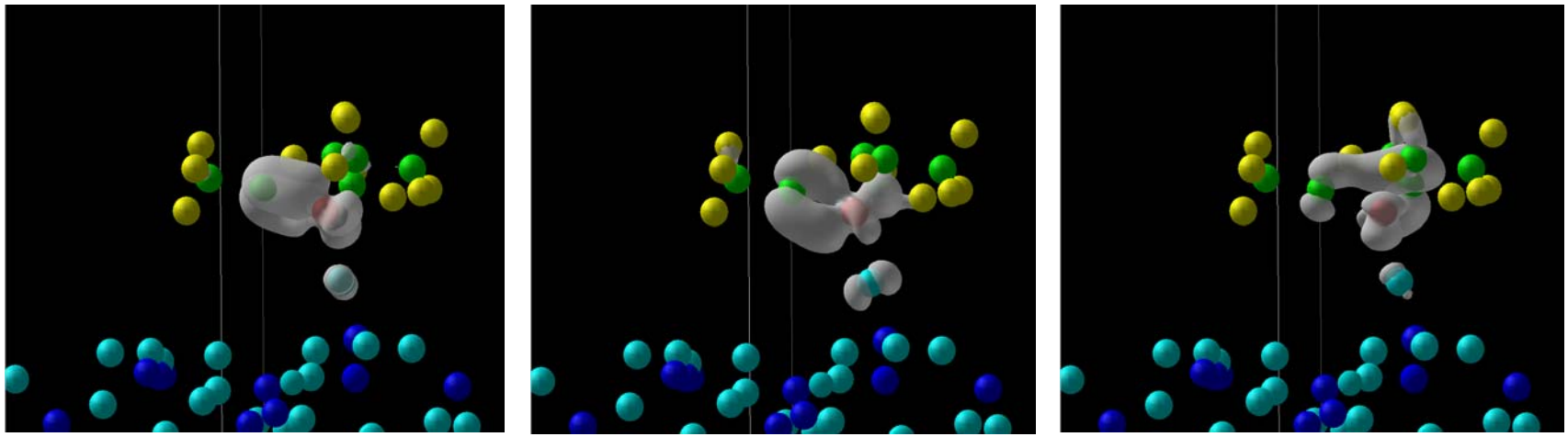


Figure S4. Band decomposed charge density for the three highest occupied bands. They correspond to the three π Re-C bonds, Re≡C (band number 244 and 245) and Re=C (band number 246). Dark blue atoms = Si, light blue = O, green = C, yellow = H and red = Re.