Part 5: Appendix

Appendix A

Potential-energy surface (PES) scan

```
# Task parameters
Calculate                       Scan_PES
Opt_energy_convergence          2.0000e-005
Opt_gradient_convergence        4.0000e-003 A
Opt_displacement_convergence    5.0000e-003 A
Opt_iterations                  1000
Opt_max_displacement            0.3000 A

# Scan PES Keywords
Scan_Option  Optimization
SCAN_DIM_1
Distance     13  14   0   0      1.532810      3.000000   25

Symmetry                        off

# Electronic parameters
Spin_polarization               restricted
Charge                          0.0000
Basis                           dnp
Pseudopotential                 none
Functional                      gga(p91)
Aux_density                     octupole
Integration_grid                medium
Scf_density_convergence         1.0000e-006
Scf_charge_mixing               0.2000
Scf_iterations                  500
Scf_diis                        6 pulay
Occupation                      fermi

# Print options
Print                           eigval_last_it

# Calculated properties
```

Fig. A.1. Input file for the potential-energy surface (PES) scan.

Appendix B

Precatalyst tables:

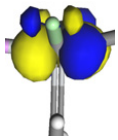
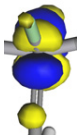
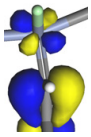
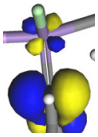
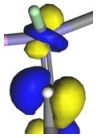
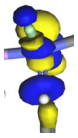
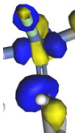
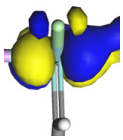
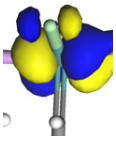
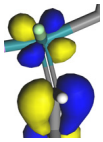
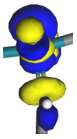
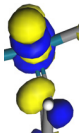
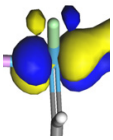
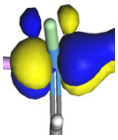
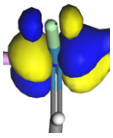
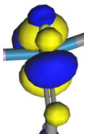
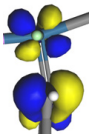
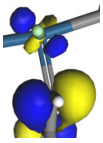
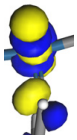
Table B.1 Energy values (Ha) of transition metals in the Grubbs second generation precatalyst framework

4	5	6	7	8	9	10
Ti -4013	V -4107	Cr -4208	Mn -4314	Fe -4427	Co -4546	Ni -4672
Zr -6705	Nb -6919	**Mo** -7141	-	**Ru** -7608	Rh -7852	Pd -8104
Hf -17490	Ta -17969	**W** -18456	Re -18953	Os -19460	Ir -19975	Pt -20500

Table B.2 LUMO energy values (eV) of transition metals in the Grubbs second generation precatalyst framework

4	5	6	7	8	9	10
Ti -2.4	V -2.5	Cr -2.3	Mn -2.8	Fe -2.9	Co -2.6	Ni -3
Zr -2.1	Nb -2.3	**Mo** -2.6	-	**Ru** -2.8	Rh -2.4	Pd -3.4
Hf -2.1	Ta -2.3	**W** -2.6	Re -3	Os -2.7	Ir -2.3	Pt -3.4

Table B.3 LUMO of transition metals in the Grubbs 2 precatalyst framework

4	5	6	7	8	9	10
Ti 	V 	Cr 	Mn 	Fe 	Co 	Ni 
Zr 	Nb 	**Mo** 	-	**Ru** 	Rh 	Pd 
Hf 	Ta 	**W** 	Re 	Os 	Ir 	Pt 

Catalyst tables:

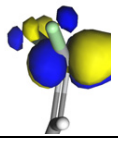
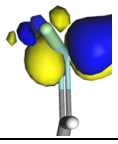
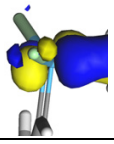
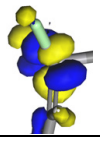
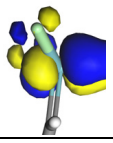
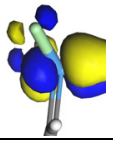
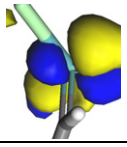
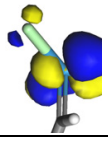
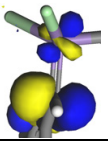
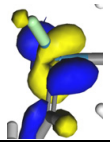
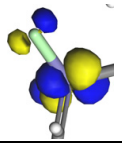
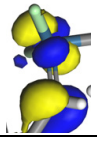
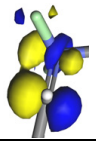
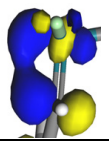
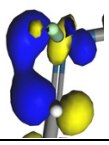
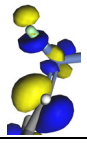
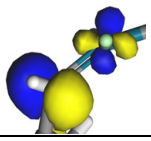
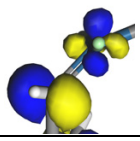
Table B.4 Energy values (Ha) of transition metals in the Grubbs second generation catalyst framework

4	5	6	7	8	9	10
Ti	V	Cr	Mn	Fe	Co	Ni
-2966	-3060	-3161	-3267	-3380	-3499	-3625
Zr	Nb	**Mo**	-	**Ru**	Rh	Pd
-5658	-5872	-6094		-6560	-6805	-7057
Hf	Ta	**W**	Re	Os	Ir	Pt
-16443	-16922	-17409	-17906	-18412	-18928	-19453

Table B.5 LUMO energy values (eV) of transition metals in the Grubbs second generation catalyst framework

4	5	6	7	8	9	10
Ti	V	Cr	Mn	Fe	Co	Ni
-2.9	-2.8	-3	-3.1	-3.5	-3.3	-3.6
Zr	Nb	**Mo**	-	**Ru**	Rh	Pd
-2.6	-2.9	-3.2		-3.3	-3.4	-3.9
Hf	Ta	**W**	Re	Os	Ir	Pt
-2.6	-2.9	-3.3	-3.4	-3	-3.3	-3.8

Table B.6 LUMO of transition metals in the Grubbs 2 catalyst framework

4	**Ti**	Zr	Hf
			
5	V	Nb	Ta
			
6	Cr	**Mo**	**W**
			
7	Mn	-	Re
			
8	Fe	**Ru**	Os
			
9	Co	Rh	Ir
			
10	Ni	Pd	Pt
			

Appendix C

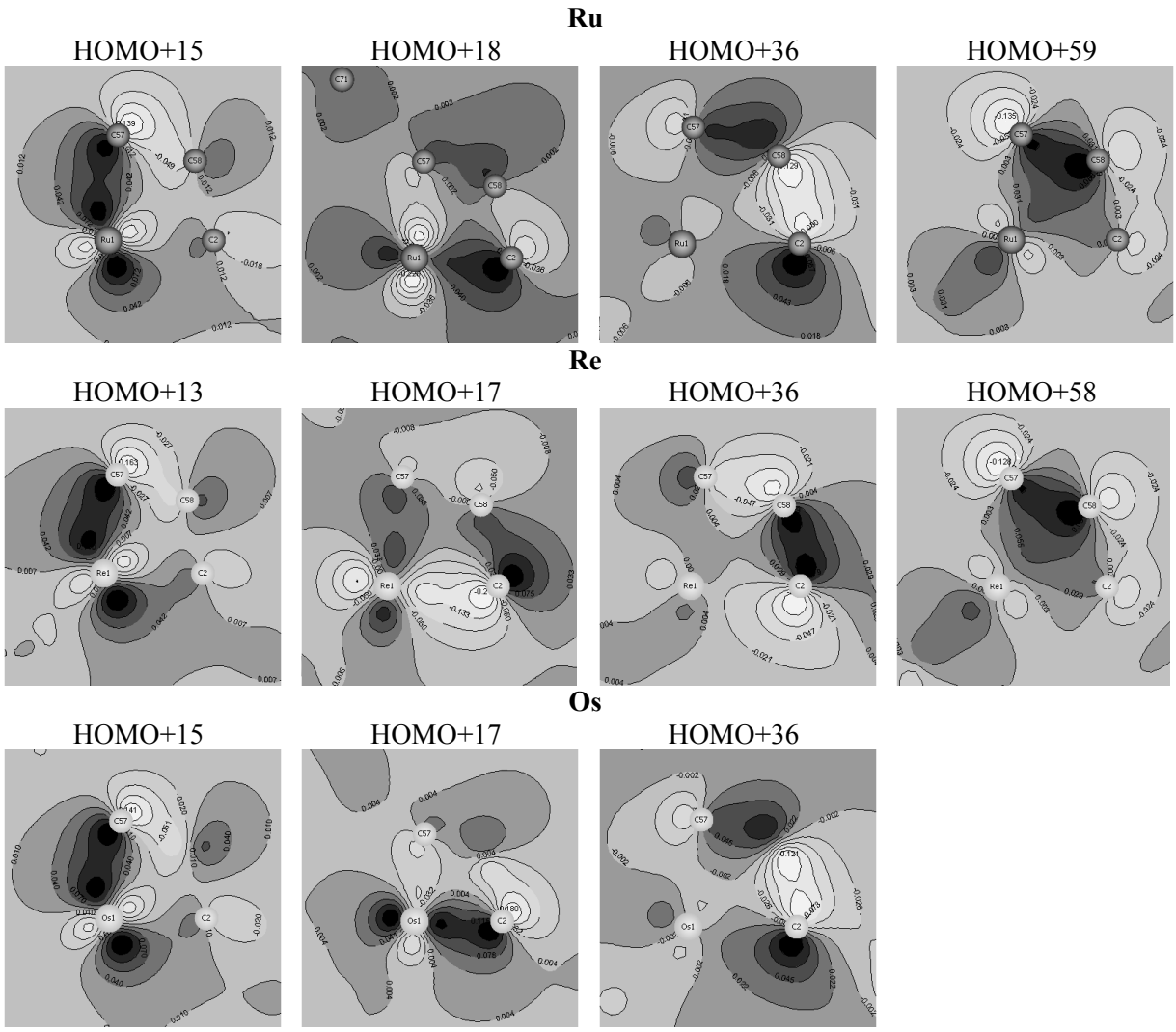


Fig. C.1. Bonding molecular orbitals of the metallacyclobutane intermediates of Ru, Re and Os. Only bonding orbitals with contributions by the metal atom, carbene carbon atom and alkene atoms were considered.

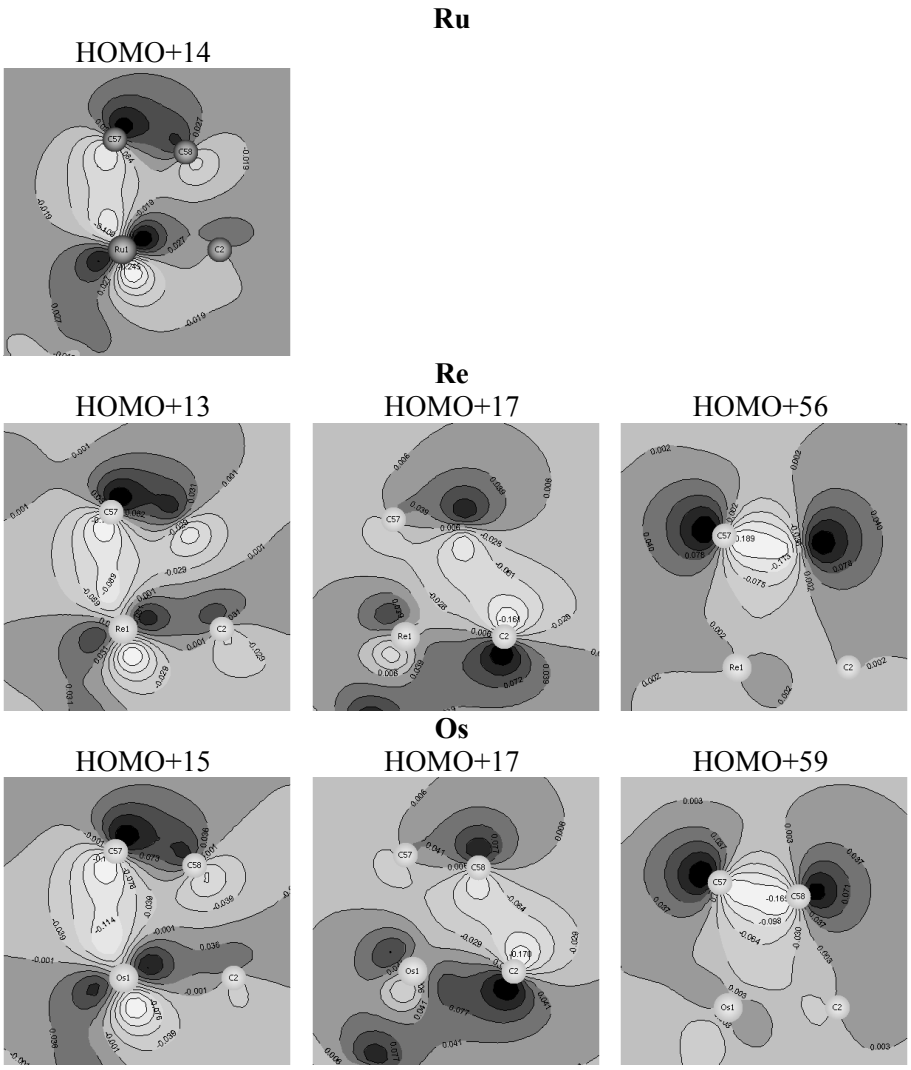


Fig. C.2. Bonding molecular orbitals of the transition states of Ru, Re and Os. Only bonding orbitals with contributions by the metal atom, carbene carbon atom and alkene atoms were considered.